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THERMODYNAMIC PROPERTIES OF ACETALDEHYDE

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ABSTRACT

The thermodynamic properties—entropy and enthalpy—of acetaldehyde have been computed for the temperature range 293.32 to 800 °K and for the pressure range 1.0 to 300 atm. A temperature-entropy diagram based on the data is presented.

The common thermodynamic properties of acetaldehyde are not available in the literature. In the present study volume, entropy and enthalpy of acetaldehyde (mol. wt. 44.052) have been computed for the saturated vapour, saturated liquid and superheated gaseous regions.

Compressibility data. Maass and Boomer[1] determined liquid density for the temperature range 273.26 to 323.16 °K. As no other data are available for the gaseous region, the modified Martin and Hou[2] equation of state was used for evaluating the PVT data in this region. The constants of this equation were evaluated from the available vapour pressure data and the critical constants.

Specific heat of superheated gas. The specific heat of acetaldehyde at constant pressure has been determined by Smith[3] and Pitzer and Weltner[4]. In the present study, the specific heat of real gaseous acetaldehyde at a constant pressure of 1.18 atm.—the corresponding vapour pressure at 298.16°K

—has been calculated using the specific heat equation for ideal gas with the Berthelot correction $2.5313\ (RT_c^3/P_c T^2)\ P$. 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 Pitzer and Weltner[4] for specific heat of ideal gaseous acetaldehyde. Thus the specific heat values used in the present study follow the relationship

$$C_{p \text{ at } P=1.15} = 3.6028 + 0.0349\ T - 1.092 \times 10^{-5}\ T^2 - 6.8617 \times 10^{-10}\ T^3 + 0.8822 \times 10^{7}\ T^{-3}$$

which fits the corrected data of Pitzer and Weltner[4] with an average deviation of 0.14 per cent.

Vapour Pressure. Kirk and Othmer[5] reported vapour pressure data in the temperature range 223.16 to 373.16 °K. In the present study the smoothened values reported by Kirk and Othmer[5] have been used and have been fitted to an empirical equation,

$$\ln P = -47.1942 - \frac{0.1434 \times 10^4}{T} + 9.7487 \ln T - 0.0113\ T$$

with an average deviation of 1.63 per cent.

Latent heat of vaporization. Kirk and Othmer[5] reported latent heat of vaporization at one temperature. In the present study, the latent heat of vaporization was calculated from Clapeyron equation using the vapour pressure equation reported above and the accepted values of saturated vapour and liquid volumes.

Normal boiling point and critical constants. From the values reported by various authors[1, 5, 6] the following have been accepted for the present study:

Normal boiling point	=	293.32 °K
Critical temperature	=	454.66 °K
Critical pressure	=	63.2 atm.

From the correlation suggested by Kulkarni-Jatkar and Laxminarayanan[6] the critical volume for acetaldehyde was calculated as 0.1555 litres/mole.

Specific volume of saturated liquid and vapour phase in equilibrium. Experimental liquid density for the temperature range 273.26 to 323.16 °K has been reported by Maass and Boomer[1]. In the present study the saturated vapour volume was calculated using the modified Martin-Hou equation[2]. The

calculated and reported values[1] were plotted and a smooth curve was drawn. The smoothened values which follow the law of rectilinear diameter have been used in the present study.

Calculation of thermodynamic functions in the homogeneous region from the PVT data. Absolute entropy at 298.16 °K was calculated by applying the Berthelot correction to the ideal entropy reported by Pitzer and Weltner[4]. Absolute enthalpy at 298.16 °K was calculated[7] from the ideal heat content value[4] and heat of formation at 0 °K[4] after applying the Berthelot correction. The values for entropy and enthalpy at 298.16 °K and 1.18 atm., the vapour pressure at 298.16 °K, thus obtained, are 63.04 cal./mole °K and −34128.4 cal./mole, respectively.

The entropy and enthalpy values of 1.18 atm. isobar were calculated following the same mathematical treatment as in the case of n-butane[8].

The modified Martin and Hou equation[2] is,

$$P = \frac{RT}{(V-b)} + \frac{A_2 + B_2 + C_3 \exp.\ (-KT/T_c)}{(V-b)^2} + \frac{A_3 + B_3\,T + C_3 \exp.\ (-KT/T_c)}{(V-b)^3}$$

$$+ \frac{A_4}{(V-b)^4} + \frac{B_5\,T + C_5 \exp.\ (-KT/T_c)}{(V-b)^5}$$

The values of the constants are as follows:

b	= 0.02971	K	= 5.475		
A_2	= −12.1152	B_2	= 0.9441×10^{-2}	C_2	= -0.2410×10^{3}
A_3	= 1.1995	B_3	= -0.6395×10^{-3}	C_3	= 0.3351×10^{2}
A_4	= −0.0626	B_5	= 0.3768×10^{-5}	C_5	= -0.5062×10^{-1}

The entropy and enthalpy values for the saturated vapour and liquid, calculated as in the case of n-octane[9], are given in Table I.

Discussion. The thermodynamic properties of acetaldehyde computed for the pressure range 1 to 300 atm. and the temperature range 293.32 to 800 °K are given in Tables I to IV*. The temperature-entropy diagram is shown in Fig. 1. As the Martin-Hou 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 evaluating the coefficients of this equation, it was used in the present case for evaluation of the PVT data with the assumption that the equation would hold good for acetaldehyde also. 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

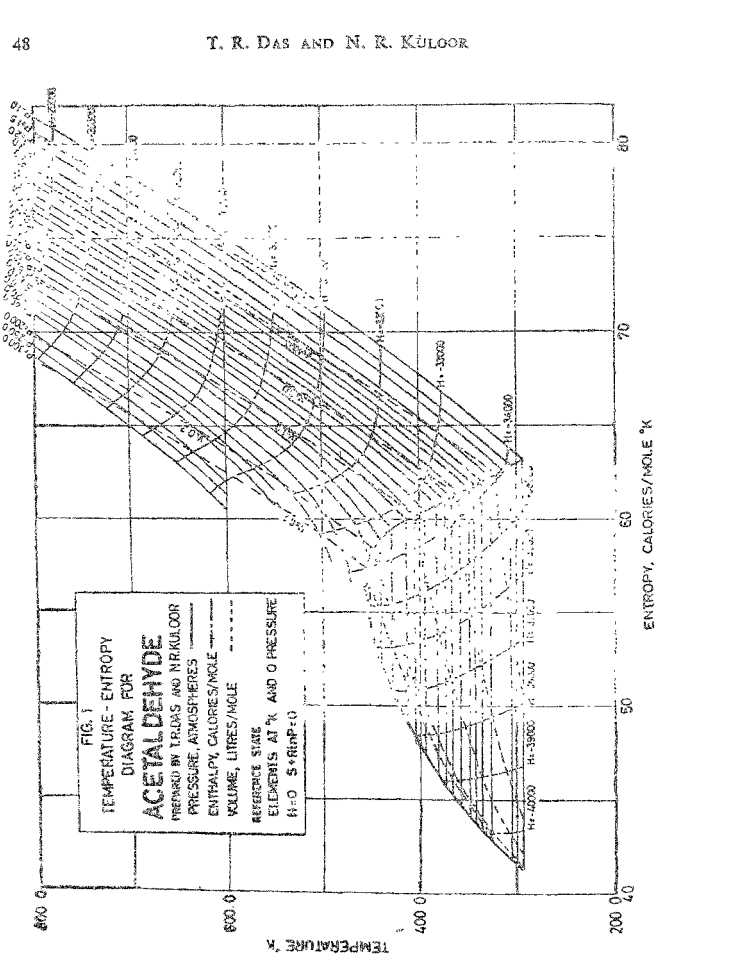
FIG. 1
TEMPERATURE - ENTROPY DIAGRAM FOR
ACETALDEHYDE
PREPARED BY T.R.DAS AND N.R.KULOOR
PRESSURE, ATMOSPHERES
ENTHALPY, CALORIES/MOLE
VOLUME, LITRES/MOLE
REFERENCE STATE
ELEMENTS AT °K AND 0 PRESSURE
H=0 S=RlnP=0
TEMPERATURE °K
ENTROPY, CALORIES/MOLE °K
800 0
600 0
400 0
200 0
40
50
60
70
80
H=-33000
H=-34000
H=-38000
H=-40000

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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	Vapori-zation	Vapour	Liquid	Vapori-zation	Vapour
293.32	1.00	0.05668	23 40	41 30	21.87	63.17	– 40598.2	6414 9	– 34183 3
300.00	1.27	0.05736	18 65	41 57	21 38	62 95	– 40523.1	6414.0	– 34109.1
310 00	1.82	0.05839	13.40	42.03	20 63	62 66	– 40394.4	6395.3	– 33999.1
320.00	2.51	0.05951	9.98	42.51	19 86	62.37	– 40245.0	6355.2	– 33889 8
330.00	3.37	0.06072	7.56	43.10	19 03	62.13	– 40060 9	6279 9	– 33781.0
340.00	4.61	0 06200	5.62	43 64	18 21	61.85	– 39866.8	6191 4	– 33675.4
350.00	6 33	0.06344	4.10	44.20	17 36	61.56	– 39668.5	6076.0	– 33592.5
360 00	8.51	0 06501	3 06	44 80	16.46	61.26	– 39437.4	5925.6	– 33511 8
370.00	11.07	0.06669	2.35	45 48	15 52	61.00	– 39177.1	5742.4	– 33434.7
380 00	14.30	0 06871	1 80	46.24	14.52	60 76	– 38889 6	5517.6	– 33372.0
390.00	18.10	0.07088	1 41	47.05	13.46	60.51	– 38568 5	5249.4	– 33319.1
400.00	22 50	0 07340	1 11	47.95	12 31	60 26	– 38201 5	4924.0	– 33277 5
410.00	27.76	0 07650	0 872	48.87	11.13	60 00	– 37822.8	4563.3	– 33259.5
420.00	33 87	0 08026	0.682	49.90	9.80	59 70	– 37385.0	4116.0	– 33269 0
430.00	40.90	0.08528	0.529	51.00	8.36	59.36	– 36914.0	3594.8	– 33319 2
440.00	49.05	0.09275	0.3977	52 26	6.60	58 86	– 36352.0	2904.0	– 33448 0
450.00	58.41	0.11029	0.2633	54.17	3 79	57.96	– 35527.5	1705 5	– 33822.0
454.66	63.20	0.15550	0.1555	56.26	0.00	56.26	– 34516.7	0.00	– 34516.7

TABLE II

Volume (litres/mole)

Pressure atm.	Temp. °K. 293.32	320.0	360.0	400.0	430.0	440.0	450.0
1.0	23.40	25.74	29.16	32.54	35.04	35.88	36.71
1.5		16.98	19.31	21.59	23.28	23.84	24.40
2.0		12.60	14.39	16.12	17.40	17.83	18.25
3.0			9.46	10.65	11.52	11.81	12.09
4.0			7.00	7.91	8.58	8.80	9.02
6.0			4.52	5.17	5.64	5.79	5.94
8.0			3.28	3.80	4.16	4.28	4.40
10.0				2.98	3.28	3.38	3.47
15.0				1.87	2.09	2.17	2.24
20.0				1.30	1.50	1.56	1.61
30.0					0.887	0.938	0.985
40.0					0.553	0.611	0.659
50.0							0.444
60.0							
63.2							
70.0							
80.0							
100.0							
120.0							
140.0							
160.0							
200.0							
300.0							

TABLE II (*concld.*)

Pressure atm.	Temp. °K. 460.0	470.0	480.0	500.0	600.0	700.0	800.0
1.0	37.54	38.37	39.20	40.86	49.13	57.37	65.60
1.5	24.96	25.52	26.07	27.19	32.72	38.23	43.72
2.0	18.67	19.09	19.51	20.35	24.51	28.65	32.78
3.0	12.38	12.66	12.95	13.51	16.31	19.08	21.84
4.0	9.23	9.45	9.66	10.07	12.20	14.29	16.37
6.0	6.09	6.23	6.38	6.67	8.10	9.51	10.90
8.0	4.51	4.62	4.74	4.96	6.05	7.11	8.17
10.0	3.57	3.66	3.75	3.93	4.82	5.68	6.53
15.0	2.30	2.37	2.44	2.56	3.18	3.76	4.34
20.0	1.67	1.72	1.78	1.88	2.36	2.18	3.24
30.0	1.03	1.07	1.11	1.19	1.54	1.85	2.15
40.0	0.701	0.740	0.777	0.844	1.13	1.37	1.60
50.0	0.493	0.534	0.570	0.630	0.880	1.09	1.28
60.0	0.334	0.386	0.426	0.490	0.716	0.895	1.06
63.2	0.283	0.345	0.388	0.453	0.675	0.847	1.00
70.0	0.132	0.263	0.316	0.386	0.599	0.760	0.904
80.0		0.149	0.224	0.305	0.512	0.658	0.788
100.0				0.192	0.391	0.517	0.626
120.0					0.306	0.424	0.519
140.0					0.257	0.358	0.443
160.0					0.218	0.310	0.386
200.0					0.168	0.246	0.308
300.0					0.120	0.164	0.208

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TABLE III

Entropy (cal./mole °K)

Pressure atm.	Temp. K° 293.32	320.0	360.0	400.0	430.0	440.0	450.0
1.0	63.17	64.38	66.09	67.72	68.90	69.28	69.67
1.5		63.51	65.25	66 89	68.08	68.46	68 85
2.0		62.88	64 64	66,30	67.49	67 88	68.26
3.0			63.77	65.45	66.65	67.04	67.43
4.0			63.12	64 83	66.04	66.44	66 83
6.0			62.16	63.93	65.17	65.57	65.96
8 0			61.43	63.26	64.52	64.93	65.33
10.0				63.71	64,01	64.42	64.83
15.0				61.62	63.00	63.43	63 86
20.0				60 71	62.21	62.67	63.11
30 0					60 87	61.40	61.90
40.0					59 50	60.21	60.82
50.0							59.64
60.0							
63.2							
70.0							
80.0							
100.0							
120.0							
140.0							
160 0							
200 0							
300.0							

TABLE III (*concld.*)

Pressure atm.	Temp. °K 460.0	470.0	480.0	500.0	600.0	700.0	800.0
1.0	70 04	70.42	70.80	71 54	75.01	78 33	81.45
1.5	69.23	69.61	69.98	70.72	74.20	77.52	80.64
2.0	68 64	69.02	69.40	70.14	73.62	76.94	80.06
3.0	67 81	68.19	68.57	69 31	72 81	76.13	79 25
4.0	67.21	67.60	67.98	68.72	72.22	75.55	78 68
6.0	66.36	66.74	67.12	67 88	71 40	74.73	77.86
8.0	65.73	66.12	66.51	67 27	70 80	74.14	77 28
10.0	65.23	65.62	66.02	66.78	70 34	73.68	76 82
15.0	64 28	64.68	65.09	65.87	69.47	72 84	75.99
20.0	63.55	63 97	64 38	65.19	68 84	72.23	75.39
30.0	62.38	62.84	63.29	64.14	67 92	71.35	74.53
40 0	61.38	61.90	62.39	63.31	67.22	70.70	73.90
50.0	60.37	60.99	61 55	62.57	66.65	70.17	73 40
60.0	59.12	60.01	60.70	61 86	66 15	69 73	72.98
63.2	58.55	59 65	60.42	61.64	66.00	69.60	72 86
70.0	55.62	58.71	59.75	61.16	65.71	69.35	72 62
80 0		56.57	58.55	60.42	65.30	69.00	72.30
100.0				58.81	64.57	68.40	71.75
120 0					63.96	67.88	71.28
140.0					63.32	67 42	70.87
160.0					62.78	67.00	70.50
200.0					61.85	66.28	69 87
300.0					60.42	64.91	68 65

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TABLE IV

Enthalpy (cal./mole)

Pressure atm.	Temp. K° 293.32	320.0	360.0	400.0	430 0	440.0	420.0
1.0	– 34183.3	– 33814.8	– 33233.0	– 32613.6	– 32124.0	– 31956.0	– 31785.6
1 5		– 33839.1	– 33249.8	– 32625.9	– 32134.0	– 31965.4	– 31794 5
2.0			– 33864.0	– 33266.9	– 32638.3	– 32144.1	– 31803.4
3.0			– 33301.6	– 32663.5	– 32164.5	– 31994.0	– 31821.4
4 0			– 33337 3	– 32689.0	– 32185 1	– 32013 4	– 31839.6
6 0			– 33411.7	– 32741.4	– 32227.2	– 32052.7	– 31876.5
8.0			– 33490.8	– 32795.7	– 32270 3	– 32093.0	– 31914.2
10 0				– 32852.1	– 32314.6	– 32134.2	– 31952 7
15.0				– 33004.5	– 32431.2	– 32242.0	– 32053.0
20 0				– 33178.7	– 32557.8	– 32357.9	– 32159.7
30.0					– 32854 9	– 32622 8	– 32399.0
40.0					– 33269.4	– 32962.8	– 32690.5
50.0							– 33089.7
60.0							
63.2							
70.0							
80 0							
100.0							
120.0							
140.0							
160 0							
200.0							
300 0							

TABLE IV (*concld.*)

Pressure atm.	Temp. °K 460.0	470.0	480 0	500.0	600.0	700.0	800.0
1.0	– 31612.9	– 31437.8	– 31260.4	– 30898.5	– 28676.0	– 26822.0	– 24484.0
1.5	– 31621.3	– 31445.7	– 31267.9	– 30905.4	– 28980 0	– 26826.0	– 24486.0
2 0	– 31629.7	– 31453.7	– 31275.5	– 30912 2	– 28985.0	– 26829 0	– 24489.0
3.0	– 31646.7	– 31469 8	– 31290.7	– 30926.0	– 28994 0	– 26836.0	– 24495.0
4 0	– 31663 8	– 31486.0	– 31306.0	– 30939.8	– 29004 0	– 26843.0	– 24500.0
6.0	– 31698.6	– 31518.7	– 31337 0	– 30967.8	– 29022.0	– 26857.0	– 24511.0
8.0	– 31743 0	– 31552.1	– 31368.5	– 30996.1	– 29041.0	– 26871 0	– 24522.0
10 0	– 31770.1	– 31586.0	– 31400.6	– 31024.9	– 29060 0	– 26885.0	– 24533.0
15.0	– 31863.7	– 31673.7	– 31483.0	– 31098.4	– 29107.0	– 26920.1	– 24560.4
20.0	– 31962.6	– 31765.8	– 31569.1	– 31174.6	– 29155.4	– 26955.3	– 24587.8
30.0	– 32180.7	– 31966.4	– 31754.7	– 31336.1	– 29253.5	– 270 5.7	– 24642.2
40.0	– 32437.2	– 32196.0	– 31962.9	– 31512.0	– 29354.0	– 27096.5	– 24696.3
50 0	– 32759.2	– 32469 8	– 32202.7	– 31706 0	– 29456 9	– 27167.5	– 24750.1
60.0	– 33232 6	– 32821.1	– 32490.3	– 31923.1	– 29562.2	– 27238.5	– 24803.4
63.2	– 33471.1	– 32962.0	– 32597.0	– 31998.5	– 29596.3	– 27261.2	– 24820.3
70.0	– 34783.8	– 33350 4	– 32858 1	– 32170.0	– 29669.5	– 27309.4	– 24856.2
80.0		– 34306.9	– 33369.2	– 32455.2	– 29778.7	– 27380.2	– 24908 4
100.0				– 33140.4	– 30001.0	– 27520 4	– 25011.0
120.0					– 30178 0	– 27658.2	– 25110.7
140 0					– 30444 9	– 27792.3	– 25207.2
160 0					– 30655.3	– 27921.7	– 25300.2
200 0					– 31027.5	– 28100.0	– 25475 0
300 0					– 31549.3	– 28642.6	– 25842.3

NOMENCLATURE

A, B, C, and D = C_p heat equation constants.

A_2, A_3, A_4, B_2, B_3, B_5, C_2, C_3, C_5, b and K – Martin-Hou equation of state constants.

C_p° ideal gaseous sp. heat at constant [illegible]

C_p real gaseous specific heat at constant pressure.

H enthalpy, cal./mole.

P [illegible] atm. (international)

P_c critical pressure, atm.

R gas constant, 0.082054 litre, atm./mole °K.

S entropy, cal./mole °K.

T temp., °K (Kelvin scale with ice point at 273.16 °K).

T_c critical [illegible] °K.

V volume, litres/mole.

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