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PARAMETERS OF THE MODIFIED SOAVE-REDLICH-KWONG EQUATION OF STATE FOR SOME CHLOROFLUOROCARBONS, HYDROFLUOROCARBONS AND FLUOROCARBONS

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SUMMARY

This work presents a compilation of the two parameters of the modified Soave-Redlich-Kwong equations of state (MSRK) for 41 fluorine-containing compounds. Vapor pressures data were compiled, tested, screened, and subsequently used for the evaluation of the parameters. Satisfactory results are obtained for the representation of vapor pressures and enthalpies of vaporization.

INTRODUCTION

The set of chlorofluorocarbons derived from methane, known commercially as Freons, are important in the refrigeration industry [1]. The perfluorocarbons are utilized in Rankine Organic Cycle (ROC) as working fluids [2]. These applications require complete and accurate knowledge of the thermodynamic properties of the fluids of interest which can be estimated through the use of an equation of state.

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However the available information on fluoro-compounds required for the application of equations of state method is very much limited.

Soave [3] suggested a modified form for the temperature dependent parameter α (T) in terms of two parameters m and n which was found to result in improved behavior for polar systems. The adjustable parameters m and n, specific for each substance, have been determined using a simplified least squares fit [3]. Camporese *et al.* [4] and Sandrusi *et al.* [5] evaluated the MSRK parameters from vapor pressure data for eighteen fluoro-compounds only. Tabulation of the parameters m and n for other components of interest should be available, in order to extend the application of the equation for the evaluation of thermodynamic properties. The objective of the present study is to extend and facilitate the use of Soave equation of state and its modified form for the representation of thermodynamic properties of fluorine-containing materials.

The required vapor pressures and critical properties, found in the literature, on fluorinated and fluorinated-chlorinated hydrocarbons, are compiled and screened through examination of the experimental errors and the techniques involved in these measurements. Once the proper vapor pressure data set and critical properties have been selected for each compound, the acentric factor is calculated according to the procedure of Passut and Danner [6]. The acentric factors are required in the original form of Soave-Redlich-Kwong method.

THEORY

The original SRK equation is given by

$$P = \frac{R\,T}{v-b} - \frac{a(T)}{v(v+b)} \qquad (1)$$

where

$$a(T) = a_c\,\alpha\,(T) \qquad (2)$$

$$a_c = 0.42747\,R^2 T^2{}_c/P_c \qquad (3)$$

$$\alpha\,(T) = [1+k(1-T_r^{0.5})]^2 \qquad (4)$$

$$k = 0.48 + 1.574\,\omega - 0.176\omega^2 \qquad (5)$$

and

$$b = 0.08664\,R\,T_c/P_c \qquad (6)$$

Soave [3] proposed an alternative form for the temperature dependent parameter α (T), for polar substances, expressed according to the following equation:

$$\alpha\,(T) = 1 + (1-T_r)(m+n/T_r) \qquad (7)$$

The parameters m and n are evaluated for each individual substance investigated, using the 'simplified procedure' of weighted least squares fit. In this method, developed by Soave [3], the following two linear equations are solved simultaneously for m and n:

$$m \sum_k \delta^2_k (1-T_{r,k})^2 + n \sum_k \delta^2_k \frac{(1-T_{r,k})^2}{T_{r,k}}$$

$$= \sum_k \delta^2_k (1-T_{r,k}) (\alpha_{exp,k} -1) \qquad (8)$$

$$m \sum_k \delta^2_k \left(\frac{1-T_{r,k}}{T_{r,k}} \right)^2 + n \sum_k \delta^2_k \left(\frac{1-T_{r,k}}{T_{r,k}} \right)^2$$

$$= \sum_k \delta^2_k \left(\frac{1-T_{r,k}}{T_{r,k}} \right) (\alpha_{exp,k} -1) \qquad (9)$$

where δ_k indicates the error in the measured vapor pressure and it is given by:

$$\delta_k = \frac{\partial \ln P^\circ_{exp}}{\partial \alpha} = [\ln (1+\delta)]/(\alpha` -\alpha_{exp}) \qquad (10)$$

The value of δ is typically 0.001-0.1. $\alpha`$is calculated when the experimental vapor pressure, $P_{exp,k}$, is increased or decreased by a value of $(1+\delta)$.

An attempt was also made in this work to obtain m and n for each substance using unweighted least squares fit. The procedure is fairly simple and direct. The values of m and n are calculated solving the following two equations simultaneously

$$m \sum_k (1-T_{r,k})^2 + n \sum_k \frac{1-T_r}{T_{r,k}} = \sum_k (1-T_{r,k})(\alpha_{exp,k} -1) \qquad (10a)$$

$$m \sum_k \frac{(1-T_{r,k})^2}{T_{r,k}} + \sum_k \frac{(1-T_{r,k})^2}{(T_{r,k})^2} = \sum_k \frac{(1- T_{r,k})}{T_{r,k}} (\alpha_{exp,k}-1) \qquad (11)$$

The correlated parameters are tested by performing vapor pressure and enthalpy calculations. The enthalpy departure function for the MSRK equation of state at a given temperature and pressure is given by:

$$\frac{H-H^*}{RT} = Z-1 - \frac{A}{B} [1 +(\frac{1}{\alpha}) (m \, T_r + \frac{n}{T_r})] \ln (1+ \frac{B}{Z}) \quad (12)$$

where

$$Z = PV/RT \quad (13)$$

$$A = aP/R^2T^2 \quad (14)$$

$$B = bP/RT \quad (15)$$

Enthalpy of vaporization is, thus, calculated using the following equation:

$$\Delta H^{vap.} = (H-H^*)^V - (H-H^*)^L \quad (16)$$

RESULTS AND DISCUSSION

Table 1 shows a compilation of the alternative names (refrigerant No.), structural formulae, normal boiling point, critical parameters, temperature ranges, pressure ranges, the acentric factor and the source of the data of the components studied in this work. The compounds are arranged in an increasing order of the acentric factor. Most of the vapor pressure data of the components studied in this work are taken from Engineering Sciences Data Unit [7, 8]. In the absence of experimental vapor pressure data, multi-constant vapor pressure equations were used.

The parameters m and n of the MSRK equation have been determined, for the 41 compounds using the simplified

TABLE 1

Summary of the available data on fluorinated hydrocarbons used in this work

No	Component Name (Refrigerant No.)	Structural formulae	Normal boiling point k	Critical Parameters				Vapor Pressure Data			Acentric Factor	
				P_c atm	T_c k	V_c cm^3/gmole	Ref. No.	Temp. Range k	Pressure range atm	Ref. No. for PVT	ω	Ref. No.
1.	1,1 Difluoroethylene (R1132a)	$H_2C=CF_2$	187.5	44.016	302.9	151.1	9	145-290	0.05-33.1	9	0.14	9
2.	Fluoroethylene (R1141)	$H_2C=CHF$	225.6	51.714	327.9	144	9	159-319	0.05-43.09	9	0.157	9
3.	Chlorotrifluoromethane (R13)	CF_3Cl	191.72	38.599	302.29	180.4*	7	150-273	0.949-19.7	7	0.173	7
4.	Tetrafluoromethane (R14)	CF_4	145.16	36.93	227.5	140	10	90-220	0.001-29.5	10	0.17987	Calc.$
5.	Dichlorodifluoromethane (R12)	CF_2Cl_2	243.4	40.71	384.95	216.7*	1	214-293	0.22-5.58	1	0.1801	Calc.$
6.	Trichlorofluoromethane(R11)	$CFCl_3$	297	43.5	471.2	248	11	240-300	0.076-1.117	11	0.18824	Calc.$
7.	Fluoromethane (R41)	CH_3F	194.8	58	317.8	124	11	141-206	0.013-11.78	11	0.1896	Calc.$
8.	Dichlorofluoromethane(R21)	$CHFCl_2$	282.05	51.1	451.5	196.4*	7	222-394	0.49-19.7	7	0.207	7
9.	Fluoroethane (R161)	H_3CCH_2F	235.5	49.54	375.3	169	9	266-361	3.3-37.9	9	0.215	9

10.	Chloro-1,1-difluoroethelyne(R1122)	$ClHC=CF_2$	254.55	44.067	400.5	197*	8	200-394	0.049-39.4	8	0.22	8
11.	Chlorodifluoromethane (R22)	CHF_2Cl	232.4	49.05	369.3	165.6	9	170-350	0.014-33.8	9	0.221	9
12.	1,1,1-Trichlorotrifluoroethane(R113a)	F_3CCCl_3	320.73	30.12	486	-	8	300-457	0.49-19.7	8	0.225	8
13.	1-Chloro-2-fluoroethane(R151)	FH_2CCH_2Cl	326.15	47.37	515	-	8	285-401	0.04-39.47	8	0.23	8
14.	Tetrafluoroethylene (R1114)	$F_2C=CF_2$	197.53	39.748	306.5	172*	8	142-277	0.01-19.7	8	0.235	8
15.	Chlorotrifluoroethylene(R1113)	$F_2C=CFCl$	244.79	39.08	379	212*	8	193-344	0.049-19.7	8	0.237	8
16.	1-Chloro-1,1-difluoroethane(R142b)	H_3CCF_2Cl	263.35	40.68	410.25	231.025	12	264-404	1.0-36.7	12	0.2373	Calc.$
17.	Fluorobenzene	C_6H_5F	358.5	44.9	560.1	271	11	250-370	0.0063-1.4	11	0.24424	Calc.$

(Continued)

TABLE 1 (cont.)

No	Component Name (Refrigerant No.)	Structural formulae	Normal boiling point k	Critical Parameters				Vapor Pressure Data			Acentric Factor	
				P_c atm	T_c k	V_c cm^3/gmole	Ref. No.	Temp. Range k	Pressure range atm	Ref. No. for PVT	ω	Ref. No.
18.	1,2-Dichlorodifluoroethylene(R1112)	ClFC=CFCl	293.81	45.211	460	-	8	232-451.2	0.049-39	8	0.23736	8
19.	1,1,1-Trifluoroethane(R143a)	H_3CCF_3	225.89	36.354	346.6	194*	8	167.5-318	0.019-19.7	8	0.246	8
20.	1,1-Dichlorotetrafluoroethane(114a)	F_3CCFCl_2	276.15	32.568	418.65	294.2*	8	216.390	0.049-19.7	8	0.251	8
21.	Chloropentafluoroethane(R115)	F_3CCF_2Cl	234.01	31.2	353.2	252	11	175-230	0.024-0.83	11	0.2529	Calc.$
22.	1,1,2-Trichlorotrifluoroethane(R113)	ClF_2CCFCl_2	320.71	33.7	487.3	325.5*	8	252-452	0.049-19.7	8	0.255	8
23.	1,2-Dichlorotetrafluoroethane(R114)	$F_2ClCCClF_2$	277.06	32.14	418.9	293.8*	8	179.8-391	.0019-19.7	8	0.256	8
24.	1,1-Difluoroethane (R152a)	H_3CCHF_2	248.15	44.362	386.65	181*	8	157-380	0.00098-39	8	0.256	8
25.	Hexafluoroethane (R116)	F_3CCF_3	194.9	30.1199	292.9	222*	8	182-276	0.49-19.7	8	0.256	8
26.	Trifluoromethane (R23)	CHF_3	191.04	47.66	299.06	132.7*	7	121-265	0.00098-19.7	7	0.264	7

27.	1,2-Dichloro-1,1-difluoroethane(R132b)	ClH_2CCF_2Cl	319.78	43.9378	496	-	8	202-488	.00098-39	8	0.268	8
28.	1,2-Difluoroethane (R152)	FH_2CCH_2F	283.65	45.497	441	-	8	266.8-432	0.49-39.4	8	0.273	8
29.	Difluoromethane(R32)	CH_2F_2	221.5	57.4	351.5	120.8*	7	140.7-344	.00098-49	7	0.276	7
30.	1,1,2-Trifluoroethane(R143)	FH_2CCHF_2	278.15	38.37	425	-	8	191.2-388	.0049-19.7	8	0.28	8
31.	Chloro-1,1,2,2-tetrafluoroethane(R124a)	F_2HCCF_2Cl	263.0	36.674	399.85	244*	8	160-367.5	.00049-19.7	8	0.283	8
32.	Tetrachloro-1,2-difluoroethane(R112)	$Cl_2FCCFCl_2$	365.81	38.105	551	-	8	304.5-505.6	0.098-19.7	8	0.334	8
33.	Chloropentafluoroacetone	C_3F_5ClO	280.95	28.2319	410.65	-	13	233-403	0.098-24.7	13	0.34203	Calc.$
34.	Perfluorocyclobutane (RC318)	C_4F_8	267.3	27.5	388.35	325	13	242-267	0.3-0.99	14	0.3571	Calc.$

(Continued)

TABLE 1 (cont.)

No	Component Name (Refrigerant No.)	Structural formulae	Normal boiling point k	Critical Parameters				Vapor Pressure Data			Acentric Factor	
				P_c atm	T_c k	V_c cm^3/gmole	Ref. No.	Temp. Range k	Pressure range atm	Ref. No. for PVT	ω	Ref. No.
35.	Perfluorobutane	C_4F_{10}	270.95	23	386.45	378	13	233-263	0.16-0.713	14	0.3726	Calc.$
36.	Perfluorobenzene	C_6F_6	353.4	32.6	516.7	377.087	11	270-385	0.023-2.5	11	0.4	11
37.	Perfluoropentane	C_5F_{12}	302.35	20.198	422.15	512	13	282-332	0.44-2.64	14	0.41948	Calc.$
38.	Perfluorocyclohexane	C_6F_{12}	323.8	24	457.2	459*	14	336-344	1.48-1.89	14	0.4367	Calc.$
39.	Perfluoromethyl-cyclohexane	C_7F_{14}	349.5	23	486.8	-	11	290-385	0.0937-2.7	11	0.48459	Calc.$
40.	Perfluoro-n-hexane	C_6F_{14}	330.3	18.8	451.7	442	11	270-330	0.07-0.989	11	0.49401	Calc.$
41.	Perfluoro-n-heptane	C_7F_{16}	355.7	16	474.8	664	11	270-390	0.02-2.68	11	0.55676	Calc.$

* From Reference No.9

$ Calculated using Pitzer definition of acentric factor.

weighted and unweighted least square fit. The values are presented in Table 2. In testing the capability of the equations to represent the thermodynamic properties of a substance, it is preferable to assess the deviation through the average absolute deviation, Δ , especially in the low vapor pressure range. The large percentage deviations that might be obtained in this range can lead to difficulties in the comparison between the different correlations. Therefore Δ is used as basis of comparison over the whole pressure range. A summary of the calculated results for vapor pressures using MSRK equation and the original SRK is shown in Table 3 for the whole pressure range and for pressures above 1 atm. It is shown that the proposed MSRK equation reproduces the experimental vapor pressure data with better accuracy than that of the original SRK equation over the whole pressure range. The overall average deviation, Δ , is 0.018 and 0.0169 atm for the weighted and the unweighted MSRK respectively compared to 0.0576 atm for the original SRK. At pressures above 1 atm MSRK also yields a better agreement with the experimental data. The overall average absolute percentage deviations obtained were 0.44% and 0.38% for weighted and unweighted MSRK respectively compared to 1.15% given by the original SRK. The relatively higher percentage deviation obtained can be attributed to the generalized nature of the original SRK and because it was developed mainly for hydrocarbons.

Moreover, parameters obtained in this work are different from those previously reported in the literature by

TABLE 2

Modified SRK Parameters for the Fluorocompounds under study

No	Component	No. of data points	Reduced Temp. Range	Modified SRK Parameters		Unweighted MSRK Parameters	
				m	n	m	n
1	$C_2H_2F_2$	30*	0.47-0.95	0.7381	0.0553	0.7293	0.0603
2	C_2H_3F	33*	0.48-0.97	0.5176	0.2169	0.5209	0.2149
3	$CClF_3$	9	0.49-0.9	0.6176	0.1737	0.6176	0.1737
4	CF_4	16	0.39-0.96	0.6635	0.1515	0.659	0.1536
5	CCl_2F_2	48	0.55 -0.76	0.6129	0.1848	0.6127	0.1849
6	CCl_3F	13*	0.51-0.63	0.6336	0.1819	0.6328	0.1823
7	CH_3F	14*	0.44 -0.65	0.7056	0.1372	0.7028	0.1387
8	$CHFCl_2$	9	0.49-0.87	0.6310	0.2083	0.6284	0.2097
9	C_2H_5F	20*	0.71 0.96	0.7054	0.1775	0.7044	0.1782
10	C_2HClF_2	10	0.5 - 0.98	0.6449	0.2152	0.6484	0.2133
11	CHF_2Cl	37*	0.46- 0.94	0.666	0.2001	0.6638	0.2017
12	$C_2Cl_3F_3$	6	0.62-0.94	0.674	0.2018	0.6828	0.1959
13	C_2ClH_4F	10	0.5 - 0.97	0.6628	0.2163	0.6658	0.2145
14	C_2F_4	11	0.46-0.91	0.6867	0.207	0.684	0.2084
15	C_2ClF_3	9	0.51-0.9	0.6747	0.2165	0.6786	0.2143
16	$C_2H_3ClF_2$	29	0.64-0.98	0.71165	0.1866	0.6995	0.1953
17	C_6H_5F	25*	0.44-0.66	0.7393	0.1941	0.7321	0.1978
18	$C_2Cl_2F_2$	10	0.5 - 0.98	0.6902	0.2164	0.6937	0.2144
19	$C_2H_3F_3$	10	0.48-0.92	0.6964	0.2136	0.6977	0.2129
20	$C_2Cl_2F_4$	9	0.52-0.93	0.7008	0.2167	0.7056	0.2139
21	C_2ClF_5	12*	0.49-0.65	0.7076	0.2137	0.7065	0.2143
22	$C_2Cl_3F_3$	9	0.52-0.93	0.7076	0.2167	0.7124	0.2139
23	$C_2Cl_2F_4$	13	0.43-0.93	0.7074	0.2168	0.7097	0.2156
24	$C_2H_4F_2$	15	0.41-0.98	0.7484	0.1952	0.7398	0.1993
25	C_2F_6	6	0.62-0.94	0.7372	0.1977	0.7459	0.1918
26	CHF_3	14	0.40-0.88	0.7962	0.1723	0.7853	0.1775
27	$C_2Cl_2H_2F_2$	15	0.41-0.98	0.7868	0.1869	0.7683	0.1957
28	$C_2H_4F_2$	7	0.60-0.98	0.7584	0.2043	0.7663	0.1992
29	CH_2F_2	15	0.4-0.979	0.8503	0.1498	0.8392	0.1549
30	$C_2H_3F_3$	12	0.45-0.9	0.7692	0.2072	0.7671	0.2082
31	C_2ClHF_4	15	0.4-0.9	0.7998	0.1938	0.791	0.1979
32	$C_2Cl_4F_2$	8	0.55-0.9	0.8590	0.2122	0.8663	0.2078
33	C_3F_5ClO	35*	0.57-0.98	0.7018	0.3309	0.7006	0.3317
34	C_4F_8	6*	0.62-0.68	0.7198	0.3375	0.7199	0.3374
35	C_4F_{10}	10*	0.6 - 0.68	0.8271	0.2845	0.826	0.2851
36	C_6F_6	24*	0.52-0.74	0.8516	0.3009	0.8517	0.3009
37	C_5F_{12}	11*	0.66-0.78	0.6569	0.4611	0.6538	0.4634
38	C_6F_{12}	5*	0.73-0.75	1.1143	0.1635	1.1143	0.1635
39	C_7F_{14}	20*	0.59-0.79	1.2063	0.1657	1.2214	0.1557
40	C_6F_{14}	13*	0.59-0.73	0.8998	0.3877	0.9002	0.3874
41	C_7F_{16}	25*	0.56-0.82	0.9354	0.4432	0.9346	0.4436

* Data points were generated from vapor pressure equations (See Table 1)

Sandarusi et al. [5]. This is expected since the parameters obtained are dependent on the quality and the range of the data used for their evaluation. The values of m and n, obtained using unweighted least squares fit, are not significantly different from those obtained by the weighted least squares technique which requires more computation time. In addition, their subsequent use in vapor pressure calculations produces nearly the same results. In brief, no significant improvement has been obtained by using the weighted least squares fit as shown in Table 3. This may be attributed to the fact that vapor pressure data available in the literature on halocarbons in the low range are not too many compared to those reported in the higher range.

Finally, the enthalpy of vaporization at the normal boiling point for fifteen fluorocompounds, selected arbitrarily, have been calculated and compared with the literature values. A summary of the results is shown in Table 4. The results show that MSRK yield better results over the original SRK, where the average absolute percentage deviation is 1.13 compared to 1.91% given by original SRK.

CONCLUSIONS

A new tabulation of the parameters m and n of the MSRK for fluorine-containing compounds has been carried out which would broaden the application of this equation for thermodynamic property evaluation of these components.

TABLE 3

Comparison between MSRK and SRK equation of state for vapor pressure calculations

No.	Component	WEIGHTED MSRK			UNWEIGHTED MSRK			ORIGINAL SRK		
		For whole Press. range		For P>1 atm	For whole press. range		For P>1 atm	For whole press. range		For P>latm
		δ %	|Δ P| atm	δ %	δ %	|Δ P| atm	δ %	δ %	|Δ P| atm	δ %
1	$C_2H_2F_2$	0.476	0.0314	0.403	0 460	0.0227	0.327	3.970	0.1614	1.851
2	C_2H_3F	0.451	0.0764	0.522	0.467	0.0744	0.535	1.240	0.0920	0.857
3	$CClF_3$	0.186	0.0107	0.192	0.186	0.0106	0.191	1.143	0.0480	0.807
4	CF_4	0.426	0.0152	0.367	0.429	0.0132	0.253	2.638	0.0594	0.873
5	CCl_2F_2	0.084	0.0013	0.062	0.084	0.0013	0.062	0.647	0.0091	0.394
6	CCl_3F	0.074	0.0004	0.144	0.078	0.0003	0.128	1.540	0.0054	0.798
7	CH_3F	0.292	0.0018	0.454	0.295	0.0015	0.362	5.427	0.0116	1.414
8	$CHFCl_2$	0.332	0.0134	0.278	0.382	0.0132	0.259	0.474	0.0386	0.546
9	C_2H_5F	0.034	0.0045	0.097	0.033	0.0043	0.096	2.110	0.2820	2.111
10	C_2HClF_2	0.300	0.0359	0.408	0.314	0.0347	0.426	0.690	0.0747	0.868
11	CHF_2Cl	0.304	0.0216	0.262	0.298	0.0216	0.232	1.140	0.0804	0.775
12	$C_2Cl_3F_3$	0.349	0.0309	0.359	0.371	0.0289	0.359	0.880	0.0847	0.934
13	C_2ClH_4F	0.282	0.0377	0.388	0.291	0.0364	0.402	0.919	0.0864	0.919
14	C_2F_4	0.514	0.0172	0.482	0.502	0.0178	0.453	0.966	0.0525	1.035
15	C_2ClF_3	0.278	0.0257	0.413	0.315	0.0247	0.439	1.034	0.0660	1.053
16	$C_2H_3ClF_2$	0.400	0.0511	0.465	0.397	0.0462	0.461	0.832	0.0633	0.832
17	C_6H_5F	0.699	0.0032	1.414	0.720	0.0028	1.186	1.270	0.00419	0.845
18	$C_2Cl_2F_2$	0.282	0.0355	0.388	0.302	0.0342	0.405	1.170	0.0874	1.025
19	$C_2H_3F_3$	0.336	0.0222	0.434	0.718	0.3420	0.0219	0.447	1.2960	0.097
20	$C_2Cl_2F_4$	0.293	0.0265	0.436	0.329	0.0248	0.439	1.376	0.0691	1.150
21	C_2ClF_5	0.092	0.0003	-	0.094	0.00027	-	2.016	0.0039	-
22	$C_2Cl_3F_3$	0.289	0.0263	0.433	0.325	0.0245	0.435	1.544	0.0703	1.160
23	$C_2Cl_2F_4$	0.323	0.0175	0.343	0.315	0.0171	0.342	1.770	0.0434	0.929
24	$C_2H_4F_2$	0.397	0.0188	0.729	0.805	0.0179	0.544	1.990	0.0594	1.091
25	C_2F_6	0.345	0.0305	0.355	0.366	0.0286	0.355	1.193	0.1000	1.181

26	CHF_3	0.920	0.0159	0.964	0.908	0.0098	0.609	5.967	0.0480	1.330
27	$C_2Cl_2H_2F_2$	1.312	0.0405	1.400	1.336	0.0286	0.899	2.805	0.0282	0.535
28	$C_2H_4F_2$	0.325	0.0436	0.330	0.332	0.0400	0.317	1.388	0.1400	1.256
29	CH_2F_2	0.872	0.0232	0.872	0.872	0.0168	0.548	9.740	0.0740	1.540
30	$C_2H_3F_3$	0.443	0.0170	0.503	0.443	0.0174	0.477	3.429	0.0617	1.390
31	C_2ClHF_4	0.841	0.0130	0.822	0.842	0.0117	0.612	4.700	0.0497	1.370
32	$C_2Cl_4F_2$	0.338	0.0298	0.434	0.377	0.0272	0.436	3.080	0.1160	1.793
33	C_3F_5ClO	0.111	0.0068	0.087	0.108	0.0068	0.083	0.387	0.1425	0.369
34	C_4F_8	0.008	0.00005	-	0.008	0.00008	-	0.190	0.0012	-
35	C_4F_{10}	0.076	0.00031	-	0.074	0.00029	-	1.107	0.0032	-
36	C_6F_6	0.023	0.00028	0.043	0.024	0.00028	0.043	2.030	0.006	0.460
37	C_5F_{12}	0.155	0.00213	0.157	0.155	0.00210	0.153	0.333	0.0062	0.485
38	C_6F_{12}	0.002	0.00017	0.002	0.002	0.00014	0.002	2.182	0.0372	2.182
39	C_7F_{14}	0.802	0.00930	0.853	0.823	0.00869	0.788	4.396	0.0402	4.260
40	C_6F_{14}	0.024	0.00012	-	0.025	0.00012	-	0.957	0.0023	-
41	C_7F_{16}	0.079	0.00061	0.089	0.077	0.00058	0.084	1.036	0.0085	1.348
	Average	0.345	0.0185	0.443	0.363	0.0169	0.383	1.800	0.0576	1.150

For any property x

$$\delta\% = \frac{1}{N}\sum_{i=1}^{N} \mid x_{exp.} - x_{calc.} \mid / x_{exp.} * 100$$

$$\Delta = \frac{1}{N}\sum_{i=1}^{N} \mid x_{exp.} - x_{calc.} \mid$$

where N is the number of experimental points.

TABLE 4

Absolute percentage deviations in calculated enthalpy of vaporization at normal boiling point.

Component	Literature Values			δ %	
	Normal Boiling point K	$\Delta H^{Vap.}$ Cal/gmole	Ref. No.	Original SRK	Unweighted MSRK
C_2F_6(R116)	194.9	3860	11	1.100	0.640
CF_3Cl(R13)	191.7	3706	11	2.013	1.030
$C_2H_4F_2$(R152a)	248.4	5100	11	3.300	1.890
$C_2Cl_3F_3$(R113)	320.7	6462.72	15	1.100	0.093
$C_2H_3F_3$(R143a)	225.5	4580	11	1.200	0.140
CHF_3(R23)	191.0	4004	16	3.060	0.760
$C_2Cl_2F_4$(R114)	276.9	5560	11	0.806	0.460
$CHCl_2F$(R21)	282	5960	11	0.576	0.970
$CHCl_2F$(R21)	232.4	4826	11	1.595	0.510
CCl_3F(R11)	297	5920	11	1.690	0.685
CCl_2F_2(R12)	243.4	4772	11	1.900	1.080
CF_4(R14)	145.16	2822.66	10	1.260	0.516
C_4F_8(RC318)	267	5565	16	0.720	0.425
$C_2H_3F_2Cl$(R142b)	264	5137	16	6.500	4.670
$C_2Cl_3F_3$(R113a)	319.2	6417.3	13	1.900	3.060
Average				1.91	1.13

The MSRK equation generates satisfactory results for vapor pressure data and enthalpy of vaporization of fluorocompounds and better than the original SRK equation. For thermodynamic properties calculations using MSRK, the parameters presented in this work should be used in the temperature range they were evaluated from and in conjunction with the tabulated critical parameters. The weighted least squares fit used for generating the MSRK parameters does not give any significant improvement over the unweighted procedure which is simpler and requires much less computation time.

NOMENCLATURE

a and b = parameters in equation of state

$a(T)$ = parameter at temperature T

A and B = constants defined by eqns. (14) and (15)

H = Enthalpy

k = parameter defined by eqn. (5)

m and n = MSRK correlation parameters

N = number of data points

P = pressure

R = gas constant

T = temperature

v = volume

Z = compressibility factor

α = temperature-dependent term in equation of state

ω = acentric factor

χ = property

Δ = deviation

δ = percentage deviation

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