Thermodynamic Properties of Methyl Chloride

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The previous work on the thermodynamic properties of methyl chloride was reported in the Data Book of American Society of Refrigerating Engineers (*1*). The original source of the data was the Electrochemicals Department, E. I. du Pont de Nemours and Company, Inc. (*10*). Since they were primarily interested in the refrigerating operation, the data were limited to the temperature range of −60° to 170°F. at pressures from 4.0 to 300 lb./sq. in. abs. This present work is to evaluate the thermodynamic properties from experimental P-V-T data (*5*), in conjunction with other literature values, in order to extend the data for temperatures up to 420°F. and pressures up to 4,500 lb./sq. in. abs. A Mollier diagram was prepared to represent the enthalpies and entropies of methyl chloride, the saturated properties, and the properties in the two-phase region. All of the calculations were carried out numerically with a high speed CDC-1604 digital computer.

METHOD EMPLOYED

The basic equations and the methods employed here for the evaluation of thermodynamic properties from volume residual data were given in detail by Kang and McKetta (*6*). Equations (1) to (6) are the fundamental relationships used to evaluate the changes of enthalpy and entropy at any pressure and temperature P and T with respect to the reference state P_o and T_o:

$$\Delta H_{P,T} = H^\circ_T + H_P + (\Delta H_v)_{T_o} \tag{1}$$

$$\Delta S_{P,T} = S^\circ_T + S_P + (\Delta S_v)_{T_o} \tag{2}$$

$$H^\circ_T = \int_{T_o}^{T} C^\circ_P \, dT \tag{3}$$

$$S^\circ_T = \int_{T_o}^{T} \frac{C^\circ_P}{T} \, dT \tag{4}$$

$$H_P = J\left[\int_o^P \left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma \right]_T dP - \int_o^{P_o} \left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma \right]_{T_o} dP \right] \tag{5}$$

$$S_P = J\left\{ \int_o^P \left[\left(\frac{\partial \gamma}{\partial T}\right)_P \right]_T dP - \int_o^{P_o} \left[\left(\frac{\partial \gamma}{\partial T}\right)_P \right]_T dP \right\} \tag{6}$$

The fugacity coefficients were calculated from the following equation:

$$\nu = \frac{f}{p} = e^{-\frac{1}{RT}\int_o^P \gamma dp} \tag{7}$$

REFERENCE STATE

The saturated methyl chloride liquid at −40°F. is taken as the reference state. Here the vapor pressure is 7.043 lb./sq. in. abs. in accordance with the correlation of Messerly and Aston (*9*).

SOURCES OF DATA

P-V-T Data

The volume residuals used in evaluating the pressure effect on the enthalpy and entropy were derived from Hsu and McKetta's P-V-T data (*5*) of methyl chloride for temperatures from 35° to 225°C. For the lower temperatures the P-V-T data were taken from the Methyl Chloride Manual (*10*). Since these latter data were scattered at low pressures, they were fitted to a Berthelot type of equation of state and then the volume residuals were calculated accordingly.

Latent Heat of Vaporization

Latent heat of vaporization was calculated from the correlation of Hsu and McKetta (*5*) for temperatures above 35°C. Below this temperature, data were taken from the Methyl Chloride Manual. The results were smoothed before they were adopted for the evaluation.

Vapor Pressures

The vapor pressure correlation of Hsu and McKetta (*5*), Ganeff and Jungers (*2*), and the data from the Methyl Chloride Manual were used in this work. They were smoothed before they were used for evaluation.

Orthobaric Densities

The orthobaric densities were taken from the correlation of Hsu and McKetta (*5*) for temperatures above 35°C. For temperatures below 30°C. the data given in the Methyl Chloride Manual were used. Again they were smoothed.

Ideal Gas Heat Capacities

The ideal gas heat capacities were calculated by statistical mechanical methods. The product of the principle moments of inertia of methyl chloride was 17.9 × 10^{-177}

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Table 1. Thermodynamic Properties of Gaseous Methyl Chloride

Reference State: $S = 0$ and $H = 0$ for the saturated liquid of methyl chloride at —40°F. and 7.043 lb./ sq. in. abs.

T	P	V	H	S	ν
300	50	3.173	258.7	0.4953	0.9828
	100	1.558	256.8	0.4661	0.9657
	200	0.7486	252.7	0.4350	0.9316
	500	0.2581	238.9	0.3850	0.8305
	1,000	0.07024	195.8	0.3088	0.6469
	1,500	0.02694	141.5	0.2299	0.4797
	2,000	0.02515	131.0	0.2137	0.3895
	2,500	0.02376	128.1	0.2083	0.3360
	3,000	0.02306	125.8	0.2038	0.3011
	3,500	0.02239	124.0	0.2000	0.2768
	4,000	0.02181	122.7	0.1969	0.2593
	4,500	0.02145	121.6	0.1942	0.2465
340	50	3.352	268.5	0.5079	0.9861
	100	1.651	266.8	0.4790	0.9723
	200	0.7998	263.4	0.4485	0.9446
	500	0.2838	251.6	0.4014	0.8591
	1,000	0.1094	218.7	0.3392	0.7113
	1,500	0.03987	176.4	0.2763	0.5770
	2,000	0.02909	160.7	0.2529	0.4765
	2,500	0.02660	153.9	0.2421	0.4134
	3,000	0.02493	149.8	0.2349	0.3716
	3,500	0.02408	147.0	0.2296	0.3424
	4,000	0.02332	145.0	0.2254	0.3212
	4,500	0.02278	143.4	0.2218	0.3054
380	50	3.522	278.6	0.5202	0.9869
	100	1.737	277.1	0.4917	0.9736
	200	0.8446	274.1	0.4619	0.9478
	500	0.3093	264.6	0.4147	0.8745
	1,000	0.1214	242.4	0.3693	0.7504
	1,500	0.06108	212.4	0.3224	0.6450
	2,000	0.03729	191.6	0.2919	0.5514
	2,500	0.03066	180.7	0.2756	0.4844
	3,000	0.02787	174.7	0.2658	0.4378
	3,500	0.02626	170.9	0.2590	0.4049
	4,000	0.02516	168.2	0.2537	0.3807
	4,500	0.02420	166.1	0.2493	0.3625
420	50	3.701	289.0	0.5323	0.9899
	100	1.831	287.9	0.5041	0.9798
	200	0.8972	285.5	0.4750	0.9595
	500	0.3312	278.5	0.4335	0.8977
	1,000	0.1534	267.9	0.3992	0.7943
	1,500	0.08021	250.6	0.3683	0.6999
	2,000	0.04933	224.4	0.3307	0.6209
	2,500	0.03691	209.3	0.3088	0.5559
	3,000	0.03212	201.4	0.2964	0.5079
	3,500	0.02925	196.5	0.2881	0.4723
	4,000	0.02742	193.1	0.2818	0.4457
	4,500	0.02605	190.4	0.2765	0.4257

See footnote on this page for complete data of Table 1.

cu. g. cm.^{6} (3), and the vibrational frequencies were taken from infrared spectra (7). The heat capacity data so calculated have an accuracy of at least ± 0.1 cal./°K.-mole according to Gelles and Pitzer (3). The results were correlated into Equation (8):

$$C^\circ_P = 10.627859 - 2.27966038 \times 10^{-2}\,T + 6.30662169 \times 10^{-5}\,T^2 - 5.25162189 \times 10^{-8}\,T^3 + 1.56653557 \times 10^{-11}\,T^4 \quad (8)$$

In the temperature range of 419.7° to 960°R. the maximum difference between the values calculated from the above equation and those calculated directly from spectroscopic data was 0.0003 B.t.u./lb. °R.

The numerical method of evaluation was similar to that used by Kang and McKetta (*6*).

THERMODYNAMIC PROPERTIES AND MOLLIER DIAGRAM

Enthalpies, entropies, volumes, and fugacity coefficients of methyl chloride in the gas phase are presented in Table 1.[*]

The enthalpy, entropy, and fugacity coefficient of the saturated vapor were obtained by extrapolating each isotherm to the corresponding vapor pressure. The results were smoothed graphically.

The quantities for the saturated liquid were obtained by subtracting the latent heat of vaporization or the entropy of vaporization from the enthalpy or entropy of the saturated vapor. The specific volume of both saturated vapor and liquid were taken from reference 5 and *10*. The thermodynamic properties of saturated methyl chloride are tabulated in Table 2.[*]

In the two-phase region, the quality lines listed in Table 3[*] were obtained from the following two equations:

$$H_x = H_g - (1 - x)\,\Delta H_v \quad (9)$$

$$S_x = S_g - (1 - x)\,\Delta H_v \quad (10)$$

The resulting data are plotted as a Mollier diagram in Figure 1 giving the enthalpy and entropy isotherms, the isobars, the saturation curve, and the quality lines.

DISCUSSION

Internal Consistency

Equation (11) is usually used to check the internal consistency of a Mollier diagram:

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad (11)$$

In accordance with this equation the slope of an isobar

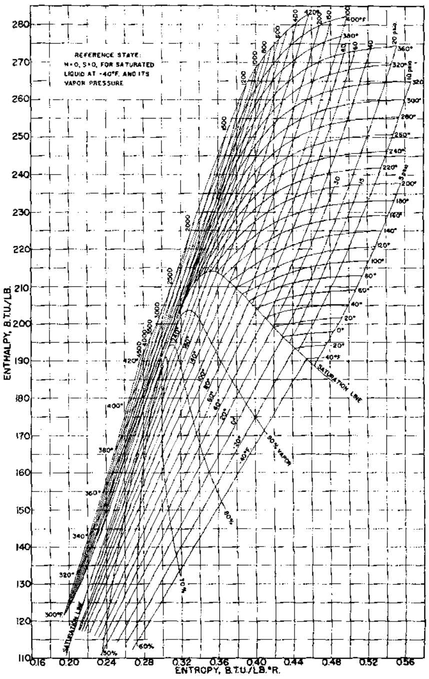

Fig. 1. Mollier diagram for methyl chloride.

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[*] Only a small part of Table 1 and Table 4 are presented here. A reprint of this article (including a large copy of Figure 1 and complete tables) is available for \$1.00 from Director, Bureau of Engineering Research, The University of Texas, Austin 12, Texas.

TABLE 4. DETAILS FOR INTERNAL CONSISTENCY CHECK

	Pressure, lb./sq. in. abs.			
	50	500	3,000	4,000
S at 300°F.	0.4953	0.3850	0.2038	0.1969
320°	0.5016	0.3932	0.2194	0.2112
340°	0.5079	0.4014	0.2349	0.2254
360°	0.5141	0.4095	0.2504	0.2396
380°	0.5202	0.4147	0.2658	0.2537
400°	0.5263	0.4255	0.2811	0.2678
420°	0.5323	0.4335	0.2964	0.2818
T_1, °R.	759.688			
T_2, °R.	879.688			
T_1S_1	376.273	298.480	154.824	149.583
T_2S_2	468.258	381.345	260.740	247.896
$\int_{T_1}^{T_2} SdT$	61.679	49.090	30.035	28.742
H_1 Table 1	258.7	238.9	125.8	122.7
H_2 Equation (12)	289.0	278.7	201.7	192.3
H_2 Table 1	289.0	278.5	201.4	193.1

in the enthalpy-entropy diagram should equal T. For practical application this equation may be rearranged into an integral form, that is

$$\Delta H = H_2 - H_1 = \Delta(TS) - \int_{T_1}^{T_2} SdT \qquad (12)$$

From Equation (12) the internal consistency can be checked. The enthalpy change because of the change of temperature at constant pressure, calculated from Equation (12), should check with the values from Table 1.

The enthalpies at four different pressures, 50, 500, 3,000, and 4,000 lb./sq. in. abs., were calculated by means of Equation (12) from the entropy data of Table 1. The integration involved in the second term on the right-hand side of Equation (12) was evaluated by the parabolic rule. The detail calculation is given in Table 4.

Comparison with Literature Values

The only reliable thermodynamic data for methyl chloride available in the literature, which can be used to check the calculated values in this work, are those in the Methyl Chloride Manual (*10*). Since these data were reported only for low pressures, all the data for pressures higher than 200 lb./sq. in. abs. were compared with Lydersen's generalized correlation (*8*). The results from this work show a complete agreement with the data given in the Methyl Chloride Manual. The comparison with the generalized charts shows the latter agree fairly well with the values obtained in this work except at 1,000 lb./sq. in. abs. and 300°F. This state is in the neighborhood of the critical point.

Reliability of Data

In the light of the internal consistency check of the data the agreement with the literature values, and the accurate P-V-T data, it can be expected that the accuracy of the enthalpy and entropy data varies from 0.1% at the low presures to 0.5% at the high pressure.

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NOTATION

C°_P = heat capacity at constant pressure in the ideal gas state, B.t.u./lb. °R.

e = base of the natural logarithm

f = fugacity

H = enthalpy, B.t.u./lb.

ΔH = change in enthalpy, B.t.u./lb.

H_g = enthalpy of the saturated vapor, B.t.u./lb.

H_L = enthalpy of the saturated liquid, B.t.u./lb.

H_v = latent heat of vaporization, B.t.u./lb.

$(\Delta H_v)_{T_0}$ = latent heat of vaporization at the reference temperature T_0, 190.5 B.t.u./lb.

H_P = change in enthalpy relative to zero pressure due to the change in pressure, B.t.u./lb.

H°_T = change in enthalpy in the ideal gas state relative to the reference temperature due to the change in temperature, B.t.u./lb.

$\Delta H_{P,T}$ = change in enthalpy relative to the reference state due to the changes in pressure and temperature, B.t.u./lb.

H_x = enthalpy of the vapor-liquid mixture, B.t.u./lb.

J = dimensional constant, 0.0029642452 B.t.u./(lb.) (cc. g.) (lb./sq. in. abs.)

P = absolute pressure, atm.

P_0 = reference pressure, 7.043 lb./sq. in. abs.

R = gas constant, 0.039359603 B.t.u./(°R.) (lb. of CH_3Cl) or 13.2694282 (lb./sq. in. abs.) (cc./g. of CH_3Cl)/°R.

S = entropy, B.t.u./lb. °R.

ΔS = change in entropy, B.t.u./lb. °R.

S_g = entropy of the saturated vapor, B.t.u./lb. °R.

S_L = entropy of the saturated liquid, B.t.u./lb. °R.

ΔS_v = entropy of vaporization, B.t.u./lb. °R.

$(\Delta S_v)_{T_0}$ = entropy of vaporization, at the reference temperature T_0, B.t.u./lb. °R.

S_P = change in entropy relative to zero pressure due to the change in pressure, B.t.u./lb. °R.

S°_P = change in entropy in the ideal-gas state relative to the reference temperature T_0 due to the change in temperature, B.t.u./lb. °R.

$\Delta S_{P,T}$ = change in entropy relative to the reference state due to the changes in pressure and temperature, B.t.u./lb. °R.

S_x = entropy of the vapor-liquid mixture, B.t.u./lb. °R.

T = absolute temperature, °R.

T_0 = reference temperature, −40°F.

x = quality of the vapor-liquid mixture, lb. vapor/lb. of mixture

$\Delta(TS)$ = $T_2S_2 - T_1S_1$

γ = volume residual, cc./g.

ν = fugacity coefficient

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