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Second Virial Coefficients of Mixtures of Nonpolar Molecules from Correlations on Pure Components

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The empirical correlations of the second virial coefficient of pure compounds as a function of temperature are shown to be satisfactory for mixtures of gases. From the London theory of dispersion attraction, the Lennard-Jones potential energy function, and the theory of corresponding states, the critical-pressure and critical-temperature characteristic of an unlike pair interaction are obtained in terms of the critical values of the two species involved in the pair interaction. These unlike pair critical values are used directly in the empirical relationships for pure compounds to obtain the second virial coefficient of a mixture of two or more molecular species. The average of the absolute per cent deviation of the calculated cross coefficient from its experimental value in 21 binary systems is 9.7 per cent.

THE SECOND virial coefficient depends on the interaction between only two molecules at a time. Statistical thermodynamics allows one to calculate the second virial coefficient from a knowledge of the isolated pair potential energy. Recently, Hudson and McCoubrey (*10*) have shown that theoretically sound combining rules for the potential energy between nonpolar molecules can be used in the statistical calculation of the second virial coefficient.

An alternate procedure for calculating the second virial coefficient in mixtures is to use empirical corresponding state correlations for pure components together with mixing rules to obtain the critical-constants characteristics of the interaction of an isolated pair. Heretofore the simple geometric mean assumption for the energy of interaction and the arithmetic mean rule for the characteristic intermolecular distance have been used to obtain the critical temperature and the critical volume, respectively, for a mixture (*1*, *7*). Prausnitz and Gunn (*18*) have used empirical combining rules for the energy of interaction and the single-component correlations of Pitzer and Curl (*14*) to calculate virial coefficients in mixtures. This last method requires a restatement of Pitzer's correlations in terms of the critical volume rather than in terms of the critical pressure as it originally appears.

Empirical correlations of second virial coefficients, B, are in the form of B/V_c *vs.* reduced temperature, T/T_c, or BP_c/RT_c *vs.* T/T_c. The use of correlations of this sort, obtained on pure components, for the calculation on the virial coefficients of mixtures requires values for V_{c12}, P_{c12}, and T_{c12}. These parameters are the critical constants characteristic of interaction of unlike molecules 1 and 2. The purpose of this work is to show that T_{c12} and P_{c12} for the unlike isolated pair interaction are not, in general, given by the geometric mean rule. These parameters may, however, be estimated from the critical properties of the pure components. The parameters so obtained give reliable values for the second virial coefficient of mixtures from correlations for single component systems.

CRITICAL CONSTANTS FOR UNLIKE MOLECULAR PAIRS

Hudson and McCoubrey (*10*) have shown from the London theory of dispersion forces and the Lennard-Jones 6, 12 potential energy function that corresponding state theory requires that the critical temperature characteristic of an unlike pair of interacting molecules be given by

$$T_{c12} = (T_{c11}\,T_{c22})^{1/2} f_I f_s^6 \qquad (1)$$

where

$$f_s = 2(V_{c11}/V_{c22})^{1/6}/[1 + (V_{c11}/V_{c22})^{1/3}] \qquad (2)$$

$$f_I = 2(I_1/I_2)^{1/2}/(1 + I_1/I_2) \qquad (3)$$

It can also be shown (*11*) that the characteristic critical pressure for unlike pair interactions is

$$P_{c12} = (P_{c11}\,P_{c22})^{1/2} f_I f_s^9 \qquad (4)$$

and that

$$V_{c12} = (V_{c11}\,V_{c22})^{1/2}/f_f^3 \qquad (5)$$

Equation 5 is merely a transformation of the arithmetic mean rule for V_{c12}:

$$V_{c12} = [(V_{c11}^{1/3} + V_{c22}^{1/3})/2]^3 \qquad (6)$$

Equations 1 and 4 are the mixture rules for evaluating the characteristic critical constants for an unlike isolated pair.

EMPIRICAL B CORRELATION

Pitzer and associates (*14–16*) have developed an empirical correlation for single component virial coefficients, which together with the critical-constants characteristics of an isolated unlike pair of molecules (Equations 1 and 4), allows the calculation of the cross coefficient, B_{12}, for that particular pair. This correlation is in terms of the critical temperature, the critical pressure, and the acentric factor, ω, defined (*16*) by

$$\omega = -\log_{10} P^0/P_c - 1.000 \qquad (7)$$

The pressure, P^0, is the vapor pressure at $T/T_c = 0.7$. The parameter ω is a measure of the deviation of intermolecular potential from that of a simple (monatomic) fluid. The acentric factor for the mixture may be calculated by

$$\omega_{12} = (\omega_{11} + \omega_{22})/2 \qquad (8)$$

This average is arbitrary.

Table I demonstrates the agreement between the coefficients obtained from this correlation and those from experiment for the pure components included in the various mixtures. The deviations of the calculated values from the experimental ones are within 10% on most cases and within 30% for the greatest difference, $n-C_6F_{14}$.

Table I. Calculated and Experimental Second Virial Coefficients of Pure Compounds

Compound	Temp., ° K.	$-B$, Cc./Mole Lit.	$-B$, Cc./Mole Calcd.	Ref. No.
CH_4	273.2	54.1	53.7	(*8*)
	303.2	41.6	41.2	
	323.2	34.6	34.3	(*9*)
	343.2	29.1	28.2	
	363.2	24.2	23.2	
	383.2	19.5	18.6	
	403.2	15.4	14.6	
	444.3	8.1	7.6	
	477.6	3.6	3.0	
	510.9	0.0	+0.9	
C_2H_6	273.2	222.2	225	(*8*)
	298.2	186.9	188	
	323.2	157.5	158	
	377.6	109.4	110.8	
	410.9	89.6	89.8	
	444.3	74.0	72.4	
	477.6	61.6	58.8	
	510.9	51.0	46.8	
C_3H_8	310.9	335.8	367	(*8*)
	344.3	280.4	294	
	377.6	235.9	240	
	444.3	167.0	163	
	510.9	117.2	112	
C_3H_6	377.6	207.9	211	(*8*)
	410.9	170.9	174	
	444.3	143.9	144	
	477.6	121.6	119	
n-C_4H_{10}	283.2	846	821	(*20*)
	303.0	715	684	
	323.2	619	607	
	344.3	505.7	527	(*8*)
	377.6	424.9	429	
n-C_4H_{10}	410.9	353.6	353	(*8*)
	427.6	322.1	322	
	444.3	293.4	294	
	460.9	272.2	278	
	477.6	245.9	246	
	510.9	199.9	207	
i-C_4H_{10}	344.3	414.0	477	
	377.6	358.0	388	
	410.9	310.6	320	
	444.3	267.8	266	
	477.6	230.2	222	
	510.9	191.6	187	
n-C_5H_{12}	307.8	1115	1115	(*6*)
	338.1	872	889	
	377.5	666	687	(*23*)
	384.2	634	660	(*6*)
	410.9	547	564	(*23*)
	444.2	460	469	(*23*)
	477.5	396	393	(*23*)
	510.8	343	332	(*23*)
neo-C_5H_{12}	303.2	842	885	(*9*)
	323.2	734	766	
	343.2	643	670	
	363.2	566	591	
	383.2	507	523	(*9*)
	403.2	452	467	
Cy-C_6H_{12}	308.2	1457	1413	(*2*)
	323.2	1309	1272	
	343.2	1121	1103	
C_6H_6	308.7	1338	1394	
	315.7	1300	1308	(*4*)
	323.2	1186	1226	(*2*)
	333.7	1130	1127	(*4*)
	343.2	1028	1049	(*2*)
	349.2	1050	1004	(*4*)
n-C_4F_{10}	283.2	1098	1210	(*20*)
	303.0	900	940	
	323.2	770	796	
n-C_5F_{12}	307.8	1358	1478	(*6*)
	338.1	1030	1155	
	383.3	716	830	
n-C_6F_{14}	308.0	1920	2343	
	338.1	1518	1820	
	384.2	1047	1294	
CCl_4	315.7	1445	1355	(*5*)
	323.2	1330	1262	
	333.7	1225	1170	
	343.2	1120	1090	
$CHCl_3$	315.7	1010	959	
	323.2	1005	930	
	333.7	927	836	
	343.2	860	802	
	349.2	837	752	
N_2	277.6	8.5	8.7	(*8*)
	298.2	4.84	4.30	
	310.9	2.0	1.8	
	323.2	0.52	−0.24	
	348.2	−3.31	−4.04	
	373.2	−6.19	−7.26	
	398.2	−9.05	−10.02	
	427.6	−11.6	−12.8	
	444.3	−13.1	−14.2	
	460.9	−14.2	−15.4	
	477.6	−15.4	−16.7	
	510.9	−17.4	−18.8	
CO_2	298.2	124.6	127	
	310.9	112.7	115	
	323.2	103.0	104	
	344.3	88.8	88.5	
	377.6	70.7	68.5	
	398.2	61.2	58	
	410.9	56.5	53	
	444.3	44.6	40.5	
	477.6	34.9	30.4	
	510.9	26.4	22.1	
SF_6	313.2	253	258	(*9*)
	333.2	223	230	
	353.2	192	193	
	373.2	163	168	
	393.2	145	146	

Table II. Pure Component Properties (12, 21).

Component	T_c, ° K.	P_c, Atm.	V_c, Cc./Mole	I, E.V.	ω	RT_c/P_c, Cc./Mole
Methane	191.1	45.8	99.0	13.16	0.010	342.5
Ethane	305.5	48.2	148.2	11.65	0.099	520.0
Propane	370.0	42.0	200.6	11.08	0.153	723.1
Propylene	365.0	45.6	180.5	9.73	0.143	657.0
n-Butane	425.2	37.5	255.1	10.63	0.202	930.2
iso-Butane	408.1	36.0	262.7	10.08	0.186	930.2
n-Pentane	469.8	33.3	311.5	10.55	0.251	1157.4
Neopentane	433.8	31.6	303.5	10.55	0.198	1126.1
Cyclohexane	553.4	40.4	308	9.88	0.150	1124
Benzene	562.16	48.6	260.4	9.24	0.212	949.3
Chloroform	536.6	54.0	238.8	11.42	0.214	815.4
CCl_4	556.3	45.0	275.7	11.47	0.191	1014.4
n-C_4F_{10}	386.4	22.93	397	15.7	0.372	1383
n-C_5F_{12}	419	19.4	490	15.8	0.434	1772
n-C_6F_{14}	447.7	16	575	15.4	0.469	2296
SF_6	318.7	37.1	199	19.3	0.210	704.7
Nitrogen	126.2	33.5	84.6	15.51	0.041	309.1
Carbon dioxide	304.2	72.9	94.2	13.79	0.263	342.5

Table III. Cross Coefficient B_{12} in Various Mixtures

			$-B_{12}$(Cc./Gm. Mole)			
				Calculated		
System No.	Mixture Components	Temp., ° K.	Exptl.	Eq. 1, 4, 8	Geom. mean	Ref. No.
1	Methane + Ethane	273.2	111.9	108	111	(8)
	$f_s = 0.998$	298.2	92.0	89	92	
	$f_l = 0.998$	323.2	75.6	73	76	
2	Methane + Propane	310.9	122.5	110	121	(8)
	$f_s = 0.992$	344.3	98.6	86	95	
	$f_l = 0.996$	377.6	80.2	67	75	
		444.3	55.1	39	46	
		510.9	34.8	20	26	
3	Methane + n-Butane	344.3	128.1	113	127	(8)
	$f_s = 0.992$	377.6	97.9	89	101	
	$f_l = 0.994$	410.9	79.1	70	80	
		444.3	60.4	54	64	
		477.6	49.7	44	50	
		510.9	42.9	30	37	
4	Methane + i-Butane	344.3	125.5	101	121	(8)
	$f_s = 0.987$	377.6	96.6	78	96	
	$f_l = 0.991$	410.9	81.3	60	76	
		444.3	63.4	46	60	
		477.6	48.9	34	48	
		510.9	40.4	23	36	
5	Methane + n-Pentane	310.9	196	163	200	(22)
	$f_s = 0.982$	344.2	142	126	159	
	$f_l = 0.993$	377.5	107	98	126	
		410.9	83	76	101	
		444.2	67	58	81	
		477.5	55	43	64	
		510.8	46	31	50	
6	Methane + Neopentane	303.2	165	158	194	(9)
	$f_s = 0.983$	323.2	138	136	168	
	$f_l = 0.993$	333.2	132	126	157	
		343.2	118	117	147	
		353.2	113	109	137	
		363.2	106	101	128	
		383.2	93	87	112	
		403.2	78	75	98	
7	Ethane + Propylene	377.6	146	151	152	(8)
	$f_s = 1.000$	410.9	120.7	124	124	
	$f_l = 0.996$	444.3	102.7	101	102	
		477.6	82.3	83	84	
8	Benzene + Cyclohexane	308.2	1346	1350	1350	(2)
	$f_s = 1.00$	323.2	1215	1190	1190	
	$f_l = 1.00$	343.2	1041	1110	1110	

CALCULATIONS AND RESULTS

The pure component properties used in the calculations are given in Table II. Many of the ionization potentials are taken from Watanabe (*21*). Table III and IV compare experimental and calculated values for the single cross coefficient in various binary mixtures. Calculated B_{12}'s in these tables obtained from the mixing rules in Equations 1, 4, and 8 are compared with those obtained from the geometric mean rule.

The values of B_{12} calculated for systems 1 through 8 (except system 6), which are composed of two hydrocarbons, are best represented by the geometric mean rule in spite of the fact that f_l and f_s values are different from unity in all but systems 7 and 8. System 6 (CH_4 + neo-C_5H_{12}) is best represented by the new rules.

Systems 9 through 12, containing CO_2 and a hydrocarbon, are best represented by the new rules. The exception is CO_2 + C_3H_8 in which neither the geometric mean nor the new rules seem to reproduce the data.

Systems 13 and 14 containing N_2 and a hydrocarbon are best represented by the new rules.

Table III. Cross Coefficient B_{12} in Various Mixtures *(Continued)*

			$-B_{12}$ (Cc./Gm. Mole)			
				Calculated		
System No.	Mixture Components	Temp., ° K.	Exptl.	Eq. 1, 4, 8	Geom. mean	Ref. No.
9	Methane + Carbon Dioxide	310.9	63.6	64.7	64.7	(*22*)
	$f_s = 1.000$	344.2	48.2	48.9	48.9	
	$f_l = 1.000$	377.5	36.6	36.7	36.7	
		410.9	27.4	26.9	26.9	
		444.2	19.8	19.0	19.0	
		477.5	13.6	12.5	12.5	
		510.8	8.4	7.0	7.0	
10	Ethane + Carbon Dioxide	310.9	103	135	140	(*22*)
	$f_s = 0.997$	344.2	87.5	105	112	
	$f_l = 0.997$	377.5	73.3	83	87	
		410.9	60.4	65	69	
		444.2	48.2	51	54	
		477.5	37.0	39	42	
		510.8	26.0	30	32	
11	Propane + Carbon Dioxide	310.9	154.5	209	207	(*8*)
	$f_s = 0.994$	344.3	128.7	164	164	
	$f_l = 0.994$	377.6	94.3	130	131	
		444.3	61.2	82	84	
		477.6	51.0	64	68	
		510.9	42.0	51	54	
12	*n*-Butane + Carbon Dioxide	377.6	130.6	144.5	177	(*8*)
	$f_s = 0.986$	410.9	100.3	114.6	143	
	$f_l = 0.992$	444.3	80.6	90.8	116	
		477.6	65.0	71.5	94	
13	Ethane + Nitrogen	277.6	65.4	57	62	(*8*)
	$f_s = 0.996$	310.9	38.6	41.1	45	
	$f_l = 0.990$	377.6	20.1	18.8	22	
		444.3	3.8	4.4	7	
		510.9	−5.9	−5.7	−3	
14	*n*-Butane + Nitrogen	427.6	17.7	16.0	30	(*8*)
	$f_s = 0.984$	444.3	12.7	11.0	25	
	$f_l = 0.982$	460.9	8.2	6.6	20	
		477.6	2.3	2.5	15	
15	Carbon + Nitrogen Dioxide	298.2	44.1	37.4	37.7	(*8*)
	$f_s = 1.000$	323.2	33.6	28.1	28.3	
	$f_l = 0.998$	348.2	27.4	20.5	20.7	
		373.2	21.5	14.2	14.4	
		298.2	17.7	8.8	9.0	
16	Benzene + Chloroform	315.7	1300	1167	1135	(*5*)
	$f_s = 0.990$	323.2	1130	1038	1064	
	$f_l = 0.995$	333.7	1040	958	981	
		343.2	960	893	915	
		349.3	950	856	824	
17	Carbon Tetrachloride + Chloroform	309.5	1310	1247	1247	(*5*)
	$f_s = 0.999$	315.7	1215	1147	1147	
	$f_l = 1.000$	323.2	1160	1072	1072	
		333.7	1120	989	989	
		337.2	1070	963	963	
		343.2	1000	923	923	
18	Methane + SF_6	313.2	85	82	93	(*9*)
	$f_s = 0.993$	333.2	68	69	80	
	$f_l = 0.982$	353.2	57	58	68	
		373.2	45	49	58	
		393.2	33	40	49	

Table IV. Cross Coefficient B_{12} in Fluorocarbon plus Hydrocarbon Mixtures

System No.	Components	Temp. °K.	Exptl.	$-B_{12}$ (Cc./Gm. Mole) Calculated *a*	*b*	*c*	Ref. No.
19	*n*-Butane + C_4F_{10}	283.2	766	890	747	836	(*20*)
		303.0	666	756	636	711	
		323.2	604	649	545	609	
20	*n*-Pentane + *n*-C_5F_{12}	307.8	969	1187	1017	1064	(*6*)
		338.1	693	1015	806	842	
		383.3	625	687	586	615	
21	*n*-Pentane + *n*-C_6F_{14}	308.0	1184	1466	1262	1338	(*6*)
		338.1	895	1151	1001	1046	
		384.2	643	840	724	758	

[a] f_I and f_s from I and V_c.
[b] $f_I f_s^6$ and $f_I f_s^9$ by Equations 9b and 10b.
[c] $f_I f_s^6$ and $f_I f_s^9$ by Equations 9a and 10a.

System 15, CO_2 + N_2, like systems 7 and 8, is no test of the rule comparison, since f_I and f_s are essentially unity.

Systems 16 and 17 contain the polar molecule $CHCl_3$. The f factors in 17 are unity and the calculated B_{12}'s are 10% lower than the experimental values. For system 16 the geometric mean rule seems to be somewhat more satisfactory than the new rules.

For system 18, CH_4 + SF_6, the new rules are a considerable improvement over the geometric mean rule.

In these 18 systems, except in those containing a hydrocarbon plus a hydrocarbon (1–5, 7), the values of f_I, of f_s, and of their combinations as $f_I f_s^6$ and $f_I f_s^9$ give satisfactory results when evaluated directly from ionization potentials and critical volumes. (If critical volume data are not available, corresponding state theory allows the ratio V_{c11}/V_{c22} to be obtained as $T_{c11}P_{c22}/T_{c22}P_{c11}$.) Further exceptions are binary mixtures containing a fluorocarbon plus a hydrocarbon. From the thermodynamics of such solutions (*13*, *19*), $f_I f_s^3$ should be 0.93, whereas the value from ionization potentials and critical volumes is 0.96. The value 0.93 gives much better results for the cross coefficients B_{12} in the mixtures of these compounds. The factors $f_I f_s^6$ and $f_I f_s^9$, required in Equations 1 and 4, may be computed from $f_I f_s^3 = 0.93$ by two alternate ways, one using only f_s:

$$f_I f_s^6 = (f_I f_s^3)\, f_s^3 = 0.93\, f_s^3 \tag{9a}$$

$$f_I f_s^9 = (f_I f_s^3)\, f_s^6 = 0.93\, f_s^6, \tag{10a}$$

and the other using only f_I:

$$f_I f_s^6 = (f_I f_s^3)^2/f_I = (0.93)^2/f_I \tag{9b}$$

$$f_I f_s^9 = (f_I f_s^3)^3/f_I^2 = (0.93)^3/f_I^2 \tag{10b}$$

For the fluorocarbon plus hydrocarbon systems shown in Table IV, B_{12} is calculated from each of the three possible ways for arriving at the values of $f_I f_s^6$ and $f_I f_s^9$ for this particular kind of system. The results obtained from evaluating these factors from the critical volumes and ionization potentials directly are less satisfactory than those obtained using the empirical value, $f_I f_s^3 = 0.93$. There seems to be little basis for choosing between the B_{12} calculated using the factors from Equations 9b and 10b *vs.* 9a and 10a, although the former seem to give calculated results closer to the experimental B_{12}. Equations 9b and 10b assume that f_I is correctly evaluated from ionization potentials whereas Equations 9a and 10a assume that f_s is correctly evaluated from the critical volumes. These results might indicate that the arithmetic mean rule for V_{c12} in terms of V_{c11} and V_{c22} is not as good an assumption for the larger V_{c11} and V_{c22} difference in these systems as when the pair of molecules have similar sizes.

Prausnitz and Gunn (*17*, *18*) have obtained empirical values for the factor $f_I f_s^6$ in Equation 1 (which they called k_{ij}) from virial coefficient data on binary mixtures. A figure showing k_{ij} *vs.* the critical volume ratio given by Prausnitz (*17*) is reproduced as Figure 1 here. Assuming that f_I is always unity the points on this plot should follow Equation 2 raised to the sixth power—i.e.,

$$k_{ij} = f_s^6 = 64(V_{c11}/V_{c22})/[1 + (V_{c11}/V_{c22})^{1/3}]^6.$$

This function drawn in Figure 1 shows that most of the data is in reasonable agreement with this expression. One of the systems which is below this curve is methane plus sulfur hexafluoride for which f_I is 0.98. (For the other systems on this plot f_I is greater than 0.99).) The calculated values of B_{12} for methane plus sulfur hexafluoride shown in Table III are essentially identical with the experimental values. The theoretical relationship of k_{ij} given by Prausnitz (*17*) gives a value for k_{ij} that is too small; this is true even for fluorocarbon plus hydrocarbon systems.

CONCLUSIONS

Of the 21 systems examined four (8, 9, 15, and 17) are no test of the comparison, since the f factors are unity, and

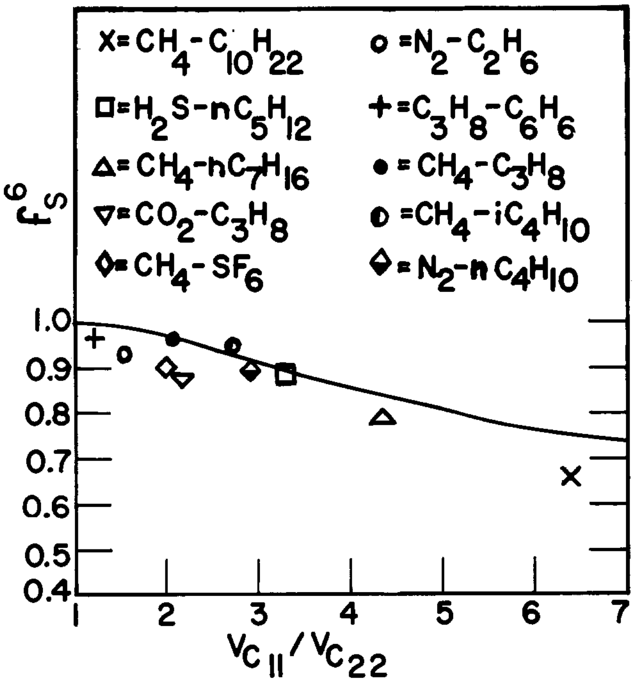

Figure 1. Comparison of theoretical and experimental f_s

system 11 is not significant. Of the remaining sixteen systems, which should all follow the new rule, seven (1–5, 7, and 16, all containing hydrocarbons of $CHCl_3$) follow the geometric mean rule, three (19–21, all containing a hydrocarbon plus a fluorocarbon) follow an empirical modification of the new rules, and only six (6, 10, 12, 13, 14, and 18) follow the new rules strictly.

The best calculated values for B_{12} are quite close to the experimental values. The mean of the absolute per cent deviation of the calculated value from experimental value is 9.7%.

Since the absolute per cent deviation in the calculated values for B_{12} and for B_{11} and B_{22} are all approximately 10, the maximum mean deviation in B_m for a binary mixture calculated in the ways described will be 10%:

$$B_m = B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2$$

$$\delta B_m = x_1^2\delta B_{11} + 2x_1x_2\delta B_{12} + x_2^2\delta B_{22}$$

$$\delta B_{11}/B_{11} = \delta B_{22}/B_{22} = \delta B_{12}/B_{12} = \Delta = 10\%$$

$$\delta B_m = (x_1^2B_{11} + 2x_1x_2B_{12} + x_2^2B_{22})\Delta$$

$$\delta B_m = B_m\Delta$$

$$\delta B_m/B_m = \Delta = 10\%$$

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Equation of State Prediction of Thermodynamic Properties of Carbon Dioxide

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A table and graph of the thermodynamic properties for CO_2 are presented for the critical ragion. Graphs are given for the effect of pressure on enthalpy for CO_2 for reduced temperature of 1.1 and 1.4 and for reduced pressures up to 6.0. All values are calculated from an equation of state and a low-pressure heat capacity equation. Comparisons are made with experimental data where available.

THE TWO objectives of this work are: to show how an accurate equation of state can safely predict changes in thermodynamic properties, and to present a completely consistent set of thermodynamic properties for CO_2 in the critical region. Fortunately, there are some experimental data available to which the predictions of the equation of state may be compared.

CALCULATION OF THE THERMODYNAMIC PROPERTIES

Few compounds have been studied more extensively than CO_2. There have been many investigations of the *P-V-T* and thermal behavior. A recent investigation by Koppel and Smith (*1*) is of particular importance because it includes thermal data for the region around the critical point. This region also was the object of considerable study in the development of an equation of state (*3*, *4*) to represent the *P-V-T* behavior. The equation which was designed specifically to have the correct curvature in the neighborhood of the critical point is

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2\exp(-kT)}{(V-b)^2} + \frac{A_3 + B_3T + C_3\exp(-kT)}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{A_5 + B_5T + C_5\exp(-kT)}{(V-b)^5} \quad (1)$$

where for *P* in p.s.i.a., *T* in °R., and *V* in lb./ft.³, the constants are for CO_2.