

THERMODYNAMIC PROPERTIES OF ETHYL CHLORIDE

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ABSTRACT

The thermodynamic properties—entropy and enthalpy—of ethyl chloride have been computed for the temperature range 285.56 (*b.p.*)—800°K and for the pressure range 1–300 atm. A temperature-entropy diagram based on the data is presented.

The common thermodynamic properties of ethyl chloride are not available in the literature. In the present study volume, entropy and enthalpy of ethyl chloride (mol. wt. 64.517) have been computed for saturated vapour, saturated liquid and superheated gaseous regions.

Compressibility Data. International Critical Tables¹ report the vapour and liquid densities for the temperature range 285.36 to 460.16 °K. As no other data are available for the gaseous region, the Martin and Hou² equation of state was used for the evaluation of the PVT-data in this region. The constants for this equation were evaluated from the available data. The calculated data agree with the available data¹ for saturated gas region with an average deviation of 1.73 per cent.

Specific heat of superheated gas.—The specific heat at constant pressure of ethyl chloride has been determined by Green and Holden³. In the present study, the specific heat of real gaseous ethyl chloride at a constant pressure of 1.57 atm. — the corresponding vapour pressure at 298.16 °K — has been calculated using the specific heat equation for ideal gas with the Berthelot correction $2.5313 (RT_c^3 / P_c T^3) P$. The constants of the ideal gas equation

$$C_p^0 = A + BT + CT^2 + DT^3$$

were evaluated by the method of least squares using the smoothened data of Green and Holden³ for specific heat for ideal gaseous ethyl chloride. Thus, the specific heat values used in the present study follow the relationship,

$$C_{p \text{ at } P=1.57} = -1.5481 + 0.0744 T - 7.1906 \times 10^{-5} T^2 + 3.0663 \times 10^{-8} T^3 \\ + 14.75196 \times 10^6 T^{-3}$$

which fits the corrected data of Green and Holden³ with an average deviation of 0.3 per cent.

Vapour Pressure.—Stull⁴, Gordon and Giauque⁵, O'hara and Fahien⁶, International Critical Tables¹ and Kirk and Othmer⁷ reported vapour pressure data for different ranges of temperatures. Gordon and Giauque⁵, O'hara and Fahien⁶ and International Critical Tables¹ reported empirical equations to fit their respective data. In the present study, the data available in the literature have been smoothened and accepted. The accepted data have been fitted to an empirical equation,

$$\ln P = 50.3156 - \frac{0.422 \times 10^4}{T} - 6.7269 \ln T + 0.8782 \times 10^{-2} T$$

with an average deviation of 0.45 per cent.

Latent heat of vaporization.—For the temperature range 183.36 to 440.16°K, O'hara and Fahien⁶ calculated heat of vaporization from Clapeyron equation making use of Antoine equation for vapour pressure and Haggemacher⁸ equation for vapour and liquid volumes. Green and Holden³ reported heat of vaporization at 298.16°K. In the present study the latent heats of vaporization were calculated from Clapeyron equation using the vapour pressure equation reported above and the accepted values of saturated vapour and liquid volumes. The values thus obtained were smoothened and used.

Normal boiling point and critical constants—From the values reported by various authors^{1, 4, 5, 7, 9-11}, the following have been accepted for the present study:

Normal boiling point	=	285.56°K
Critical temperature	=	459.76°K
Critical pressure	=	52.0 atm.
Critical volume	=	0.1949 litres/mole.

Specific volume of saturated liquid and vapour phase in equilibrium.—Wismer⁹, Ramsay¹² and Gilbert and Lagemann¹³ determined saturated liquid densities. International Critical Tables¹ reported vapour and liquid densities for the temperature range of 285.36 to 460.16°K. The values reported by International Critical Tables¹ have been accepted for the present work.

Calculation of thermodynamic functions in the homogeneous region from the PVT data.—Absolute entropy at 298.16°K was calculated by applying Berthelot correction to the ideal entropy reported by Green and Holden³. Absolute enthalpy at 298.16°K was calculated¹¹ from ideal heat content³ and heat of formation at 0°K,³ after applying the Berthelot correction. The values are:

Entropy of real gaseous ethyl chloride at 298.16°K and 1.57 atm.	=	65.80 cal./mole°K.
Enthalpy of real gaseous ethyl chloride at 298.16°K and 1.57 atm.	=	-20101.0 cal./mole.

The entropy and enthalpy values at 298.16 °K along 1.57 atm. isobar were calculated following the same mathematical treatment as in the case of n-butane¹⁵. The Martin and Hou equation is,

$$P = \frac{RT}{(V-b)} + \frac{A_2 + B_2 T + C_2 e^{-KT/T_c}}{(V-b)^2} + \frac{A_3 + B_3 T + C_3 e^{-KT/T_c}}{(V-b)^3} \\ + \frac{A_4}{(V-b)^4} + \frac{B_5 T + C_5 e^{-KT/T_c}}{(V-b)^5}$$

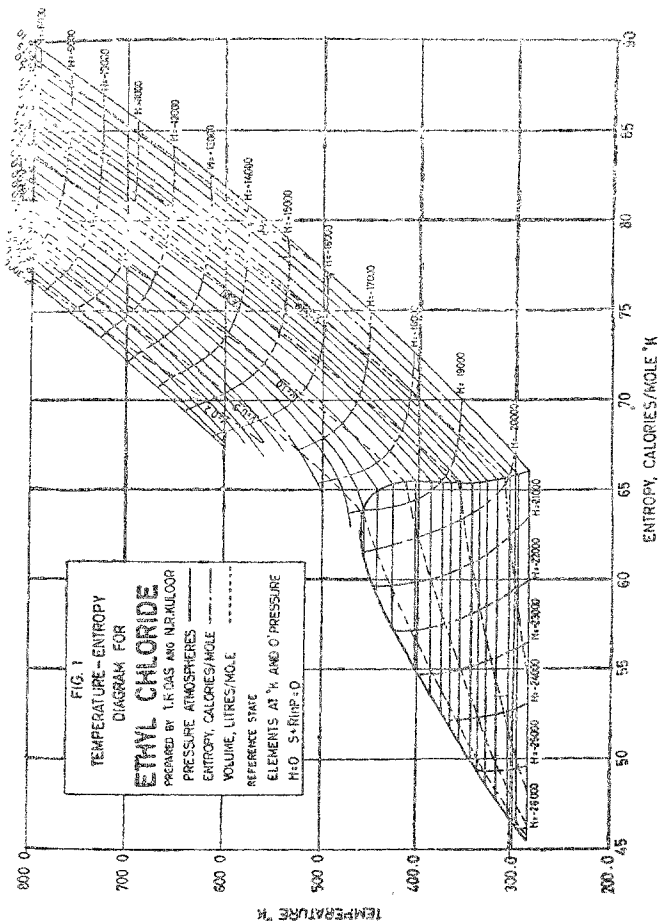
The values of the constants are as follows :

$$\begin{array}{lll} b = 0.0394 & K = 5.475 & \\ A_2 = -15.6862 & B_2 = 0.012 & C_2 = -0.1921 \times 10^3 \\ A_3 = 2.1211 & B_3 = -0.1429 \times 10^{-2} & C_3 = 0.3291 \times 10^2 \\ A_4 = -0.1174 & B_5 = 0.8199 \times 10^{-5} & C_5 = -0.7331 \times 10^{-1} \end{array}$$

The entropy and enthalpy values for the saturated vapour and liquid, calculated as in the case of n-octane¹⁶, are given in Table I.

Discussion. The thermodynamic properties of ethyl chloride computed for the pressure range 1 to 300 atm. and the temperature range 285.56 to 300°K are given in Tables I to IV*. The temperature-entropy diagram is shown in Fig 1. As the Martin and Hou² equation of state yields reliable PVT data in the superheated and saturated vapour region for a number of substances and as only vapour pressure data and critical properties are needed for the evaluation of the coefficients of this equation, it was used in the present study for the calculation of the PVT data. A comparison of the PVT data calculated in the present study for the saturated vapour region with the experimental data of other authors shows good agreement. The comparison is, however, limited to the temperature and pressure ranges covered by these authors. A check by the usual methods shows the data in Tables II, III and IV to be internally consistent.

* Complete tabular material can be obtained from the authors.



ETHYL CHLORIDE

TABLE I

Properties of the saturated liquid and vapour.

Temp. °K.	Vapour pressure atm.	Volume, lit./mole		Entropy, cal./mole °K.		Enthalpy, cal. mole			
		Liquid	Vapour	Liquid	Vapour- zation	Vapour	Liquid	Vapour- zation	Vapour
285.56	1.00	0.07125	22.63	45.36	20.67	66.03	-26188.2	5902.5	-20385.7
290.00	1.19	0.07177	19.30	45.06	20.27	65.93	-25903.8	5878.3	-20086.8
300.00	1.67	0.07300	13.76	46.34	19.39	65.73	-25679.5	5738.1	-19941.4
310.00	2.31	0.07430	10.16	47.09	18.51	65.60	-25439.5	5641.6	-19797.9
320.00	3.11	0.07568	7.67	47.88	17.63	65.51	-25187.6	5524.2	-19663.4
330.00	4.12	0.07718	5.81	48.67	16.74	65.41	-24908.7	5392.4	-19516.3
340.00	5.36	0.07877	4.56	49.52	15.86	65.38	-24613.2	5243.0	-19370.2
350.00	6.86	0.08050	3.63	50.39	14.98	65.37	-24315.7	5086.8	-19228.9
360.00	8.67	0.08240	2.91	51.23	14.13	65.36	-24004.2	4902.5	-19101.7
370.00	10.8	0.08447	2.33	52.10	13.25	65.35	-23654.9	4704.4	-18950.5
380.00	13.3	0.08678	1.94	53.03	12.38	65.41	-23301.5	4488.9	-18812.6
390.00	16.2	0.08922	1.61	53.94	11.51	65.45	-22932.2	4236.0	-18696.2
400.00	19.6	0.09256	1.321	54.87	10.59	65.46	-22549.6	3936.0	-18613.6
410.00	23.4	0.09577	1.067	55.80	9.60	65.40	-22126.8	3591.0	-18535.8
420.00	27.8	0.10000	0.869	56.80	8.55	65.35	-21685.9	3199.2	-18486.7
430.00	32.7	0.10526	0.702	57.82	7.44	65.26	-21224.9	2719.2	-18505.7
440.00	38.2	0.11254	0.547	58.85	6.18	65.03	-20624.2	2002.5	-18621.7
450.00	44.5	0.12420	0.406	60.16	4.45	64.61	-19477.1	0.00	-
459.76	52.0	0.19490	0.1949	62.61	0.00	62.61	-	-	-

TABLE II—(contd.)

Pressure Atm.	Temp. °K							
	460.0	470.0	480.0	520.0	560.0	600.0	700.0	800.0
1.0	37.49	38.32	39.16	42.48	45.79	49.10	57.35	65.59
1.5	24.91	25.47	26.03	28.25	30.47	32.68	38.20	43.71
2.0	18.62	19.04	19.46	21.14	22.81	24.48	28.63	32.77
3.0	12.33	12.61	12.90	14.03	15.15	16.27	19.06	21.83
4.0	9.18	9.40	9.61	10.47	11.33	12.17	14.27	16.56
6.0	6.03	6.18	6.33	6.92	7.50	8.07	9.49	10.89
8.0	4.46	4.57	4.69	5.14	5.58	6.02	7.09	8.15
10.0	3.51	3.61	3.70	4.07	4.43	4.79	5.6	6.51
25.0	2.25	2.31	2.38	2.65	2.90	3.14	3.74	4.32
20.0	1.61	1.67	1.72	1.93	2.13	2.32	2.78	3.23
30.0	0.958	1.01	1.05	1.22	1.36	1.50	1.83	2.14
40.0	0.611	0.661	0.705	0.853	0.978	1.09	1.35	1.59
50.0	0.345	0.478	0.483	0.633	0.746	0.845	1.06	1.25
60.0		0.182	0.308	0.482	0.591	0.681	0.874	1.05
80.0				0.288	0.336	0.476	0.637	0.776
100.0								
120.0				0.281	0.281	0.355	0.496	0.614
140.0				0.209	0.209	0.277	0.404	0.507
160.0				0.167	0.167	0.223	0.338	0.431
200.0						0.187	0.290	0.374
300.0						0.151	0.225	0.296
						0.127	0.154	0.196

TABLE III (concl'd.)

Pressure atm.	460.0	470.0	480.0	Temp. °K. 500.0	560.0	600.0	700.0	800.0
1.0	75.44	75.93	76.41	78.30	80.11	81.87	86.00	89.84
1.5	74.62	75.11	75.59	77.48	79.30	81.06	85.20	89.03
2.0	74.03	74.52	75.01	76.90	78.72	80.48	84.62	88.46
3.0	73.20	73.69	74.18	76.07	77.90	79.66	83.80	87.65
4.0	72.60	73.09	73.58	75.48	77.31	79.07	83.22	87.07
6.0	71.73	72.23	72.72	74.63	76.47	78.24	82.40	86.25
8.0	71.09	71.60	72.09	74.02	75.87	77.64	81.81	85.66
10.0	70.58	71.09	71.59	73.35	75.39	77.17	81.34	85.20
15.0	69.60	70.12	70.64	72.61	74.49	76.29	80.49	84.36
20.0	68.84	69.37	69.90	71.92	73.83	75.64	79.87	83.75
30.0	67.57	68.16	68.73	70.86	72.83	74.68	78.96	82.87
40.0	66.35	67.05	67.70	70.00	72.04	73.95	78.29	82.23
50.0	64.58	65.78	66.62	69.22	71.37	73.33	77.74	81.71
60.0		62.90	65.21	68.47	70.77	72.79	77.27	81.28
80.0				66.90	69.65	71.84	76.49	80.56
100.0					68.60	71.00	75.84	79.98
120.0					67.63	70.23	75.27	79.48
140.0					66.84	69.54	74.76	79.04
160.0						68.93	74.29	78.64
200.0						68.12	73.48	77.95
300.0						67.34	72.14	76.61

TABLE IV (concl'd.)

Pressure atm.	Temp. K°							
	460.0	470.0	480.0	520.0	562.0	600.0	700.0	800.0
1.0	-16806.2	-16579.6	-16350.3	-15407.6	-14426.4	-13409.3	-10722.7	-7847.3
1.5	-16816.0	-16588.9	-16359.2	-15415.3	-14433.0	-13415.1	-10727.2	-7830.9
2.0	-16826.0	-16598.4	-16368.3	-15422.9	-14439.7	-13421.0	-10731.7	-7824.5
3.0	-16846.0	-16617.5	-16386.5	-15438.3	-14453.0	-13422.6	-10740.6	-7861.6
4.0	-16866.2	-16636.8	-16404.9	-15453.8	-14466.3	-13444.4	-10749.6	-7868.7
6.0	-16907.5	-16675.9	-16442.2	-15485.1	-14493.3	-13468.0	-10767.5	-7883.0
8.0	-16949.7	-16716.0	-16480.3	-15516.9	-14520.5	-13491.8	-10785.6	-7897.3
10.0	-16993.1	-16757.0	-16519.2	-15549.1	-14548.0	-13515.8	-10803.6	-7911.5
15.0	-17106.7	-16864.0	-16620.3	-15631.9	-14618.1	-13576.5	-10848.9	-7947.1
20.0	-17229.5	-16978.6	-16727.7	-15717.9	-14690.0	-13638.3	-10894.5	-7982.7
30.0	-17513.3	-17238.0	-16966.9	-15901.7	-14839.9	-13765.3	-10986.3	-8053.7
40.0	-17887.5	-17561.2	-17253.5	-16104.0	-14998.9	-13896.9	-11078.8	-8124.5
50.0	-18583.2	-18026.8	-17625.6	-16330.2	-15167.7	-14033.3	-11172.0	-8194.8
60.0		-19302.6	-18208.1	-16587.1	-15347.3	-14174.3	-11265.5	-8264.6
80.0				-17220.5	-15739.7	-14468.8	-11457.9	-8402.4
100.0					-16166.6	-14774.8	-11639.2	-8537.3
120.0					-16593.0	-15082.4	-11822.3	-8668.5
140.0					-17943.5	-15378.7	-12040.7	-8775.7
160.0					-15644.3	-12172.8	-8918.8	
200.0					-15969.2	-12493.2	-9151.8	
300.0					-16113.1	-12994.8	-9641.9	

Nomenclature:

$A, B, C,$ and D = specific heat equation constants.

$A_2, A_3, A_4, B_2, B_3, B_4, C_2, C_3, C_4, b$ and K = Martin-Hou equation of state constants.

C_p^0 = ideal gaseous specific heat at constant pressure.

C_p = real gaseous specific heat at constant pressure.

H = enthalpy, cal./mole.

P = pressure, atm. (international)

P_c = critical pressure, atm.

R = gas constant, 0.082054 litre, atm./mole $^{\circ}$ K.

S = entropy, cal./mole $^{\circ}$ K.

T = temperature, $^{\circ}$ K (Kelvin scale with ice point at 273.16 $^{\circ}$ K).

T_c = critical temperature, $^{\circ}$ K.

V = volume, litres/mole.

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