LETTERS TO THE EDITOR

To the Editor:

McElroy, et al. (1983), have presented new cross second virial coefficient data for the system acetone-methyl acetate. They show comparisons with the correlations of Tsonopoulos (1974) and Hayden and O'Connell (1975). The latter method appears to be good for pure component, but poor for cross, coefficients. McElroy, et al., attribute these errors in the Hayden-O'Connell method to the nonpolar parameter mixing rules in the model. While these are certainly subject to revision, their inadequacy would appear primarily in polar-nonpolar systems, not in this kind of system involving "chemical" effects.

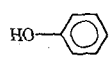
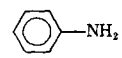
Instead, the errors arise from a wrong value of the solvation parameter. Although not explicitly noted by McElroy, et al., the value of 1.1 that appears in Appendix C-4 of the book by Prausnitz, et al. (1980) must have been used. Unfortunately, that number was not based on any data. A value 0.75 gives cross coefficients within 5 cc/gmol of the data of McElroy, et al.

As the extensive and careful work of Stein and Miller (1980) on amine-methanol systems show, erroneous guesses of the binary solvation parameter can yield very poor results. In their case, the estimate in the book was 0.2 while the experimental values ranged from 2.0 to 2.4!

It is unfortunate that Prausnitz, et al., listed all of the association and solvation parameters in the same way rather than denoting guesses differently from estimates based on data. Table I presents the groups for which Table II gives parameter values that do make such a distinction. (Some revisions have been made to versions of this table previously distributed to some individuals; the groups are related to those in the UNIFAC activity coefficient correlation of Skjold-Jorgensen, et al., 1980). Most values are based on data for only one system; 0″ in the cases where more data were available, the optimum parameter values were never strictly constant for the proposed groups. This is due to imperfections in the model and errors in the data. Along with the above references, the 100 pages of tabulated material that accompanied the original Hayden-O'Connell article document these values.

In systems where accurate results are essential, no predictive method is likely to be reliable enough when chemical effects are involved. In the system of McElroy, et al., variations of 0.1 in the solvation parameter yield virial coefficient changes of 35–45 cc/gmol. Changes of 0.01 in the binary parameter of the Tsonpoulos method yield variations of about 50 cc/gmol. In the systems of Stein and Miller, changes of 0.05 in the solvation parameter give variations of 400 cc/gmol. Thus, with this kind of sensitivity, it is easy to see how predictions may be poor. While the proposed mixing rule of McElroy, et al., appears to work in the present case, until it is used in considerably more systems,

TABLE 1 GROUP IDENTIFICATIONS FOR HAYDEN-O'CONNELL CORRELATION (BASED ON UNIFAC GROUPS OF SKJOLD-JORGENSEN, ET AL., 1980)

Number	Name	Formula
2	Alkene	C=C
3	Phenyl	
5	Hydroxyl	—OH
6	Methanol	CH_3OH
7	Water	H_2O
8	Phenyl Hydroxyl	
9	Keto	C=O
10	Aldehyde	CHO
11	Ester(Nonformate)	COO—
12	Ether	—O—
13	Monoalkylamino	$—NH_2$
14	Dialkylamino	—NH—
15	Phenylamino	
16	Cyano	—CN
16a	Hydrogen Cyanide	HCN
17	Alkanoic Acid	—COOH

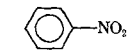
Number	Name	Formula
18	Monochloro	CCl
19	Dichloro	CCl_2
20	Chloroform	$HCCl_3$
21	Tetrachloromethane	CCl_4
23	Nitro	$—NO_2$
24	Phenyl Nitro	
25	Carbon Disulfide	CS_2
26	Trialkylamino	—N=
27	Formate	HCOO—
30	Thiol	—SH
33	Pyridine	
34	Diol	$—(COH)_2$
36	Alkyne	—C=C—
37	Carbon Dioxide	CO_2
38	Nitrous Oxide	N_2O
39	Sulfur Dioxide	SO_2
40	Hydrogen Chloride	HCl

TABLE 2 ESTIMATED GROUP ASSOCIATION AND SOLVATION PARAMETERS FOR HAYDEN-O'CONNELL CORRELATION (GROUP NUMBERS IDENTIFIED IN TABLE I)

	2	3	5	6	7	8	9	10	11	12	13	14	15	16	16a	17
2	0+	0.1	0.1	0.10+	0.1	0.15	0	0	0	0	0.20+	0.2	0.1	0.2	0.2	0.3
3		0+	0+	0+	0	0	0.50+	0+	0.6	0+	0	0	0	0.7	0.7	0.4
5			1.55+	1.6	1.6	1.0	1.0	0.8	1.8	0.5	2.4+	2.4+	2.0	1.5	1.5	2.8
6				1.63+	1.65	1.0	1.0	0.8	1.8	0.5	2.4+	2.4+	2.0	1.5	1.5	2.8
7					1.70+	1.0	1.0	0.8	1.8	0.5	2.5	2.5	2.1	1.6	1.6	2.9
8						0.32+	0.6	0.9	1.8	0.5	2.0	2.0	1.5	1.2	1.2	2.4
9							0.9+	1.0	0.75+	0	1.0	1.0	0.8	1.3	1.3	1.8
10								0.58+	0.75	0.4	0.9	0.9	0.7	2.5+	2.2	1.6
11									0.70+	0	0.6	0.6	0.5	1.4	1.2	1.5
12										0+	0.7	0.7	0.5	1.0	1.0	1.2
13											0.2+	0.2+	0.2	1.4	1.2	2.2
14												0.2+	0.1	1.4	1.2	2.2
15													0.1	1.2	1.0	2.0
16														1.65+	1.0	2.5
16a															0.12+	2.0
17																4.5+
18																
19																
20																
21																
23																
24																
25																
26																
27																
30																
33																
34																
36																
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18	19	20	21	23	24	25	26	27	30	33	34	36	37	38	39	40
0	0	0	0	0.2	0.4	0	0.2	0	0	0.3	0.1	0	0	0	0	0.2
0	0	0.12+	0.3	1.00+	1.3	0	0	0.5	0	0	0	0	0	0	0.5	0.4
0	0	0.1	0	1.2	1.6	0.2	2.0+	1.6	0.7	1.5	1.6	0.3	0.32	0.17	2.0	1.3
0	0	0.1	0	1.2	1.6	0.2	2.0+	1.6	0.7	1.5	1.6	0.3	0.32+	0.17+	2.0	1.3
0	0	0.1	0	1.2	1.6	0.2	2.1	1.6	0.7	1.5	1.6	0.3	0.32+	0.17+	2.2	1.38+
0	0	0.1	0.30+	1.3	1.5	0.1	1.5	1.0	0.5	1.2	1.3	0.2	0.3	0.1	1.5	1.0
0.2+	0.92+	1.26+	0.2	1.63+	2.0	0.13+	0.8	0.7	0.2	0.3	1.0	0.3	0+	0	0.9	0.5
0	0	1.1	0.1	1.4	1.7	0	0.6	0.7	0.1	0.6	0.8	0.2	0	0	0.8	0.4
0	0	1.65+	0.2	1.8	2.0	0	0.3	0.7+	0.3	0.3	1.8	0.2	0	0	1.0	0.6
0	0	0.95+	0.1	1.3	1.0	0	0.3	0+	0.1	0.3	0.5	0	0	0	0.58+	0.5
0.5	1.0	1.6	0	1.4	1.7	0.1	0.1	0.5	0.1	0.2	2.4	0.5	0.2	0.1	0.3	1.0
0.5	1.0	1.57+	0	1.4	1.7	0.1	0.1	0.5	0.1	0.2	2.4	0.5	0.2	0.1	0.3	1.5
0.3	0.8	1.4	0.3	1.2	1.4	0.1	0.1	0.4	0.1	0.1	2.0	0.3	0.1	0	0.1	1.2
0	0.9	1.8	0.3	2.0	2.4	0	1.0	1.3	0.7+	1.3	1.5	0.5	0	0	0.8	1.0
0	0.6	1.0	0.1	1.7	2.0	0	0.9	1.1	0.5+	1.1	1.5	0.3	0	0	0.5	0.7
0.5	0.9	1.5	0.2	2.2	2.7	0.3	1.8	1.4	0.4	2.1	2.8	0.6	0.5	0.3	1.0	3.0
0+	0+	0	0	0.3	0.5	0	0.2	0	0	0.4	0	0	0	0	0	0
	0+	0	0	0.6	0.9	0	0.6	0	0	0.9	0	0	0	0	0.8	0.2
		0+	0	0.8	1.2	0	1.2	1.2+	0.2	1.5	0.1	0	0	0	1.5	0.7
			0+	0.3	0.5	0	0	0.1	0	0.3	0	0	0	0	0.9	0.2
				1.66+	1.8	0.2	1.0	1.6	0.6	1.3	1.2	0.5	0.16+	0.1	1.2	1.3
					2.0	0.3	1.2	1.8	0.8	1.6	1.6	0.7	0.1	0	1.5	1.7
						0.34+	0	0	0	0.1	0.2+	0.2	0.3	0.2	0.2	1.7
							0.06+	0.2	0	0.1	2.0	0.2	0	0	0.1	1.0
								0.2+	0.2	0.2	1.6	0.1	0	0	0	0.4
									0.15+	0.1	0.7	0.1	0.1	0	0.1	0.7
										0.2+	1.5	0.4	0.1	0	0.2	1.4
											2.5	0.3	0.3	0.2	2.0	1.3
												0.16+	0.16	0.1	0.5	0.6
													0.16+	0.1	0.5	0.8
														0.09+	0.3	0.5
															0	0.5
																1.0

+ Based on Data

it is uncertain whether it will be adequate for all pairs of substances.

If other workers have evaluated solvation parameter values from data not used for Table II, I would be very interested in learning about the numbers.

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Reply:

Professor O'Connell in his letter referring to the paper by McElroy et al 1983 refers to errors which "arise from a wrong value of the solvation parameter" and "the value of 1.1 which appears in appendix C4 of the book by Prausnitz et al (1980)", which "must have been used". Not only was this value not used, but no value was even necessary since a major aim of the work was to avoid the use of such parmaeters which as Professor O'Connell points out are freely listed in the book referred to without reference to the fact that many values have been "guessed".

In our paper, measured critical temperatures have been employed in a two parameter equation of state to obtain an estimate of the unlike interaction critical temperature T^c_{12} for the system which is the parameter required to apply the Hayden and O'Connell correlation. No solvation parameter is required but the value implied by the T^c_{12} value thus obtained is in fact far from 1.1.

Furthermore solvation parameters are most commonly obtained by fitting a cross second virial, B_{12}, correlation to B_{12} experimental measurements. Once obtained they are then used to test B_{12} correlations against measured B_{12} values. This is plainly nonsensical particularly if the correlation used to obtain the solvation parameter is not specified and it "never" is. It would make more sense to simply leave T^c_{12} as an additional fitting parameter. Better still are estimates of T^c_{12} made independent of B_{12} measurements. Our paper describing the use of experimental mixture critical temperatures for this purpose is a first step in this direction and we are currently working on improvements to the procedure.

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P. J. McElroy, H. Hashim and W. L. Tatt, "Excess second virial coefficients and critical temperatures: acetone-methyl acetate", *AIChE J.*, **29**, 1007 (1983).

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