$Cd(NO_3)_2$, and greater consistency of results was thereby expected. The sign of the difference of the lattice energies would not be changed by substituting the other value for $CdCl_2$ into Equation 7. That is, in both instances, a negative correction for nearest-neighbor interaction is obtained.

The data for the b values of Equation 8 were obtained from phase diagrams in the literature containing quite large uncertainties. Because of the small effect of ΔE_{nn}, however, this uncertainty is not important.

NOMENCLATURE

ΔC_f = molar heat capacity difference between solid and liquid at normal freezing point, cal. per deg. mole
ΔE = molar energy of mixing, cal. per mole
$\Delta \bar{E}$ = molar partial energy of mixing, cal. per mole
$\Delta \bar{G}$ = molar partial Gibbs free energy of mixing, cal. per mole
ΔH_f = molar enthalpy of fusion at the normal freezing point, cal. per mole
K = equilibrium constant
N = number of particles
$\Delta \bar{S}$ = molar partial entropy of mixing, cal. per deg. mole
T = temperature, ° K.
T_f = normal freezing point, ° K.
R = molar gas constant, cal. per deg. mole
U = molar lattice energy at 0° K., cal. per mole
X = ion fraction
X' = equivalent ion fraction
X'' = number fraction of particles
a = activity
a^* = activity of pure component at its normal freezing point
b = interaction parameter for next-nearest-neighbors, cal. per mole
α = fraction of total Cd-containing species
γ = activity coefficient
θ = freezing point depression, ° K.

Superscripts

xs = excess; that is, exptl. – ideal

Subscripts

f = fusion
m = mixing
n = nearest-neighbor
nn = next-nearest-neighbor
a, i, j, k = generalized species

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Correlation of Thermodynamic Properties of Chloromethanes

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A correlation for entropy and enthalpy based on the two-parameter law of corresponding states and the reference substance concept has been obtained. For 199 points tested, the over-all average absolute deviation and the maximum deviations in the calculated values of entropy with the available data are 0.74 and 7.20%. The corresponding deviations of enthalpy are 1.86 and 15.0%, respectively. A compressibility chart for chloromethanes has been made and shown to be superior to existing charts. For 102 points tested, the average absolute and maximum deviations in the compressibilities were 1.80 and 19.5%, respectively.

THE pressure-volume-temperature (PVT) properties of a substance are very useful for purposes of design and are frequently used. The substances used in engineering practice include those for which the PVT data are entirely nonexistent. A generalized compressibility chart is useful in filling such a need.

An equation of state, theoretical or empirical, is advantageous mainly because it condenses the PVT data to a large extent, interpolation and possibly extrapolation are more accurate, and partial derivatives which are used in the calculation of thermodynamic properties can be calculated easily and accurately.

An equation of state such as those of Beattie-Bridgeman and Benedict-Webb-Rubin, especially the latter, represents PVT data fairly accurately up to about 1.5 times the critical density.

However, the PVT data needed for the evaluation of the constants are lacking for many substances. In such cases a generalized chart is useful, as it can predict data for all substances fairly accurately.

All the generalized charts are based on the principle of corresponding states formulated by van der Waals (*27*), that at the same reduced conditions of temperature and pressure, all substances manifest the same reduced volume.

Mathematically, this can be stated as

$$f(P_r, T_r, V_r) = 0 \tag{1}$$

or in terms of the compressibility factor, Z, as

$$Z/Z_c = f(P_r, T_r) \tag{2}$$

Based on this principle several (*3, 4, 6, 7, 8, 10, 13, 16, 20, 31, 32*) charts have been developed. The generalized charts were extended to the liquid state by Watson (*30*).

There are several modifications of the theorem of corresponding states (TCS) based on either two or three parameters. For engineering purposes, compressibility charts based on the two-parameter law of corresponding states is satisfactory. But the two-parameter charts for different homologous series may give a higher degree of accuracy. It was therefore decided to test the applicability of TCS for chloromethanes.

Further, if the two-parameter TCS holds good, it should be possible to predict enthalpy and entropy starting from one of the substances in the group—for example, methane. As the structures of chloromethanes remain the same, but their properties change by the replacement of hydrogen atoms in the parent methane molecule by chlorine atoms, any change in the property should be attributable to the number of hydrogen and chlorine atoms in the molecule. The work undertaken to test these is presented in this paper.

GENERALIZED COMPRESSIBILITY CHART FOR CHLOROMETHANES

The chloromethanes—methane, methyl chloride, methylene chloride, chloroform, and carbon tetrachloride—are substances in a homologous series. The thermodynamic properties of methylene chloride (*22*), chloroform (*23*), and carbon tetrachloride (*21*) have been evaluated. The properties of methyl chloride (*11, 26*) and methane (*5*) are available. These properties were used and a generalized chart for chloromethanes was prepared (Figure 1).

A two-parameter chart was made earlier by Viswanath (*28, 29*). For the construction of the compressibility chart he used polar and nonpolar substances. He compared the Z chart with the experimental data for substances which are highly polar, saturated and unsaturated hydrocarbons, and other substances. For these substances the value of the critical compressibility, Z_c, varied between 0.23 and 0.30. For most of the substances, the author reports an average absolute deviation of about 1%. Further, he has compared the charts with those of Nelson and Obert (*15*) and Lydersen *et al.* (*14*). Details of such a comparison are given elsewhere (*28, 29*). Reid and Sherwood (*19*) in their critical analysis of *PVT* relations say that the best Z charts are due to Viswanath (*28, 29*) and Nelson and Obert (*15*). It was therefore decided to compare the present Z chart for chloromethanes with that of Viswanath because of its accuracy and the availability of large (about 95 × 50 cm.) charts constructed by the author.

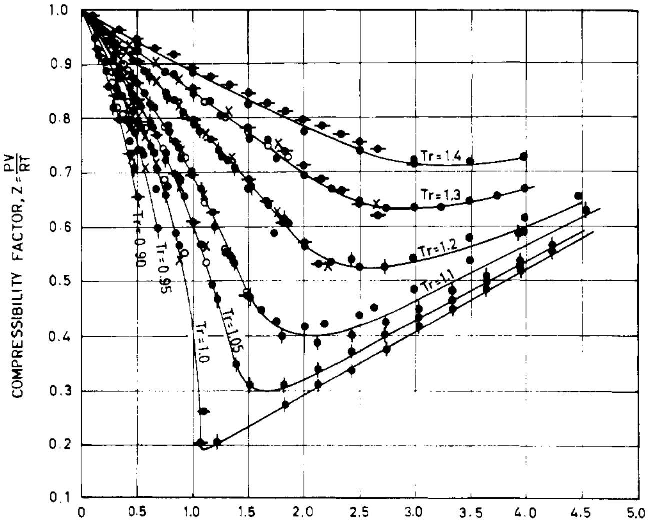

Figure 1. Generalized compressibility chart for chloromethanes

● Methane
● Methyl chloride
● Methylene chloride
O Chloroform
X Carbon tetrachloride

The present Z chart was compared with that of Viswanath (*28, 29*) for methane, methyl chloride, methylene chloride, chloroform, and carbon tetrachloride (Table I).

In general, both charts predict compressibilities with almost the same accuracy and the order of maximum deviations is of the same order of magnitude.

For 102 points tested, the present Z chart and that of Viswanath (*29*) predicted compressibilities with overall average absolute deviations of 1.79 and 2.04%, respectively.

Such a comparison indicates that the present Z chart is slightly superior to that of Viswanath (*29*). Larger deviations were found around the critical region and also in the case of methyl chloride. A few points, especially in the case of methyl chloride, did not fit the present generalized Z charts. This may be due to the error in

Table I. Comparison of Compressibility Values with Available Data

		This Work		Viswanath	
T_r	No. of Points	Av. absolute deviation, %	Max. deviation, %	Av. absolute deviation, %	Max. deviation, %
		METHANE			
1.00	3	1.618	3.237	0.429	0.854
1.05	3	0.748	1.806	0.692	1.952
1.10	6	1.789	5.839	1.910	4.889
1.20	7	0.559	2.651	1.111	2.245
1.30	6	1.777	3.135	0.620	1.441
		METHYL CHLORIDE			
1.00	6	4.227	19.52	6.593	17.07
1.05	6	0.327	0.798	3.783	7.190
1.10	6	1.953	0.913	2.990	6.250
1.20	8	1.197	2.778	1.542	4.064
		METHYLENE CHLORIDE			
1.00	3	9.617	18.46	9.456	19.48
1.05	3	6.627	15.36	0.570	1.222
1.10	3	2.002	5.063	1.518	3.754
1.20	5	2.678	11.43	2.802	10.82
		CHLOROFORM			
1.00	5	1.196	4.779	2.720	10.98
1.05	3	0.867	0.914	1.129	2.396
1.10	3	0.717	1.250	1.632	3.958
1.20	3	0.836	1.485	1.125	2.640
1.30	5	2.092	6.470	0.993	3.250
		CARBON TETRACHLORIDE			
1.00	3	0.266	0.706	0.391	0.727
1.05	3	0.026	0.078	0.182	0.301
1.10	3	0.295	0.761	0.603	0.609
1.20	4	1.305	2.392	2.274	3.828
1.30	5	1.474	3.304	0.816	2.390

Over-all average absolute deviation for 102 points = 1.79%.

experimental values in these regions. Therefore with the availability of more and accurate experimental data, the grouping of substances into homologous series might be accurate and worth the effort.

ENTROPY AND ENTHALPY CORRELATION FOR CHLOROMETHANES

Generalized tables for the evaluation of entropy and enthalpy using a knowledge of critical constants and properties of an ideal gas are available (*7, 12, 14, 18, 28, 32*).

In this work, correlation of entropy and enthalpy based on the theorem of corresponding states and using methane as the reference substance is presented.

Entropy Correlation. Equation 2 shows that Z is a function of three parameters: P_r, T_r, and Z_c.

Su (*25*) has defined a pseudocritical volume, V_{ci}, as

$$V_{ci} = \frac{RT_c}{P_c} \tag{3}$$

Using this, in the definition of the compressibility factor,

$$Z = PV/RT \tag{4}$$

we obtain

$$Z = \frac{P_r \phi_r}{T_r} \tag{5}$$

where $P_r = P/P_c$; $T_r = T/T_c$; $\phi_r = V/V_{ci}$; and $V_{ci} = RT_c/P_c$.

Thus we obtain a functional relationship between the compressibility factor, Z, and the two parameters P_r and T_r as

$$Z = f(P_r, T_r) \tag{6}$$

The pseudocritical volume definition, therefore, eliminates the use of Z_c and gives a basis for the two-parameter law of corresponding states.

From this law it follows that the values of ($S - S^*$), the entropy departure from ideality at the same values of reduced temperature and pressure, must be the same for all substances. This can be written as

$$(S_1 - S_1^*)_{P_r, T_r} = (S_2 - S_2^*)_{P_r, T_r} \tag{7}$$

Hence,

$$S_2)_{P_r, T_r} = S_1 + (S_2^* - S_1^*)_{P_r, T_r} \tag{8}$$

Hence, if the entropy of a reference substance is known, it is possible to evaluate the entropy data for any substance.

$(S_2^* - S_1^*)_{P_r, T_r}$ is a function of temperature only. In this work, methane was selected as the reference substance, as it is the first member of the chloromethanes and also because thermodynamic data are available for it over wide ranges of temperature and pressure (*5*).

Defining

$$\Delta S^* = (S_2^* - S_1^*) \tag{9}$$

we may expect a relation between ΔS^* and T_r of the form:

$$\Delta S^* = a + bT_r^n \tag{10}$$

ΔS^* for methyl chloride, methylene chloride, and chloroform were evaluated using the ideal gas thermodynamic properties of Gelles and Pitzer (*9*) and for carbon tetrachloride using the data of Albright *et al.* (*1*). Constants a, b, and n for all four substances are given in Table II.

Constants a, b, and n were correlated with molal volume at the normal boiling point (V_B) and the number of chlorine and hydrogen atoms. V_B can be easily evaluated by the knowledge of molecular structure by using the additive contributions listed by Perry (*17*). Figure 2 gives the plots of a *vs.* number of chlorine atoms, $(b/V_B^{1/2}a^{1/3}{}_{\text{calcd.}})$ *vs.* the number of hydrogen atoms, and $n^{1/2}$ *vs.* V_B. These can be represented by:

$$a^{1/3} = 1.260 + 0.745\ N \tag{11}$$

and

$$b = V_B^{1/2}a^{1/3}{}_{\text{calcd.}}[0.098 + 0.65N' - 0.17(N')^2] \tag{12}$$

Table II. Constants for Evaluation of Ideal Gas Entropy Using Equation 10

Substance	*a*	*b*	*n*
Methyl chloride	2.00	16.56	1.80
Methylene chloride	8.00	23.15	1.00
Chloroform	20.87	19.42	0.550
Carbon tetrachloride	43.43	3.43	0.350

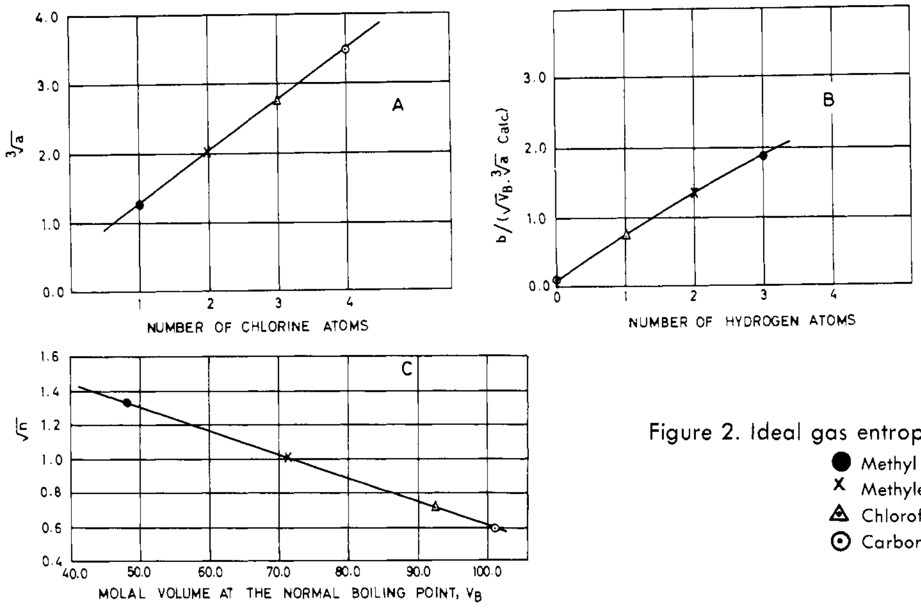

Figure 2. Ideal gas entropy correlation for chloromethanes

● Methyl chloride
X Methylene chloride
△ Chloroform
⊙ Carbon tetrachloride

$$n^{1/2} = 2.02 - (1.42 \times 10^{-2}) V_B \qquad (13)$$

where N = number of chlorine atoms and N' = number of hydrogen atoms.

Constants a and b evaluated using Equations 11 and 12 agree with the actual values with a maximum deviation of 2.5%. n evaluated using Equation 13 agrees with the actual values with a maximum deviation of 10%.

For 72 points tested over a range of $T_r = 0.60$ to $T_r = 1.50$ ΔS^* evaluated using the calculated constants were found to agree with the actual values with an over-all average absolute deviation of 1.03% and an over-all maximum deviation of 2.53%. The entropy of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride was evaluated using the calculated ΔS^* values and the entropy data of methane (*5*) by using the equation

$$S_2)_{T_r, P_r} = S_1)_{T_r, P_r} + \Delta S^*)_{T_r, P_r} \qquad (14)$$

The final correlation is:

$$\begin{aligned} S_2)_{T_r, P_r} = {} & S_1)_{T_r, P_r} + (1.260 + 0.745N)^3 \\ & + V_B^{1/2}(1.260 + 0.745N)(0.098 + 0.65N' - 0.17N'^2) \times \\ & T_r[2.02 - (1.42 \times 10^{-2})\ V_B]^2 \end{aligned} \qquad (15)$$

For methyl chloride, entropy data are available in the literature (*11, 26*). For methylene chloride (*22*), chloroform (*23*), and carbon tetrachloride (*21*) these have been evaluated. The values of entropy are compared with the available data (Table III).

For carbon tetrachloride, chloroform, and methylene chloride the deviations are in general less than 1%. For methyl chloride deviations are more, the average absolute deviation being 2.2%.

Enthalpy Correlation. From the two-parameter law of corresponding states, it follows that the values of $(H^* - H)/T_c$, where $(H^* - H)$ is the enthalpy departure from ideality, must be the same at the same values of reduced temperature and pressure. Thus it is possible to evaluate enthalpy data for any substance, if the data are available for a reference substance.

Using the concepts outlined above, the enthalpy of chloromethanes has been evaluated using the relation,

$$H_2 = \Delta H - (T_{c_2}/T_{c_1})H_1 \qquad (16)$$

where $\Delta H = H_2^* - (T_{c_2}/T_{c_1})H_1^*$, subscript 1 referring to methane.

ΔH can be evaluated as follows:

$$\begin{aligned} \Delta H = {} & (H_2^* - H_1^*) - [(T_{c_2} - T_{c_1})/T_{c_1}]H_1^* = (H^* - H_o^o)_2 - \\ & (H^* - H_o^o)_1 - [(T_{c_2} - T_{c_1})/T_{c_1}]H_1^* + [(H_o^o)_2 - (H_o^o)_1] = \\ & \Delta(H^* - H_o^o) + \Delta H_o^o - [(T_{c_2} - T_{c_1})/T_{c_1}]H_1^* \end{aligned} \qquad (17)$$

The values of $(H^* - H_o^o)$, the enthalpy function, are available for chloromethanes (*1, 9*). The values of ΔH_o^o depend on the reference point chosen.

However, for methane, the available data (*5*) use the reference point as $H = 0$ for pure crystalline solid, and the data for methyl chloride use $H = 0$ for saturated liquids at 233.3° K. These reference points were retained in the present correlation.

For methylene chloride, chloroform, and carbon tetrachloride $H = 0$ and $S + R \ln P = 0$ for elements at 0° K. and zero pressure was taken as the reference.

As in the case of entropy, the values of $\Delta(H^* - H_o^o)$ are expressed in terms of the reduced temperature, T_r, as

$$\frac{\Delta(H^* - H_o^o)}{T_r} = A + BT_r \qquad (18)$$

Constants A and B have been correlated with the number of chlorine atoms and the molal volume at the normal boiling point, respectively. The correlations represented graphically as Figure 3 can be written as

$$A = 8.605 + 2.131N \qquad (19)$$

$$B = -6028 + 1964.2\,V_B^{1/3} \qquad (20)$$

The values of H_1^* were fitted to the equation

$$H_1^* = 2191.3 + 1525T_r \qquad (21)$$

The final correlation is

$$\begin{aligned} H_2 = {} & (8.605 + 2.131N)T_r - (6028 + 1964\ V_B^{1/3})T_r^2 + \Delta H_o^o - \\ & [(T_{c_2} - T_{c_1})/T_{c_1}]\ (2191.3 + 1525\ T_r) - (T_{c_2}/T_{c_1})H_1 \end{aligned} \qquad (22)$$

Table III. Deviation of Entropy Values from Available Data

	Values of Reduced Temperature, T_r									
	0.80	0.90	0.95	1.00	1.05	1.10	1.15	1.20	1.30	1.40
METHYL CHLORIDE										
No. of points	1	2	2	2	8	9	9	...	...	...
Av. abs. deviation, %	1.88	1.78	1.55	1.49	3.04	2.59	1.72	...	...	...
Max deviation, %	1.88	1.91	1.65	7.58	7.20	5.05	3.10	...	...	...
METHYLENE CHLORIDE										
No. of points	1	3	4	6	6	8	...	10	11	11
Av. abs. deviation, %	0.03	0.18	0.24	0.55	0.21	0.21	...	0.30	0.16	0.09
Max. deviation, %	0.03	0.26	0.46	1.89	0.28	0.48	...	1.37	0.33	0.29
CHLOROFORM										
No. of points	1	3	4	6	7	7	...	9	11	11
Av. abs. deviation, %	0.59	0.40	0.34	0.20	0.22	0.21	...	0.06	0.07	0.25
Max. deviation, %	0.59	0.47	0.40	0.41	0.73	0.38	...	0.29	0.19	0.32
CARBON TETRACHLORIDE										
No. of points	1	3	4	6	6	7	...	8	11	...
Av. abs. deviation, %	0.03	0.43	0.51	0.52	0.70	0.86	...	1.04	0.97	...
Max. deviation, %	0.03	0.54	0.74	1.01	0.91	1.38	...	1.39	1.20	...

Over-all average absolute deviation for 199 points = 0.704%.

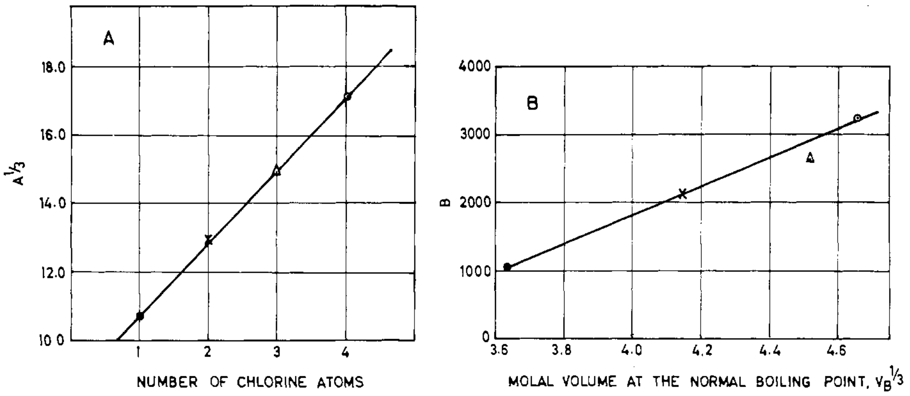

Figure 3. Ideal gas enthalpy correlation for chloromethanes

- ● Methyl chloride
- X Methylene chloride
- △ Chloroform
- ⊙ Carbon tetrachloride

Constants A and B and the values of ΔH_o° for chloromethanes are given in Table IV.

Constants A and B calculated using Equations 19 and 20 represent the actual values with maximum deviation of 1.4 and 4.7%, respectively.

Using the calculated values of A and B, values of $\Delta(H^* - H_o^\circ)$ were calculated and found to agree with the actual values within a maximum deviation of about 3.5%.

The values of enthalpy were evaluated using Equation 22 using the calculated values of $\Delta(H^* - H_o^\circ)$. Absolute values of deviations of enthalpy with actual values are shown in Table V. Except in the case of methyl chloride, the average absolute deviations in general are around 1.5%.

Isothermal Changes of Enthalpy with Pressure Using Generalized Compressibility Chart. The isothermal change of enthalpy is given by

$$\frac{H^* - H}{T_c} = -RT_r^2\left[\int_0^{P_r} \frac{1}{P_r}\left(\frac{\partial Z}{\partial T_r}\right)_{P_r}\right]dP_r \qquad (23)$$

The values of $(H^* - H)/T_c$ have been evaluated using Equation 23, and the present generalized compressibility chart (Figure 1). Graphical differentiation and integration were employed to evaluate the integral. $(\partial Z/\partial T_r)_{P_r}$ was evaluated by drawing tangents and also by the method of normals. The slopes obtained by the two methods agreed within ±2.0%. Table VI compares evaluated $(H^* - H)/T_c$ values of methane and methyl chloride with those of Pitzer and Lydersen *et al.* The Lydersen *et al.* values were taken corresponding to Z_c values of methane and methyl chloride. The values referred to as experimental are those obtained from *PVT* data by Din (*5*) in the case of methane, and Hsu and McKetta (*11*) and Tanner *et al.* (*26*) in the case of methyl chloride. It can be seen from Table VI that the present method is as good as Pitzer's and Lydersen's methods and if accurate experimental data become available, it may yield very accurate results. It is surprising that Pitzer's method is better in the case of methane and not methyl chloride. Methane comes closer to a normal fluid than methyl chloride according to the criterion given by Pitzer. But as the acentric factor takes into account the effects of nonsphericity and dipole interaction effects, and as methane is fairly spherical and nonpolar, one concludes that the acentric factor should not have a large effect. On the other hand, methane being a quantum mechanical fluid [reduced de Broglie wavelength $\Lambda^* = 2^{1/2}h/\sigma(m\epsilon)^{1/2} = 0.27$] should not conform well to generalized correlations without any other empirical corrections like Newton's correction of critical temperature and critical pressure in the case of hydrogen, helium, and neon. In the

Table IV. Constants of Equation 18

Substance	A	B	ΔH_o°
Methyl chloride	1251.7	1080.6	1228.7
Methylene chloride	2081.8	2235.0	−21913.3
Chloroform	3434.9	2652.5	−24195.3
Carbon tetrachloride	4998.0	3233.0	−27191.3

Table V. Deviations of Enthalpy Values from Available Data

	Values of Reduced Temperature, T_r									
	0.80	0.90	0.95	1.00	1.05	1.10	1.15	1.20	1.30	1.40
					METHYL CHLORIDE					
No. of points	1	2	3	4	6	11	11	...	...	...
Av. abs. deviation, %	1.30	1.07	1.99	1.96	2.70	6.52	3.27	...	...	...
Max. deviation, %	1.30	1.10	2.52	2.91	5.20	14.99	8.49	...	...	...
					METHYLENE CHLORIDE					
No. of points	1	4	4	6	6	8	...	9	11	11
Av. abs. deviation, %	0.64	0.88	1.67	0.80	0.63	0.34	...	1.06	1.40	1.50
Max. deviation, %	0.64	2.35	2.19	1.44	0.96	0.50	...	1.49	1.92	2.95
					CHLOROFORM					
No. of points	1	3	4	6	7	7	...	8	11	11
Av. abs. deviation, %	0.43	0.44	1.60	2.68	2.01	0.97	...	2.40	1.92	3.40
Max. deviation, %	0.43	0.58	1.71	5.32	3.69	1.50	...	5.77	2.15	4.56
					CARBON TETRACHLORIDE					
No. of points	1	3	4	6	6	7	...	9	11	...
Av. abs. deviation, %	0.13	0.26	0.53	0.70	0.93	0.75	...	0.88	0.97	...
Max. deviation, %	0.13	0.63	0.85	2.58	1.28	1.58	...	1.49	1.99	...

Over-all average absolute deviation for 202 points = 1.81%.

Table VI. Comparison of $(H^* - H)/T_c$ Values

T_r	Range of P_r	No. of Points	Average % Deviation[a] This work	Pitzer *et al.*	Lydersen *et al.*
			METHANE		
1.0	0.1–1.0	6	9.05	7.84[b]	3.91
1.05	0.1–1.0	6	4.4	4.25	6.43
1.1	0.1–3.0	11	13.95	9.67	8.15
1.2	0.1–3.0	11	7.01	4.39	10.67
1.3	0.1–3.0	11	11.65	1.55	10.70
1.4	0.1–3.0	11	8.85	4.93	15.63
Av. absolute deviation, %			9.59	5.31	9.98
			METHYL CHLORIDE		
0.90	0.2	1	14.63	21.95	21.95
0.95	0.2–0.3	2	23.50	23.35	22.20
1.00	0.2–0.5	3	27.36	20.78	21.89
1.05	0.5–1.0	3	23.00	21.63	18.77
1.10	0.5–3.0	8	15.00	11.86	12.06
Av. absolute deviation, %			20.70	19.91	19.37

[a] Deviation = (experimental-calculated)/experimental.

[b] $P_r = 0.1$ excluded from Pitzer's tables, since data are not available.

present correlation based on grouping of substances according to the homologous series, the abnormal effects which result from the introduction of chlorine atoms into the parent methane are taken into account as the correlation is based on the experimental data of methane and the number of chlorine atoms in the molecule. Thus this takes into account in an aggregate manner the chemical nature of the molecule. Further, the estimated values of ω by different authors (*24*) do not agree, and ω is not an experimentally determinable quantity. In the present correlation no such difficulty arises.

Table VII shows the enthalpy values calculated using all four methods—the present reference substance method, the present generalized Z-chart, Pitzer's method, and Lydersen's method. Table VII shows that the reference substance method is as good as Pitzer's method. It is less superior to Lydersen's method, which is less accurate compared to the generalized chart. At $T_r = 1.05$, a pressure range of only 0.1 to 1.0 could be used, because of the lack of data for methane. The advantage of the present method can be seen considering Equations 8 and 15. Where the ideal gas entropies are available, Equation 8 can be used to calculate the entropy of the substance in question in the homologous series. In addition, if the ideal gas entropies are correlated, the method can be extended to other members in the homologous series. This method of correlation results in equations such as Equation 15, for which even a knowledge of heat capacity is not required.

Table VII. Comparison of Calculated and Experimental Enthalpy Values

T_r	P_r Range	Average % Deviation Ref. substance	Generalized chart	Pitzer *et al.*	Lydersen *et al.*
0.80	0.1	1.30 (*1*)	. . .	. . .	0.52 (*1*)
0.90	0.1–0.2	1.07 (2)	0.60 (2)	0.41 (*1*)	0.46 (2)
0.95	0.1–0.3	1.99 (*3*)	1.10 (*3*)	1.32 (2)	1.15 (*3*)
1.00	0.1–0.5	1.96 (*4*)	1.33 (*4*)	1.26 (*3*)	0.84 (*4*)
1.05	0.1–3.0	2.70 (6)	1.58 (5)	4.20 (*10*)	2.83 (*11*)
1.15	0.1–3.0	3.27 (*11*)	. . .	1.28 (*10*)	1.50 (*11*)
Av. abs. dev., %		2.49	1.26	2.39	1.75

CONCLUSIONS

The two-parameter law of corresponding states has been applied to the homologous series of chloromethanes. A compressibility chart for chloromethanes has been constructed.

A correlation for the entropy and enthalpy of chloromethanes based on the two-parameter law of corresponding states and the reference substance concept has been obtained. The input data required to evaluate entropy and enthalpy of different members in the chloromethane homologous series are the entropy and enthalpy of the reference substance, molal volume at the normal boiling point of the substance, and the number of hydrogen and chlorine atoms in the substance. The reference substance used in the present work is methane.

NOMENCLATURE

A, B = constants in Equation 18
a, b, n = constants in Equations 11 to 13
$(H^* - H)$ = enthalpy departure from ideality, cal./gram mole
h = Planck's constant, erg. sec./molecule
m = mass, gram
N, N' = number of Cl_2 and H_2 atoms, respectively
P = pressure, atm.
P_c = critical pressure, atm.
P_r = P/P_c = reduced pressure
R = universal gas constant, liters atm./gram mole °K.
$(S - S^*)$ = entropy departure from ideality, cal./gram mole °K.
T = temperature, °K.
T_c = critical temperature, °K.
T_r = T/T_c = reduced temperature
V = volume, liters/gram mole
V_B = molal volume at normal boiling point, cc./gram mole
V_r = V/V_c = reduced volume
V_c = critical volume, liters/gram mole
Z = PV/RT = compressibility factor
$\Delta H = (H_2 - H_1)$ = difference in enthalpy of a real gas at any temperature from that of reference substance, cal./gram mole
$\Delta H^* = (H_2^* - H_1^*)$ = difference in enthalpy of an ideal gas at any temperature from that of reference substance, cal./gram mole
$\Delta H_o^o = [(H_o^o)_2 - (H_o^o)_1]$ = difference in enthalpy of an ideal gas at 0° K. from that of reference substance at 0° K., cal./gram mole
$\Delta S = (S_2 - S_1)$ = difference in entropy of a real gas at any temperature from that of reference substance, cal./gram mole °K.
$\Delta S^* = (S_2^* - S_1^*)$ = difference in entropy of an ideal gas at any temperature from that of reference substance, cal./gram mole °K.

Greek Letters

Λ^* = reduced de Broglie wavelength
ϵ = minimum potential energy, erg/molecule
σ = collision diameter, A.
ϕ_r = V/V_{ci}

Subscripts

1 = methane (reference substance)
2 = substance

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Transport Collision Integrals for Gases Using the Lennard-Jones (6, *n*) Potentials

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The three-parameter Lennard-Jones (6, *n*) intermolecular potential function was used to calculate the first six reduced collision integrals, the correction factors, and the various quantities derived from those collision integrals. The ranges of tabulation were

$$n = 8(2)20 \text{ and}$$
$$T^* = 0.001(0.005)0.02(0.01)0.1(0.05)0.5(0.1)1.0(0.2)$$
$$2.0(0.5)4.0(1.0)10(2.0)20(5)50(10)100$$

[numbers in parentheses between two numbers were interval for tabulation]. The three intermolecular potential parameters—*n*, ϵ/k, and σ—were determined from the experimental viscosity data for 12 gases: helium, argon, neon, hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, air, methane, propane, and *n*-pentane.

THE TRANSPORT properties of a dilute gas can be calculated if the intermolecular potential energy function is known, and calculations of this kind have important applications in analyzing experimental data to provide information on the potential energy function and in interpolating or extrapolating experimental data. The calculation is based on the Chapman-Enskog solution of the Boltzmann equation, which is given by Hirschfelder, Curtiss, and Bird (*9*); it involves evaluation of collision integrals which are complicated integrals requiring three stages of numerical integration. These collision integrals have been tabulated for a number of potential energy functions, including the well known Lennard-Jones (6, 12) (*9*), Buckingham exp-6 (*21*), L-J (6, 9) (*27*), and L-J (7, 28) (*27*) functions. There is a large amount of evidence that these functions are not sufficiently flexible to describe the actual interactions of real molecules accurately. With the availability of high-speed computers, we have used the L-J (6, *n*) potentials to calculate collision integrals. Thus, the potential function allows the adjustable steepness of the repulsive potential an additional degree of flexibility as compared to the L-J (6, 12) potential. The applicability of the potentials was tested for 12 gases with experimental viscosity data. Recently Klein and Smith (*17*) also tabulated collision integrals using L-J (6, *n*) with *n* = 9, 12, 15, 18, 21, 24, 30, 50, and 75.

The form of the L-J (6, *n*) potential $E(r)$ is

$$E(r) = \frac{n\epsilon}{n-6}\left(\frac{n}{6}\right)^{\frac{6}{n-6}}\left[\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (1)$$

where ϵ is the depth of the potential well, *n* is an adjustable parameter for the steepness of the repulsion potential, and $E(\sigma) = 0$. The reduced form of the potential is shown in Figure 1 for *n* = 8 and *n* = 20. This function should prove useful on several counts—it is simple in form, the repulsive index, *n*, serves as a simple indicator of the hardness of the repulsive core, the potential has been used in a number of more complicated theories (*10, 23*), this form has proved useful because the theory involves derivatives of potential which then leads to simple recursion formulas on the index *n*, and the potential functions derived