

The PFGC equation of state at the age of fourteen

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Abstract - The capabilities and application of PFGC equation of state has been reviewed. In particular, the PFGC ability in predicting pure components pressure-volume-temperature and thermodynamic properties, vapor-liquid equilibria, vapor-liquid-liquid equilibria and hydrate formation behavior have been discussed. In addition, its capabilities have been compared both with experimental data and other equation of states.

INTRODUCTION

Fourteen years ago in 1974, Cunningham and Wilson (ref. 1) introduced the Parameters From Group Contribution (PFGC) equation of state. The starting point is a description of the Helmholtz energy of a liquid lattice structure with holes:

$$A^{PFGC}/RT = A^{FH}/RT + A^W/RT \quad (1)$$

A^{FH} is a Flory-Huggins contribution (entropy effect), and A^W is an intermolecular interaction term (enthalpy effect). It is assumed that all the expressions for the Helmholtz energy are analogous to expressions for the Gibbs energy. Hence any activity coefficient expression may in principle be used for A^W , and they used a modified Wilson equation to describe the interactions between functional groups constituting the molecules rather than between molecules themselves. Based on the appropriate mathematical manipulations and using modified hole theory, Wilson and Cunningham derived the set of equations (ref. 1) for compressibility factor, chemical potential and isothermal effect of pressure on enthalpy.

Contrary to a number of successful equations of state such as SRK (ref. 2), PR (ref. 3), BWRs (ref. 4), in PFGC equations, there are no defining parameters in term of the critical properties, boiling point or any other physical property except type of groups making up the particular molecule. This is a great advantage specially when dealing with heavy fractions such as the C6+ fractions commonly encountered in natural gas, crude oil or coal tar liquids systems where the critical temperature and pressure of these compounds must be estimated using empirical correlations. Usually, the estimation are based on knowledge of the "average" molecular weight, "average" boiling point and specific gravity of the fraction. Wilson et al. (ref. 5) and later Brule et al. (ref. 6) have shown that the existing correlations have extreme sensitivity to the values used for critical properties of the C6+ fractions.

PFGC PARAMETERS

In this equation of state, the parameters are functions only of the groups making up the individual molecules present in the system. For a defined compound such as ethane or propane, the groups present in each molecule are known. For example, there are two CH₃- and one -CH₂- groups in propane. There are five parameters for each group which must be known before any thermodynamic property calculations can be made. These five parameters are:

- b_k = volume of group k
- s_k = parameter proportional to external degree of freedom of group k
- $E_k^{(0)}$ = first interaction energy coefficient of group k
- $E_k^{(1)}$ = second interaction energy coefficient of group k
- $E_k^{(2)}$ = third interaction energy coefficient of group k

Wilson and Cunningham presented only four parameters, namely, b_k , s_k , $E_k^{(0)}$, $E_k^{(1)}$ in the original version of the PFGC equation of state, but Moshfeghian et al. (ref. 7) introduced the fifth parameter, $E_k^{(2)}$, for better accuracy and extension of capabilities of this equation of state. To distinguish between the Wilson and Cunningham version of the PFGC equation of state, Moshfeghian-Erbar-Shariat have dubbed their version as PFGC-MES.

Unfortunately, Wilson and Cunningham did not give a complete set of parameters for the various groups in their equation of state. However, Moshfeghian et al. (refs. 7,8,9,10,11) developed a set of parameters for a wide variety of compounds/groups and thoroughly evaluated their approach which was different from that of Wilson and Cunningham. Table 1 presents the previously unpublished parameters for several groups.

TABLE 1. PFGC-MES group parameters

NO.	GROUP	b , ft ³ /lbmole*	s	$E^{(0)}/R$, °R*	$E^{(1)}/R$, °R	$E^{(2)}/R$, °R
1	H ₂	0.3296	1.8729	-53.6787	8.2008	1.3592
2	CH ₄	0.590	1.871	-129.0	-57.2	7.0
3	CH ₃ -	0.332	1.983	-319.3	-40.0	0.0
4	-CH ₂ -	0.268	0.507	-266.0	-63.7	0.0
5	>CH-	0.2178	-0.8975	-102.26	-86.2	0.0
6	>C<	0.191	-3.39	482.0	-115.0	0.0
7	CH ₂ =	0.354	1.340	-221.6	-54.0	0.0
8	-CH ₂ -cyc	0.3744	0.6333	-198.645	-75.76	0.3
9	-CH= rin	0.258	0.3471	-257.1	-193.8	30.0
10	>C= rin	0.0545	0.0855	-1167.7	-53.8	150.0
11	-CH=	0.344	-0.708	-100.6	-119.0	0.0
12	N ₂	0.445	2.3695	-118.3	-33.2	3.0
13	CO ₂	0.330	3.6985	-614.7	-201.2	20.2
14	CO	0.4053	2.5993	-136.27	-57.1	6.5
15	H ₂ S	0.405	3.4335	-609.6	-172.9	16.0
16	H ₂ O	0.200	2.200	-2651.3	-2779.3	858.5
17	-OH	0.1011	2.1264	-2593.30	-3053.10	1449.90
18	MeOH	0.3732	5.5992	-1407.77	-789.31	108.03
19	NH ₃	0.277	2.7065	-985.6	-838.0	210.0
20	-NH ₂	0.083	3.000	-2177.1	-626.5	271.5
21	Cl-	0.3032	1.4585	-441.9	-113.0	0.0
22	-CH- cyc	0.268	0.507	-271.0	-115.0	0.0
23	CCl ₃ F	0.994	6.5677	-453.33	-47.09	2.88
24	CCl ₂ F ₂	0.8530	6.0670	-404.87	-41.44	1.17
25	CClF ₃	0.8472	4.0990	-253.46	-70.78	9.00
26	CF ₄	0.8472	3.5000	-203.10	-69.76	8.44
27	CHCl ₂ F	0.8454	5.2309	-464.19	-110.10	12.09
28	CHClF ₂	0.6723	4.8861	-446.54	-135.12	22.57
29	CHF ₃	0.5764	3.9402	-365.24	-153.16	23.20
30	CH ₃ Cl	0.6606	3.4159	-445.93	-137.70	13.01
31	C ₂ Cl ₃ F ₃	1.4009	6.3884	-344.77	-64.46	8.03
32	C ₂ ClF ₅	1.2747	6.7136	-323.63	-53.89	7.39
33	C ₂ H ₃ ClF ₂	0.8834	-0.4543	-440.33	-164.25	60.00
34	C ₂ H ₄ F ₂	0.7705	4.7970	-419.36	-209.43	60.00
35	R500*	0.8200	5.6308	-400.32	-88.60	16.30
36	R502*	0.7264	6.6788	-455.71	-57.14	7.51
37	R503*	0.5905	5.2765	-394.93	-57.88	2.25
38	R504*	0.6305	4.8257	-428.95	-172.13	36.47
39	>N-	0.0812	4.6608	-2286.0	1000.0	84.9

rin=ring; cyc=cyclo; *=azeotropic mixtures, treated as pure compounds
 * 1 ft³/lbmole = 6.244 x 10⁻⁵ m³/mole ; 1 °R = 1.8 K

PREDICTION OF PURE COMPONENT PYT PROPERTIES

A summary of the fitting process and some predicted deviations for the PFGC-MES equation of state are reported by investigators (refs. 7,12). The results shown in these references are for selected non-hydrocarbon compounds. Parameters for most polar and non-hydrocarbon components were

derived by considering the components as a single functional group. The remaining compounds were fitted using the group contribution approach and a single interaction parameter. For the most part, these are predicted properties rather than fitted properties. With the exception of the data of the vapor pressure predictions for carbon tetrachloride, the predicted properties are in reasonable agreement with the experimentally determined values. The data for mono-chloromethane are particularly outstanding in that these data were predicted completely using only the group contribution. No fitting was done for this particular compound. With the exception of trans-2-butene, the predicted values appear to be in reasonable agreement with the literature data.

To further demonstrate the power of the PFGC-MES equation of state, Moshfeghian et al. (ref. 7) determined the group parameters for the OH-group in the normal alcohols by fitting ethanol, n-propanol and n-butanol. After they determined the OH- group parameters, the vapor pressure of remaining alcohols up to nC20-OH was predicted. Their results of these predictions are shown in Table 2. With the possible exception of the higher molecular weight alcohols, C17 and above, the predicted and experimental results were in good agreement. In that study, the upper reduced temperature limit for the pure component fitting process was approximately 0.95.

The average absolute deviation between predicted and the experimental values for pure and azeotropic mixtures of refrigerants by the PFGC-MES equation of state is reported in (ref. 10). The predicted values appear to be in excellent agreement with the experimental data. In this reference the capabilities of the PFGC-MES are also compared with that of the SRK (ref. 13) equation of state for the same components. Even though PFGC-MES covers a wider range of reduced temperature, it gives better results.

The comparison results between the experimental PVT data for coal derived compounds and those predicted by PFGC-MES are reported in (ref. 11). For some of the compounds studied in that reference, there was no experimental data available to make a complete comparison. For example, the only data on quinoline that they could find was its vapor pressure reported by Van De Rostyne and Prausnitz (ref. 14). However, the predicted properties such as the saturated liquid volume, saturated vapor volume and heat of vaporization for this compound was reported in this reference. The overall comparison results between the experimental PVT data and those predicted by PFGC-MES is very good. The maximum average absolute deviation is 5.71 percent which corresponds to that of saturated vapor volume of benzene.

TABLE 2. Summary of the average absolute percentage error for vapor pressures of aliphatic alcohols (ref. 7)

Alcohol	Temperature Range, °F *	Average Absolute Percent Error
Methanol	273 - 483	1.16
Ethanol	323 - 503	1.55
1-Propanol	343 - 523	2.13
1-Butanol	358 - 550	1.19
1-Pentanol	410 - 535	5.22
1-Hexanol	450 - 545	5.38
1-Octanol	465 - 561	4.87
1-Nonanol	485 - 661	6.44
1-Decanol	500 - 678	5.74
1-Undecanol	520 - 600	2.91
1-Dodecanol	535 - 617	2.15
1-Tridecanol	550 - 633	0.84
1-Tetradecanol	567 - 650	1.39
1-Pentadecanol	578 - 667	3.32
1-Hexadecanol	594 - 678	5.54
1-Heptadecanol	611 - 689	7.76
1-Octadecanol	628 - 706	10.38
1-Nonadecanol	633 - 717	12.79
1-Eicsanol	644 - 728	15.22

* °F = 32 + 1.8 °C

VAPOR-LIQUID-EQUILIBRIA

Data for binary mixtures of carbon dioxide, nitrogen, hydrogen sulfide, methane, ethane, propane, benzene, toluene, methanol, glycols and a variety of cycloparaffins with light hydrocarbons have been used by researchers to derive the vapor and hydrocarbon-liquid phase binary group interaction coefficients. Mixtures of water with light hydrocarbons, carbon dioxide, hydrogen sulfide, nitrogen and carbon monoxide have also been used by researchers to derive the binary group interaction coefficients for the water-rich liquid phase. Results for selected systems reported by Moshfeghian et al. (ref. 7,8), Majeed et al. (ref. 12) and later by Wagner et al. (ref. 15) are in good agreement with experimental data.

TABLE 3. PFGC-MES binary group interaction coefficient

K_{1j}	LK_{1j}	VK_{1j}	K_{1j}	LK_{1j}	VK_{1j}	K_{1j}	LK_{1j}	VK_{1j}
102	0.691	0.691	216	0.125	0.264	416	0.310	0.290
103	0.411	0.411	218	0.500	0.500	418	0.750	0.750
104	0.720	0.720	221	1.430	1.430	420	0.677	0.677
105	0.460	0.460	304	1.032	1.032	510	0.300	0.300
107	0.550	0.550	307	0.989	0.989	521	0.950	0.950
108	0.695	0.695	308	1.020	1.020	621	5.500	5.500
109	0.950	0.950	312	0.945	0.945	713	0.895	0.895
110	0.050	0.050	313	0.850	0.850	716	0.250	0.380
112	0.600	0.600	315	0.830	0.830	916	0.470	0.250
203	0.945	0.945	316	0.210	0.335	918	0.805	0.805
204	0.900	0.900	318	0.750	0.750	1113	0.980	0.980
205	0.500	0.500	405	1.395	1.395	1116	0.420	0.300
207	1.050	1.050	407	0.940	0.940	1213	0.450	0.450
208	0.880	0.880	408	1.050	1.050	1215	0.450	0.450
212	0.945	0.945	410	0.600	0.600	1218	0.500	0.500
213	0.765	0.765	412	0.650	0.650	1318	0.840	0.840
215	0.720	0.720	413	0.900	0.900	1618	0.900	0.900
216	0.125	0.264	415	0.750	0.750			

K_{1j} = 100x(ID No for group i)+(ID No for group j)

VK_{1j} = Vapor phase binary group interaction parameter

LK_{1j} = Liquid phase binary group interaction parameter

Using the binary group interaction parameters defined in Table 3, researchers (refs. 7,12,15) predicted the behavior of multi-component systems. Figure 1 presents one such comparison based on Yarbrough's data (ref. 16). The quality of agreement shown here is typical for petroleum/natural gas systems. These results are comparable with SRK and PR predictions for this system.

The ability of the PFGC-MES equation of state to describe the behavior of more non-ideal systems is illustrated in Figs. 2 and 3. These diagrams are typical of the behavior that one can expect for these kind of systems. The prediction of the liquid phase composition for methanol-benzene system (ref. 17) in Fig. 2 are not particularly good at low concentrations of benzene. However, the higher concentrations of benzene are predicted quite well.

Figure 3 shows a plot of the predicted and experimental K-values for the hydrogen sulfide-water system (ref. 18). Again, agreement between experiment and prediction appears to be satisfactory.

Figure 4 shows the effect of pressure on the solubility of water in the propane vapor phase and the solubility of propane in the liquid water phase at the approximate propane critical isotherm (ref. 19). The agreement between experimental and calculated values must be considered excellent for this system. Researchers (refs. 7,15,18) report similar agreement between predicted and experimental hydrocarbon vapor and liquid water phase solubilities for most of the available data.

VAPOR-LIQUID-LIQUID-EQUILIBRIA AND HYDRATE FORMATION

The capability of this equation of state to handle three-phase calculations has been evaluated by several investigators. The PFGC ability to predict hydrate formation condition and hydrate inhibition have been also studied (refs. 15, 21). The hydrate model described by Parish and Prausnitz (ref. 22) is used as the basis for hydrate formation calculations. The activity

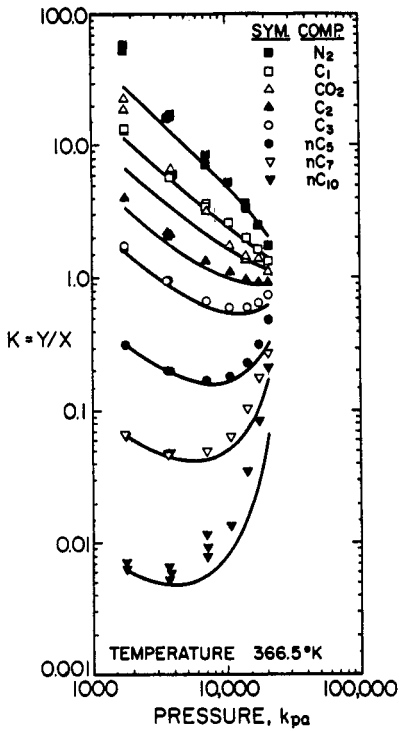


Figure 1. Comparison of predicted and experimental K-values (ref. 7) Yarborough data.

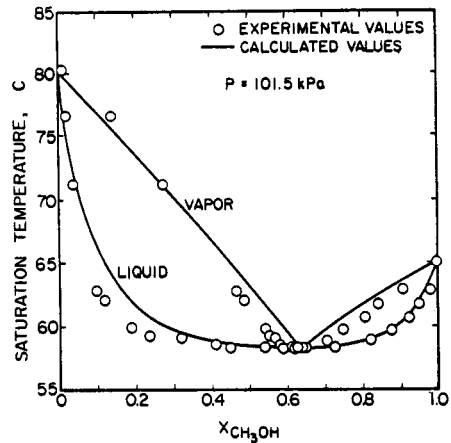


Figure 2. Comparison of predicted and experimental T-X diagram for the methanol-benzene system (ref. 7).

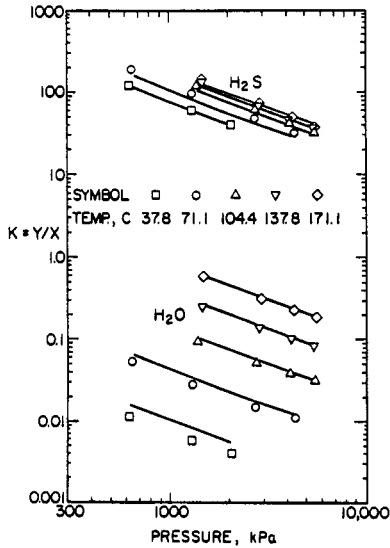


Figure 3. Comparison of experimental and calculated K-values for the H₂S - H₂O system (ref. 7)

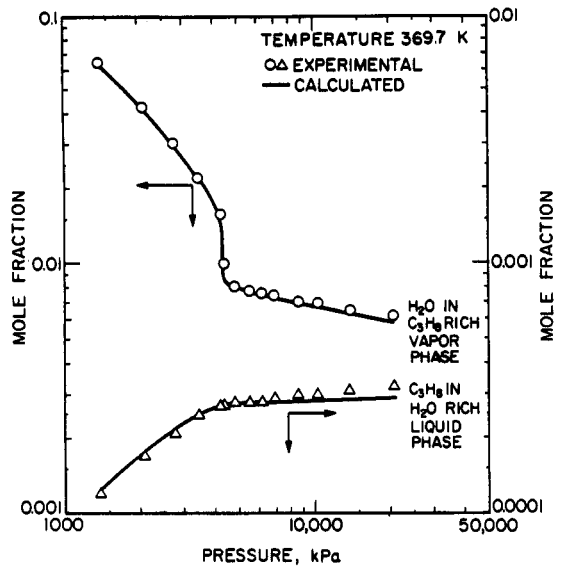
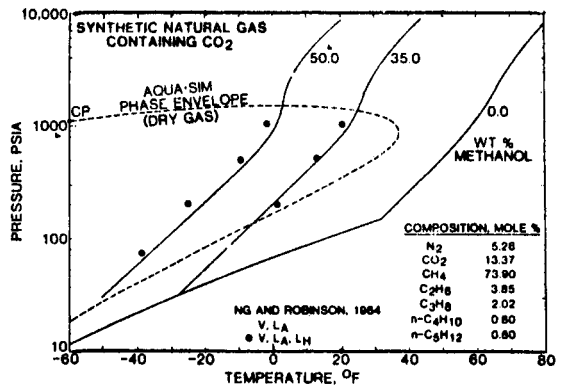


Figure 4. Mutual solubility of C₃H₈ and H₂O (ref. 7)

Figure 5. Experimental and predicted hydrate formation curves for a synthetic conditions for a natural gas (ref. 15)



coefficient corrections suggested by Menten et al. (ref. 23) were included by Wagner and co-workers to account for the effects of inhibitors such as methanol and glycols. Wagner, Erbar and Majeed (refs. 20) have developed a computer simulation program, AQUA*SIM, for process design involving three-phase calculations and hydrate formation as described above, based on PFGC. All of these investigators report good agreement between experimental and predicted hydrate formation or inhibition conditions. Figure 5 (ref. 15) shows a typical comparison between the experimental data and those predicted by PFGC.

As an example of its application for phase equilibrium and hydrate inhibition calculations, Wagner et al. (ref. 15) considered the process described by Moshfeghian et al. (ref. 20). The feed natural gas enters a separator operating at 150 OF and 2000 psia where liquid water and hydrocarbon are knocked out. The composition of the pipeline gas leaving the separator is also given in reference (ref. 15). The Hydrocarbon dew point curve for the pipeline gas is shown in Fig. 6; the water dew point curves lies inside the phase envelope. The predicted hydrate formation curve has also been plotted in Fig. 6. The pipeline temperature and pressure profile is given in (ref. 18). Pipeline gas leaves the separator saturated with water at 150 OF and 2000 psia. The pipeline operating line has been plotted on Figure 6 and crosses the hydrate formation curve between stations 3 and 4. If 25 weight percent methanol is added to the pipeline gas leaving the separator, hydrate formation is depressed; the pipeline operating line no longer intersect the hydrate formation curve.

The AQUA*SIM program was used to obtain the pipeline gas composition using a three-phase flash calculation. Three-phase flash calculations were also performed to determine the condensation of hydrocarbon liquid and distribution of water and methanol in the aqueous and vapor phases along the pipeline. The results which were obtained by Wagner et al. (ref. 18) provide an estimate of methanol vaporization losses from the solubility of methanol in the vapor phase.

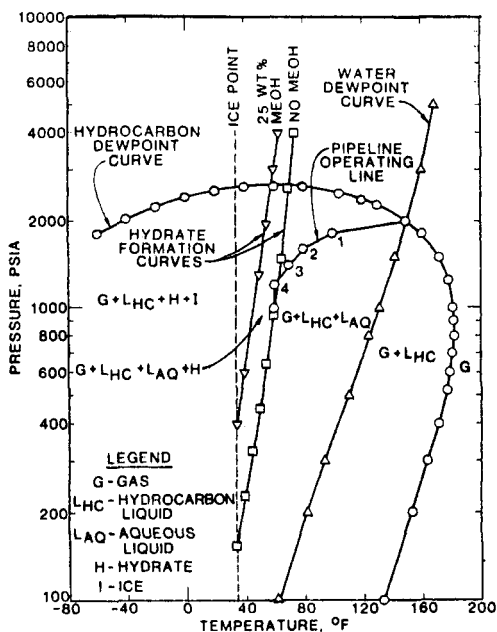


Figure 6. Example of phase behavior and process/pipeline conditions a natural gas system (ref. 15)

CONCLUSIONS

Several papers on the capabilities and applications of the PFGC equation of state have been reviewed. All of the authors who evaluated this equation of state believe that the PFGC equation of state can provide reasonable predictions for light gas components recoveries, systems involving hydrocarbon-water-methanol distribution coefficients, etc. They also believe that the PFGC approach is more specifically applicable to hydrate formation and coal liquification processing systems than any of the currently available methods of predicting thermodynamic properties. In addition, the PFGC has also been successfully applied to ionic systems by Friedemann (ref. 24).

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REFERENCES

1. J. R. Cunningham and G. M. Wilson, Paper Presented at GPA Meeting, Tech Section F, March 25, Denver, Colorado, (1974).
2. G. Soave, Chem. Eng. Sci., 27(6), 1197, (1972).
3. D. Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fundam., 15(3), 59-64, (1976).
4. K. E. Starling, Fluid Thermodynamic Properties for Light Petroleum Systems, Gulf Publishing Co., Houston, Texas, (1973).
5. A. R. Wilson, R. N. Maddox and J. H. Erbar, Oil & Gas J. August 21, (1978).
6. M. R. Brule; M. R., K. H. Kumar and S. Watanasiri, Oil & Gas J. 87-93, (1985).
7. M. Moshfeghian, A. Shariat and J. H. Erbar, Paper Presented at the A.I.Ch.E. National Meeting, Houston, Texas, April 1-5, (1979).
8. M. Moshfeghian, A. Shariat and J. H. Erbar, Paper Presented at NBS/NSF Symp. on Thermo. of Aqueous Sys., Airlie House, Virginia, (1979).
9. M. Moshfeghian, A. Shariat and J. H. Erbar, ACS Symposium Series 113, 334-359, (1979).
10. M. Moshfeghian, J. H. Erbar, A. Shariat and R. C. Erbar, Ind. & Eng. Chem. Research, (in press).
11. M. Moshfeghian, M. Taheri, A. Shariat and R. N. Maddox, Presented for Publication
12. Majeed; A. I., J. Wagner, and J. H. Erbar, Proceeding of the 1984 Summer Computer Simulation Conference, Boston, Massachusetts, 537-542, Society for Computer Simulation, July 23-25, (1984).
13. L. Asselineau, G. Bogdanic and J. Vidal, Chem. Eng. Sci., 33, 1269-1276, (1978).
14. C. Van De Rostyne and J. M. Prausnitz, JCED, (1980).
15. J. Wagner, R. C. Erbar and A. I. Majeed, Presented at Sixty-fourth Annual GPA Convention, March 18-20, Houston, Texas, (1985).
16. L. Yarborough and J. L. Vogel, Chem Eng. Prog., Sys. Series, 63(81), 1-9, (1967).
17. I. Nagata, JCED, 14(4), 418, (1969).
18. F. T. Selleck, L. T. Carmichael, and B. H. Sage, Ind. Eng. Chem., 44(9), 2219-2226, (1952).
19. R. Kobayashi and D. L. Katz, Ind. Eng. Chem., 45(2), (1953).
20. A. Shariat, M. Moshfeghian and J. H. Erbar, Oil & Gas J., 77(47), 126-133, (1979).
21. B. Roozbehani, M.S. Thesis (in Farsi), Chemical Engineering Department, Shiraz University, (1988).
22. W. R. Parish and J. M. Prausnitz, Ind. Eng. Chem. Proc. Des. Dev., 11(1), 26-35, (1972).
23. P. D. Menten, W. R. Parish and E. D. Sloan, Ind. Eng. Chem. Proc. Des. Dev., 20(2), 399-401, (1981).
24. J. D. Friedemann, Doctoral Dissertation, School of Chemical Engineering, Oklahoma State University, (1987).