

Variational Approach to the Prediction of Excess Thermodynamic Properties of Binary Liquid Mixtures. IV

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The variational technique which is proposed earlier [J. Chem. Phys. **53**, 1931 (1970)] is applied for the prediction of the excess thermodynamic properties of binary liquid mixtures. The results are compared with the experimental and machine-calculated, Monte Carlo, data. Also comparisons are made with the results of the other theories of mixtures. It is shown that the variational technique is a stronger tool for quantitative predictions of the excess thermodynamic properties of liquid mixtures than the other existing theories of mixtures.

I. INTRODUCTION

In the present report the excess thermodynamic properties of different binary liquid mixtures are calculated by the variational technique proposed earlier,¹ and the results are compared with the available experimental and machine-calculated data. Also the results of the variational technique are compared with the results of the other theories of liquid mixture, and it is shown that the variational technique consistently predicts the excess thermodynamic properties better. For all the binary systems in which the calculations are performed it is assumed that the Lennard-Jones potential function is valid. The method of calculation and the mathematical formulations of this variational technique are already presented in Paper III (Ref. 1).

II. COMPARISON WITH EXPERIMENTAL RESULTS

To be consistent with the other theories of mixtures^{2,3} in calculations of the excess properties reported in this part, the potential parameters listed in Table I are used. For argon the values of $\epsilon/K=119.8^\circ\text{K}$ and $\sigma=3.405 \text{ \AA}$ are used. In Table II the results of the variational calculations are compared with experiment and other theories for eight different binary equimolar liquid mixtures, all at zero pressure.

In Table II, G^E , H^E , and V^E are the excess Gibbs free energy, enthalpy, and volume, respectively, of the mixtures over the values for pure systems at the same temperature and zero pressure. The sources of experimental data are given in Refs. 2-4. "APM" stands for average potential model,^{2,3} vdW(a) stands for van der Waals mixing rule joined with empirical relations of Bellemans *et al.*²⁻⁴ for G , H , and V , while vdW(b) stands for van der Waals mixing rule joined with the van der Waals equation of state,⁵ Guggenheim stands for Guggenheim's equation of state joined with van der Waals mixing rule,⁵ and perturbation stands for perturbation theory.³ For all the theories compared in this table the Lorentz-Berthelot combining rule for unlike pair interaction parameters, $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$; $\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$, is used. A comparison of

the results of variational calculations with each of the other theories will indicate that the variational technique predicts the excess thermodynamic properties of these mixtures better than the other approaches.

For mixtures of real liquids the Lorentz-Berthelot rule is not satisfactory enough for unlike pair-interaction parameters. The choice of the unlike pair-interaction parameters has a very critical effect on the prediction of excess thermodynamic properties of mixtures, and an accurate *a priori* knowledge of these parameters is necessary for more quantitative predictions.⁶ For example, Fender and Halsey⁷ found that use of $\epsilon_{12} = 2\epsilon_{11}\epsilon_{22}/(\epsilon_{11} + \epsilon_{22})$ instead of $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$ for the mixtures of rare gases will improve the prediction of the prop-

TABLE I. Pair interaction parameters for pure substances.

Substance	ϵ/ϵ (argon)	σ/σ (argon)
Argon	1.000	1.000
Krypton	1.387	1.070
Nitrogen	0.836	1.063
Oxygen	1.022	0.995
Carbon monoxide	0.881	1.070
Methane	1.266	1.099

erties of these mixtures greatly. This point has been supported by Table III, in which the results of the variational calculations using both of these rules are compared with experimental results⁸ at 115.77°K and zero pressure for mixtures of argon and krypton. In Table III, for σ_{12} the arithmetic average, $\frac{1}{2}(\sigma_{11} + \sigma_{22})$, is used which is satisfactory for the mixtures of spherical molecules. Another system of interest which its unlike-pair interaction parameters are known⁹ is $\text{CH}_4 + \text{CF}_4$ as shown in Table IV along with like-pair interaction parameters.⁹ In Table V the excess properties of equimolar mixture of $\text{CH}_4 + \text{CF}_4$ as calculated by different theories (using the potential parameters of Table IV) are compared with experimental values at zero pressure and at 111°K . Among the different theories compared in Table V with experiment, Guggenheim's results are better than the others.

TABLE II. Comparison of the experimental and theoretical values of excess thermodynamic properties at $P=0$ and $x_1=x_2=0.5$ for different systems of binary liquid mixtures. G^E and H^E are in joules/mole and V^E is in cubic centimeters/mole.

	G^E	H^E	V^E		G^E	H^E	V^E
(Ar+Kr) at 116°K				(O ₂ +Ar) at 84°K			
Experiment	84		-0.52	Experimental	42	44	-0.21
APM	170		-0.44	APM	65	85	-0.11
vdW (a)	37	-50	-0.78	vdW (a)	51	54	-0.32
vdW (b)	18	-64	-1.26	vdW (b)	24	21	-0.30
Guggenheim	50	-54	-1.13	Guggenheim	46	50	-0.32
Perturbation	28	-54	-0.72	Perturbation	40	35	-0.34
Variational	42	-33	-0.71	Variational	50	58	-0.28
(Ar+N ₂) at 84°K				(O ₂ +N ₂) at 78°K			
Experiment	34	51	-0.18	Experiment	42	44	-0.21
APM	80	105	-0.07	APM	65	85	-0.11
vdW (a)	40	43	-0.32	vdW (a)	51	54	-0.32
vdW (b)	21	19	-0.36	vdW (b)	24	21	-0.30
Guggenheim	39	44	-0.36	Guggenheim	46	50	-0.32
Perturbation	32	27	-0.33	Perturbation	40	35	-0.34
Variational	39	44	-0.29	Variational	50	58	-0.28
(Ar+CO) at 84°K				(N ₂ +CO) at 84°K			
Experiment	57		0.10	Experiment	23		0.13
APM				APM			
vdW (a)	26	32	-0.20	vdW (a)	1.0	-0.4	-0.02
vdW (b)	13	16	-0.23	vdW (b)	24	21	-0.30
Guggenheim	25	34	-0.22	Guggenheim	1	-1	-0.03
Perturbation	18	14	-0.25	Perturbation	0.9	-0.4	-0.02
Variational	25	33	-0.17	Variational	1.2	0.56	-0.02
(Ar+CH ₄) at 91°K				(CO+CH ₄) at 91°K			
Experiment	74	103	0.17	Experimental	115	105	-0.32
APM	170	240	0.72	APM	105	80	-0.50
vdW (a)	-19	-53	-0.31	vdW (a)	75	23	-0.85
vdW (b)	-13	-31	-0.26	vdW (b)	41	2	-0.86
Guggenheim	-9	-43	-0.23	Guggenheim	87	45	-0.88
Perturbation	-29	-76	-0.36	Perturbation	66	23	-0.63
Variational	-11	-34	-0.14	Variational	77	35	-0.69

TABLE III. Results of the variational calculations using the Lorentz-Berthelot rule and the Fender-Halsey rule compared with experimental results at 115.77°K and zero pressure for mixtures of Ar and Kr.

x_{Ar}	G^E (J/mole)			V^E (cm ³ /mole)		
	Exptl	$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$	$\epsilon_{12} = 2\epsilon_{11}\epsilon_{22}/(\epsilon_{11} + \epsilon_{22})$	Exptl	$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$	$\epsilon_{12} = 2\epsilon_{11}\epsilon_{22}/(\epsilon_{11} + \epsilon_{22})$
0.1	29	14.7	30.2	-0.13	-0.206	-0.349
0.2	52	27.0	54.6	-0.26	-0.387	-0.546
0.3	69	36.6	73.0	-0.37	-0.538	-0.459
0.4	80	43.3	84.9	-0.46	-0.660	-0.553
0.5	84	46.7	90.1	-0.52	-0.727	-0.609
0.6	82	46.4	88.1	-0.53	-0.751	-0.621
0.7	72	42.3	78.5	-0.50	-0.715	-0.580
0.8	56	33.5	61.0	-0.40	-0.591	-0.474
0.9	32	19.6	35.0	-0.24	-0.367	-0.288

TABLE IV. Potential parameters for CH₄+CF₄.

	ϵ/ϵ (CH ₄)	σ/σ (CH ₄)
CH ₄ +CH ₄	1.000	1.000
CH ₄ +CF ₄	0.917	1.132
CF ₄ +CF ₄	1.017	1.242

 TABLE V. Comparison of the results of different theories and experiment for CH₄+CF₄ at $P=0$, $T=111^\circ\text{K}$, and $x_1=x_2=0.5$.

	G^E (J/mole)	H^E (J/mole)	V^E (cm ³ /mole)
Experiment	360		0.88
APM	870		7.1
vdW(a)	279	482	0.90
vdW(b)	171		1.11
Guggenheim	298		1.22
Perturbation	209	259	-0.97
Variational	424	770	3.13

 TABLE VI. Comparison of excess properties of equimolar mixtures of argon and krypton at 115.8°K and $P=0$ as calculated by Monte Carlo (MC) method,^a and different theories. ($\epsilon_{11}/K=119.8\text{K}$, $\sigma_{11}=3.405\text{Å}$, $\epsilon_{22}/K=167\text{K}$, $\sigma_{22}=3.633\text{Å}$).

	G^E (J/mole)	H^E (J/mole)	V^E (cm ³ /mole)
MC ^a		-80±34	-0.80±0.16
MC ^b	34±10	-34±40	-0.54±0.20
APM ^c	133	141	0.02
vdW ^c	42.2	-45.4	-0.79
Perturbation	32.7	-48.5	-0.73
Variational	46.7	-33.5	-0.73

^a Taken from Ref. 10.

^b Taken from Ref. 3.

^c Based on Bellemans' empirical equations, taken from Ref. 3.

III. COMPARISON WITH MONTE CARLO RESULTS

In comparison of the results of the variational approach with Monte Carlo data on mixtures, there is the advantage of the exact *a priori* knowledge of the unlike-pair interaction parameters. Consequently this comparison should be considered stronger than the case where experimental data are used. In Table VI the variational results are compared with Monte Carlo (MC) data,^{3,10} along with the results of other theories. In Table VI, MC^b is Monte Carlo calculations, performed by McDonald, using longer runs than MC^a and reported in Ref. 3. In Table VI, all the theories compared, except for APM, are in satisfactory agreement with MC data. In Table VII, variations of excess volume, V^{III} , excess free energy, g^{III} , and excess enthalpy, h^{III} , of the binary mixtures of Lennard-Jones fluids with respect to σ_{11}/σ_{22} and

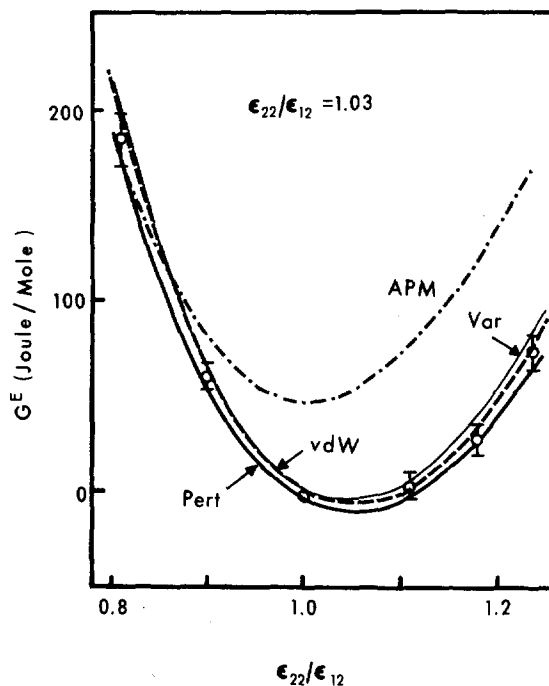


FIG. 1. Excess Helmholtz free energy of mixing vs $\epsilon_{22}/\epsilon_{12}$ for a binary mixture of Lennard-Jones liquids at 97°K , $P=0$, and $x_1=x_2=0.5$ ($\epsilon_{12}/K=133.5^\circ\text{K}$, $\sigma_{12}=3.596\text{Å}$). The data points are the Monte Carlo results of McDonald and Singer,³ the curves are results of different theories.

$\epsilon_{11}/\epsilon_{22}$ over that of a pure fluid system with Lennard-Jones parameters σ_{12} and ϵ_{12} are given. This table was originally reported in Paper III (Ref. 1), but because of the corrections which have been made, both for MC data^{11,12} and for g^{III} of the variational technique, it is

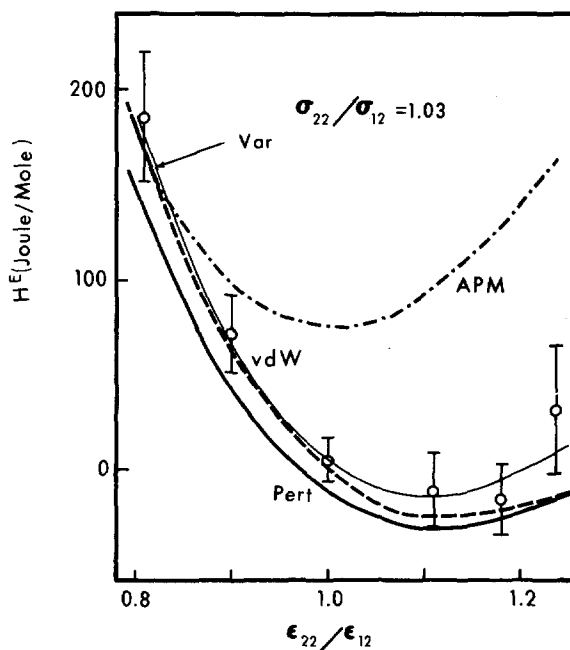


FIG. 2. Excess enthalpy of mixing vs $\epsilon_{22}/\epsilon_{12}$ for the same mixtures as in Fig. 1 and at the same conditions.

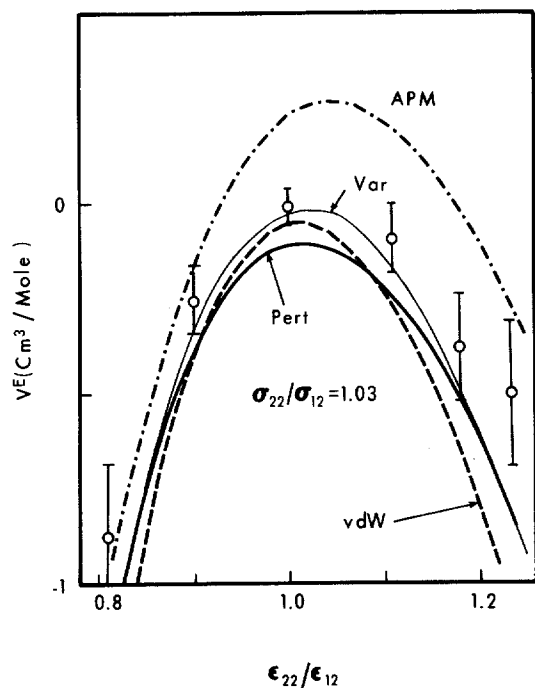


FIG. 3. Excess volume of mixing vs $\epsilon_{22}/\epsilon_{12}$ for the same mixtures as in Figs. 1 and 2, and at the same conditions.

again reported here. This table indicates that the variational results are in better agreement with MC data than vdW for the excess properties.

In Figs. 1-6 the APM, vdW, perturbation, and variational results are compared with MC curves.³

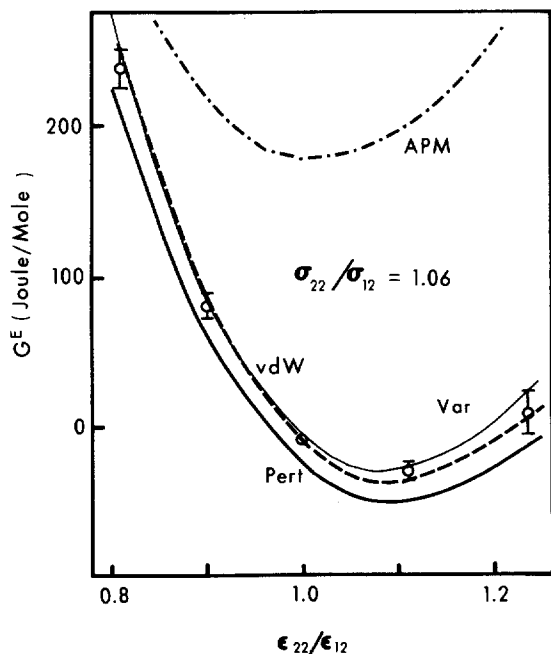


FIG. 4. Excess Helmholtz free energy of mixing vs $\epsilon_{22}/\epsilon_{12}$, for mixtures at the same conditions as Fig. 1, except for σ_{22}/σ_{12} .

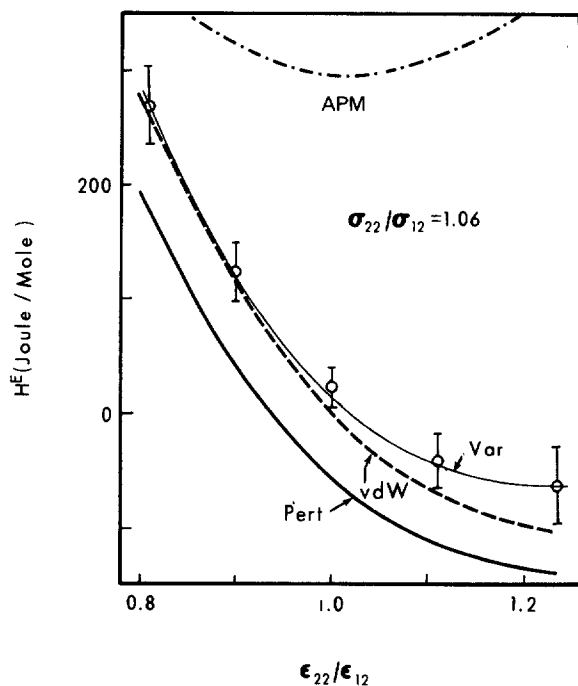


FIG. 5. Excess enthalpy of mixing vs $\epsilon_{22}/\epsilon_{12}$ for the same mixtures as in Fig. 4 and at the same conditions.

The variables in these graphs are $\epsilon_{22}/\epsilon_{12}$ and σ_{22}/σ_{12} . The conditions for these graphs are the same as in Table VII. Again, in these graphs, the consistent and clear superiority of the variational technique in predicting excess properties over the other theories compared is apparent.

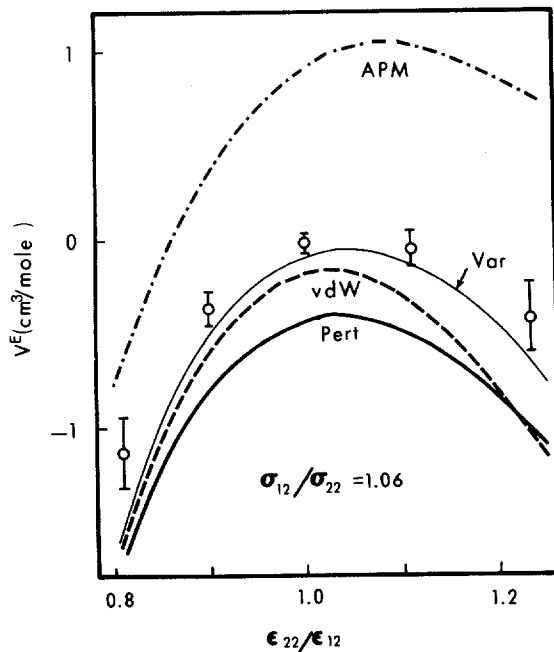


FIG. 6. Excess volume of mixing vs $\epsilon_{22}/\epsilon_{12}$ for the same mixtures as in Figs. 4 and 5 and at the same conditions.

TABLE VII. Variation of thermodynamic functions V^{III} , g^{III} , and h^{III} of the binary liquid mixtures of Lennard-Jones fluids with respect to molecular potential parameters at $P=0$, $T=97^\circ\text{K}$, $x_1=x_2=0.5$, and for $\sigma_{12}=\frac{1}{2}(\sigma_{11}+\sigma_{22})=3.596 \text{ \AA}$, $\epsilon_{12}/K=(\epsilon_{11}\epsilon_{22})^{1/2}/K=133.5^\circ\text{K}$.

σ_{11}/σ_{22}	$\epsilon_{11}/\epsilon_{22}$	ΔV^{III}			$g^{III}\times 10^3$			$h^{III}\times 10^3$		
		MC ^a	vdW ^b	Var.	MC ^c	vdW ^b	Var.	MC ^d	vdW ^b	Var.
1.000	1.000	0.00	0.00	0.00	0.0	0.0	0.0	0	0	0
1.041	1.000	0.03	0.02	0.03	-2.2	-0.6	-0.6	2	0	0
1.083	1.000	0.14	0.08	0.13	-3.9	-2.4	-2.6	11	0	0
1.128	1.000	0.34	0.18	0.30	-5.2	-5.4	-5.8	29	0	10
1.174	1.000	0.62	0.32	0.54	-6.0	-9.5	-9.5	53	0	19
1.222	1.000	0.98	0.50	0.83	-6.3	-14.9	-13.8	85	0	29
1.273	1.000	1.43	0.72	1.22	-6.2	-21.5	-18.0	125	0	48
1.000	1.235	-0.02	-0.03	-0.06	-28.7	-23.1	-24.1	-27	-31	-39
1.062	0.810	0.09	0.07	0.07	4.1	15.0	10.9	19	23	19
1.062	1.000	0.08	0.04	0.07	-3.1	-1.3	-0.9	6	0	0
1.062	1.235	-0.05	-0.04	-0.03	-66.6	-64.1	-59.5	-84	-84	-87
1.128	0.810	0.39	0.26	0.34	36.8	50.1	45.1	86	76	78
1.128	1.235	0.19	0.05	0.15	-101.	-107.6	-94.9	-117	-137	-116

^a Reference 12, standard deviation 0.045 and maximum difference 0.1.

^b Based on the McDonald's Monte Carlo curves for the reference system (see Ref. 11).

^c Reference 12, standard deviation 1.50 and maximum difference 4.

^d Reference 12, standard deviation 15 and maximum difference 33.

IV. CONCLUSION

In order to compare the results of the variational calculations for the experimental binary liquid systems of Tables III and V with the results of the other theories of mixtures, it is better to consider the root-mean-square values of deviations⁵ $[x^E(\text{calc})/x^E(\text{obs})-1]$, where $x=G$, H , or V . The root-mean-square deviation for APM is 2.16, for vdW(a) is 1.21, for vdW(b) is 1.53, for Guggenheim is 1.22, for perturbation is 1.38, and for variational is 1.12. This shows that the variational results are closer to experimental results than all the other theories. This is especially important due to the fact that the variational approach is an analytic approach, along with perturbation theory, while the other approaches which are introduced are corresponding-states approaches.

Tables VI and VII and Figs. 1-6, in which the results of variational approach, along with the other theories are compared with the Monte Carlo calculations of McDonald and Singer, clearly indicate that the variational theory is in better agreement with Monte Carlo data than the other theories compared. This is particularly encouraging because the variational theory takes care of the size and the energy

differences of the molecules of the mixtures better than the other theories compared.

ACKNOWLEDGMENT

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