

# THERMODYNAMIC PROPERTIES OF CARBON TETRACHLORIDE

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Received on February 5, 1966

## ABSTRACT

The thermodynamic properties of carbon tetrachloride have been calculated up to a temperature of 750°K and a pressure of 200 atmospheres, using Martin and Hou equation of state. Tables of thermodynamic properties and a temperature-entropy diagram are presented.

Carbon tetrachloride is a raw material in the production of Freons, and can be used as a refrigerant by itself. Therefore, a knowledge of its thermodynamic properties is necessary. A detailed literature survey revealed that thermodynamic properties of carbon tetrachloride are available only in the saturated region up to a pressure of about 0.4 atmospheres<sup>6</sup>. In the present work tables and a diagram of thermodynamic properties of carbon tetrachloride over wide ranges of temperature and pressure are presented.

## SURVEY OF EXISTING DATA

1. *Vapour Pressure.* The vapour pressure of carbon tetrachloride has been experimentally determined by various investigators like Regnault<sup>25</sup>, Mundel<sup>24</sup>, Herz and Rathmann<sup>8</sup>, Young<sup>33</sup> and Hildenbrand and McDonald<sup>10</sup>. Accurate determination of vapour pressure up to a pressure of one atmosphere has been carried out by Hildenbrand and McDonald<sup>10</sup> by twin ebulliometric method. The authors have fitted their data to an equation of the form,

$$\log P (m.m.) = a' - b'/(t + c') \quad (1.a)$$

where  $a' = 6.89406$ ;  $b' = 1219.58$ ;  $c' = 227.16$  and  $t =$  temperature, °C.

The data Hildenbrand and McDonald<sup>10</sup>, Young<sup>33</sup> and the data given in International Critical Tables<sup>11</sup> were combined and smoothed. The smoothed data of vapour pressure, over the temperature range of 273°K to the critical point were used for this investigation.

The vapour pressure data above one atmosphere was fitted to an equation of the form

$$\log P = a + b/T + c \log T + dT \quad (1.b)$$

where  $a = 61.37647$

$$b = -3632.894766$$

$$c = -21.46100899$$

$$d = 1.028807543 \times 10^{-2} \text{ with } T \text{ in } ^\circ K \text{ and } P \text{ in atmosphere}$$

The equation predicts the vapour pressure data with maximum and average deviations of 0.63% and 0.2% respectively.

Equation (1.a) has been used below 1 atmosphere and Equation (1.b) has been used above 1 atmosphere.

2. *The Critical Constants.* The critical constants used in the present work are those suggested by Kobe and Lynn<sup>16</sup>. They are,

$$T_c = 556.36^\circ K; P_c = 45.0 \text{ atms.}; V_c = 276.0 \text{ c.c./mole.}$$

3. *The Specific Volume of Saturated Liquid and Vapour.* Young<sup>34</sup> measured the saturated liquid and vapour volumes from 353°K to the critical point. These data are listed in International Critical Tables<sup>11</sup>. The densities of carbon tetrachloride have been measured by Biron<sup>2</sup>, Egerton and Lee<sup>3</sup>, and Mills and Mac Rae<sup>23</sup>.

The saturated liquid and vapour densities of several investigators<sup>2, 3, 23</sup> over the temperature range of 273 – 353°K, were combined with the data given in the International Critical Tables<sup>11</sup> over the temperature range of 353°K to the critical point, and were smoothed.

The smoothed data over the temperature range of 273°K to the critical point were used for this investigation.

4. *Transition and Melting Temperatures.* The melting and transition temperatures have been determined by various investigators like Stull<sup>29</sup>, Johnstone and Long<sup>13</sup>, Turkevich and Smyth<sup>30</sup> and Hicks *et al.*<sup>9</sup>

The melting point of 250.30°K and the transition temperature of 225.35°K reported by Hicks *et al.*, agree very well with the values of other investigators<sup>29, 13, 30</sup>. For the present work, the data of Hicks *et al.*, have been used.

5. *Heats of Transition and Fusion.* The heats of transition and fusion have been determined by Latimer<sup>17</sup>, Johnston and Long<sup>13</sup>, Stull<sup>29</sup>, and Hicks *et al.*<sup>9</sup>

The differences in the reported values of heats of fusion with those reported by Hicks *et al.*, is about  $\pm 4\%$ . At this stage it is difficult to choose the best values of heats of fusion, and hence it is necessary to redetermine the heats of fusion. For the present work, more weight was placed on the data of Hicks *et al.*

The heat of transition reported by Hicks *et al.*, agrees very well with the data of other investigators<sup>17, 13, 29</sup> and therefore, it was selected for the present work.

The values used are:

Heat of transition = 1095.0 calories/mole.

Heat of fusion = 601.0 calories/mole.

6. *Heat Capacity from Calorimetric Data.* Heat capacity of carbon tetrachloride has been determined by the calorimetric method by various investigators. Among them mention may be made of Stavely *et al.*<sup>87</sup>, Stull<sup>29</sup>,

Hicks *et al.*<sup>9</sup>, Vold<sup>31</sup>, Richards and Wallace<sup>26</sup> and Lord and Blanchard<sup>18</sup>. Harrison and Moelwyn-Hughes<sup>7</sup> have measured heat capacity of carbon tetrachloride over the range of 243°K to 303°K. Hicks *et al.*<sup>9</sup>, have reported low temperature thermal data of carbon tetrachloride over the range of temperature of 17 to 298°K. The entropy calculated at 298.15°K using the data of Hicks *et al.*, agrees very well with the spectroscopic entropy data of Albright *et al.*<sup>1</sup> Hence, among the number of low temperature investigations, the data reported by Hicks *et al.*, seem to be the most reliable and complete. Hence, for this investigation the data of Hicks *et al.*, were used.

7. *Heat Capacity of the Ideal Gas.* The heat capacity of carbon tetrachloride in the ideal gaseous state has been calculated by Gelles and Pitzer<sup>4</sup>, Albright *et al.*<sup>1</sup>, Kelley<sup>14</sup>, Stevenson and Beach<sup>28</sup> and by Gordon<sup>5</sup>. Gordon conservatively took the frequencies in order to offset the neglect of anharmonicity, rotational stretching and rotation = rotation interaction. The data of Albright *et al.*, includes a semi-empirical anharmonicity correction. Kobe and Kobe<sup>15</sup> have fitted the data of Albright *et al.*, to an equation of the form,

$$C_p = A' + B'T + C'T^2 + D'T^3 \quad (2)$$

where  $A' = 9.288$ ;  $B' = 5.099 \times 10^{-2}$ ;  $C' = -5.729 \times 10^{-5}$  and  $D' = 2.257 \times 10^{-8}$ .

The authors report average and maximum deviations of 0.2 and 0.36 per cent, respectively.

Equation (2) was verified and was found to agree with the data with the same accuracy. For this work, Equation (2) has been used.

8. *Heat of Vaporization.* Latent heats of vaporization of carbon tetrachloride have been experimentally determined by various investigators like Marshall<sup>19</sup>, Mathews<sup>21</sup>, Hildenbrand and McDonald<sup>10</sup>, Wirtz<sup>32</sup> and Young<sup>34</sup>. The values tabulated by Mills<sup>22</sup> are those of Young<sup>34</sup> and are in good agreement with the data given in the International Critical Tables<sup>12</sup>. The data of Mills<sup>22</sup> were smoothed. The heat of vaporization was calculated by using Clausius-Clapeyron equation and was compared with the values of Mills. The agreement was found to be quite satisfactory. The smoothed data of Mills over a range of temperature of 273 to 556.36°K were used in the present investigation.

#### CALCULATION OF THERMODYNAMIC PROPERTIES

For the calculation of thermodynamic properties, the Martin and Hou<sup>20</sup> equation of state,

$$P = \frac{RT}{V - b_1} + \frac{A_2 + B_2T + C_2e^{-kT/T_c}}{(V - b_1)^2} + \frac{A_3 + B_3T + C_3e^{-kT/T_c}}{(V - b_1)^3} + \frac{A_4}{(V - b_1)^4} + \frac{B_5T}{(V - b_1)^5} \quad (3)$$

with  $k = 5.475$  has been used.

The constants in Equation (3), evaluated following the procedure outlined by the authors<sup>20</sup> are :

$$\begin{aligned} b_1 &= 0.05755953 \\ A_2 &= -26.19011895 \\ A_3 &= 4.95628873 \\ A_4 &= -0.38842449 \\ B_2 &= 0.016924131 \\ B_3 &= -0.00280089 \\ B_5 &= 0.000028784 \\ C_2 &= -428.5816275 \\ C_3 &= 93.49053479 \end{aligned}$$

Table I presents the deviation of pressures calculated using Equation (3). Comparison could not be made in the superheated region because of non-availability of data over this region.

The volume of carbon tetrachloride at various temperatures and pressures were evaluated by Newton-Raphson iterative method.

The change of entropy and enthalpy are given by the relation,

$$dS = C_v \left( \frac{dT}{T} \right) + \left( \frac{\delta P}{\delta T} \right)_V dV \quad (4)$$

and

$$dH = \left[ \left\{ T \left( \frac{\delta P}{\delta T} \right)_V + V \left( \frac{\delta P}{\delta V} \right)_T \right\} \right] dV_T + C_p dT \quad (5)$$

and if  $C_v = A + BT + CT^2 + DT^3$ , (6)

using Equation (3) and taking necessary derivatives, Equations (4) and (5) become :

$$S = \left\{ A \ln T + BT + (C/2) T^2 + (D/3) T^3 + R \ln (V - b_1) - \frac{B_2}{(V - b_1)} - \frac{B_3}{2(V - b_1)^2} - \frac{B_5}{4(V - b_1)^4} + \left[ \frac{C_2}{(V - b_1)} + \frac{C_3}{2(V - b_1)^2} \right] (K/T_c) e^{-kT/T_c} \right\} + C_s \quad (7)$$

and,

$$H = \left\{ AT + BT^2/2 + CT^3/3 + DT^4/4 + PV + \frac{A_2 + (1 + kT/T_c)C_2 e^{-kT/T_c}}{(V - b_1)} + \frac{A_3 + (1 + kT/T_c)C_3 e^{-kT/T_c}}{2(V - b_1)^2} + \frac{A_4}{3(V - b_1)^3} \right\} + C_H \quad (8)$$

TABLE I  
Comparison of Calculated and Observed Pressures

$T^{\circ}K$	$P_{calc.}$	$P_{obs.}$	Per cent Deviation
280.0	0.061497	0.063289	2.831
290.0	0.1026209	0.103510	0.859
300.0	0.1629273	0.16284	-0.536
310.0	0.24344	0.247537	1.655
320.0	0.358799	0.36495	1.685
330.0	0.518653	0.523550	0.935
340.0	0.728813	0.732860	0.552
350.0	0.994190	1.003684	0.946
360.0	1.332682	1.34280	0.754
370.0	1.7633148	1.77120	0.445
380.0	2.297082	2.2962	-0.038
390.0	2.927128	2.9308	0.125
400.0	3.672161	3.68660	0.392
410.0	4.567123	4.5810	0.303
420.0	5.58585	5.625	0.696
430.0	6.777344	6.8364	0.864
440.0	8.153701	8.2328	0.961
450.0	9.7241199	9.8274	1.051
460.0	11.546851	11.638	0.783
470.0	13.59595	13.688	0.672
480.0	15.879197	16.000	0.755
485.0	17.121826	17.258	0.788
490.0	18.54208	18.584	0.226
495.0	19.87929	19.991	0.559
500.0	21.376526	21.483	0.496
505.0	22.96151	23.055	0.406
510.0	24.59378	24.711	0.474
515.0	26.2771	26.454	0.669
520.0	28.110	28.303	0.682
525.0	30.05174	30.236	0.609
530.0	32.13466	32.278	0.444
535.0	34.367786	34.434	0.192
540.0	36.62378	36.694	0.191
545.0	38.99129	39.057	0.378
550.0	41.41102	41.568	0.378
555.0	44.1673	44.194	0.060
556.36	45.00078	45.000	-0.002

$$\text{Per cent Deviation} = \frac{P_{obs.} - P_{calc.}}{P_{obs.}} \times 100$$

Maximum Deviation = 2.83 per cent.

Average Absolute Deviation = 0.654 per cent.

TABLE  
Properties of Saturated

T°K	P. Atms	$V_g$	$V_l$	$S_1$
280	0.06329	371.52	0.09497	50.034
290	0.10351	229.99	0.09615	50.893
300	0.16284	149.35	0.09734	51.871
310	0.24753	102.90	0.09854	52.858
320	0.36495	71.222	0.09978	53.810
330	0.52355	50.857	0.10108	54.837
340	0.73296	37.025	0.10238	55.761
350	1.00378	27.719	0.10375	56.688
360	1.3428	21.074	0.10523	57.592
370	1.77120	16.194	0.10677	58.485
380	2.2962	12.610	0.10834	59.355
390	2.9308	10.022	0.11006	60.210
400	3.6866	8.0756	0.11182	61.076
410	4.5810	6.5464	0.11375	61.903
420	5.6250	5.3884	0.11577	62.696
430	6.8364	4.4591	0.11783	63.486
440	8.2328	3.7115	0.12003	64.252
450	9.8274	3.1079	0.12252	65.013
460	11.638	2.6030	0.12327	65.763
470	13.688	2.1914	0.12835	66.516
480	16.000	1.8535	0.13176	67.259
485	17.258	1.7055	0.13368	67.639
490	18.584	1.5555	0.13568	67.952
495	19.991	1.4378	0.13786	68.379
500	21.483	1.3194	0.14019	68.715
505	23.055	1.2094	0.14271	69.084
510	24.711	1.1108	0.14543	69.448
515	26.454	1.0215	0.14844	69.835
520	28.303	0.93349	0.15184	70.237
525	30.236	0.84994	0.15569	70.659
530	32.278	0.76843	0.16015	71.059
535	34.434	0.68801	0.16578	71.437
540	36.694	0.61536	0.17243	71.836
545	39.057	0.54360	0.18088	72.251
550	41.568	0.47481	0.19122	72.821
555	44.194	0.37522	0.21546	73.855
556.36	45.000	0.27570	0.27570	74.815

## II

## Liquid and Vapour

$\Delta S_v$	$S_g$	$H_l$	$\Delta H_v$	$H_g$
28.251	78.285	-17949.8	7910.4	-10039.3
26.975	77.868	-17678.4	7822.8	-9855.6
25.737	77.608	-17384.6	7721.2	-9663.4
24.590	77.448	-17094.8	7622.8	-9472.1
23.485	77.295	-16796.8	7515.1	-9281.7
22.325	77.162	-16460.4	7367.4	-9093.1
21.307	77.068	-16148.9	7244.3	-8904.6
20.329	77.017	-15832.1	7115.1	-8717.0
19.392	76.984	-15512.6	6981.3	-8531.4
18.473	76.958	-15183.8	6835.1	-8348.7
17.590	76.945	-14853.4	6684.3	-8169.1
16.753	76.963	-14546.9	6533.6	-8013.3
15.922	76.998	-14184.2	6369.0	-7815.3
15.129	77.032	-13847.0	6202.8	-7644.2
14.391	77.087	-13519.1	6044.4	-7474.8
13.656	77.142	-13182.4	5872.2	-7310.3
12.944	77.196	-12846.3	5695.2	-7151.1
12.239	77.252	-12504.9	5507.5	-6997.4
11.531	77.294	-12157.4	5304.4	-6854.0
10.818	77.334	-11800.3	5084.4	-6715.9
10.112	77.371	-11440.4	4853.6	-6586.7
9.419	77.393	-11257.3	4730.6	-6526.7
9.019	77.371	-11092.5	4615.2	-6477.3
8.661	77.398	-10920.3	4464.4	-6415.9
8.289	77.376	-10708.4	4330.6	-6377.8
7.909	77.373	-10507.1	4186.0	-6321.1
7.516	77.357	-10325.7	4033.7	-6292.0
7.068	77.351	-10116.9	3870.6	-6246.3
6.587	77.305	-9906.9	3675.2	-6231.7
6.107	77.246	-9775.8	3458.3	-6217.5
5.607	77.166	-9459.2	3236.8	-6222.4
5.071	77.044	-9236.1	2999.9	-6236.2
4.460	76.907	-9024.5	2738.3	-6286.1
3.661	76.711	-8772.4	2430.7	-6341.7
2.010	76.482	-8468.7	2013.8	-6454.9
0	75.865	-7868.0	1115.3	-6752.7
0	74.815	-7329.4	0	-7329.4

TABLE  
Properties of Superheated

T°K	P, Atms. →	0.1	0.2	0.3	0.5
300.0	V	244.43	121.35		
	H	-9653.5	-9669.24		
	S	78.602	77.187		
320.0	V	261.12	129.84	86.068	51.043
	H	-9247.4	-9260.5	-9273.8	-9301.2
	S	79.911	78.505	77.669	76.592
340.0	V	277.76	138.27	91.763	54.555
	H	-8833.5	-8844.5	-8855.7	-8878.3
	S	81.167	79.767	78.937	77.874
360.0	V	294.34	146.65	97.412	58.019
	H	-8410.9	-8420.3	-8429.7	-8448.8
	S	82.374	80.978	80.153	79.100
380.0	V	310.90	155.99	103.03	61.446
	H	-7981.0	-7989.1	-7997.1	-8013.5
	S	83.545	82.142	81.322	80.276
400.0	V	327.42	163.31	108.61	64.846
	H	-7544.4	-7551.3	-7558.3	-7572.3
	S	84.654	83.264	82.447	81.407
420.0	V	343.93	171.61	114.17	68.224
	H	-7101.4	-7107.5	-7113.6	-7125.7
	S	85.734	84.347	83.531	82.495
440.0	V	360.42	179.90	119.72	71.585
	H	-6652.6	-6657.9	-6663.2	-6673.98
	S	86.777	85.392	84.578	83.546
460.0	V	376.89	188.17	125.26	74.933
	H	-6198.2	-6203.2	-6207.8	-6217.2
	S	87.787	86.403	85.590	84.561



III

Carbon Tetrachloride

0.8	1.00	1.50	2.00	3.00	5.00
33.615	26.629				
-8912.9	-8936.6				
76.865	76.370				
35.853	28.461	18.594			
-8478.0	-8497.8	-8548.6			
78.107	77.623	76.713			
38.053	30.253	19.846	14.635		
-8038.2	-8055.0	-8097.8	-8156.7		
79.295	78.819	77.931	77.181		
40.224	32.015	21.065	15.585	10.093	
-7593.6	-7607.9	-7644.4	-7693.5	-7760.1	
80.434	79.965	79.093	78.373	77.502	
42.373	33.755	22.260	16.510	10.751	6.1226
-7144.2	-7156.6	-7188.1	-7229.5	-7286.7	-7429.8
81.530	81.066	80.206	79.508	78.657	77.388
44.505	35.478	23.437	17.415	11.387	6.5503
-6690.0	-6700.9	-6728.3	-6756.2	-6813.4	-6935.0
82.586	82.125	81.275	80.657	79.757	78.539
46.623	37.185	24.600	18.306	12.007	6.958
-6231.4	-6240.9	-6265.0	-6289.5	-6339.5	-6444.3
83.605	83.147	82.304	81.694	80.810	79.629

TABLE  
 Properties of Superheated

T°K	P, Atms. →	0.1	0.2	0.3	0.5
480.0	V	393.36	196.43	130.79	78.268
	H	-5739.1	-5743.3	-5747.5	-5755.9
	S	88.763	87.381	86.569	85.542
500.0	V	409.82	204.68	136.30	81.599
	H	-5275.3	-5279.1	-5282.8	-5290.4
	S	89.710	88.328	87.517	86.492
540.0	V	442.77	221.17	147.32	88.241
	H	-4333.6	-4338.5	-4341.5	-4347.7
	S	91.518	90.137	89.328	88.305
580.0	V	475.60	237.64	158.32	94.865
	H	-3381.4	-3383.9	-3386.5	-3389.7
	S	93.242	91.862	91.054	90.033
620.0	V	508.46	254.10	169.31	101.48
	H	-2415.7	-2417.9	-2420.1	-2424.6
	S	94.832	93.452	92.644	91.625
660.0	V	541.32	270.55	180.29	108.08
	H	-1440.5	-1442.5	-1444.4	-1448.3
	S	96.356	94.977	94.169	93.151
700.0	V	574.18	286.99	191.26	114.67
	H	-457.69	-459.35	-461.08	-464.56
	S	97.802	96.423	95.616	94.598
750.0	V	615.24	307.54	204.97	122.91
	H	779.80	778.27	776.75	773.71
	S	99.509	98.131	97.324	96.306

III

Carbon Tetrachloride

0.8	1.00	1.50	2.00	3.00	5.00
48.731	38.883	25.752	19.185	12.615	7.351
- 5768.5	- 5777.0	- 5798.4	- 5820.0	- 5964.0	- 6055.7
84.590	84.134	83.297	82.693	81.822	80.669
50.830	40.572	26.895	20.055	13.213	7.734
- 5301.7	- 5309.2	- 5328.3	- 5347.6	- 5386.8	- 5467.8
85.542	85.088	84.256	83.657	82.796	81.664
55.007	43.932	29.161	21.775	14.388	8.475
- 4357.0	- 4363.2	- 4378.8	- 4394.5	- 4426.3	- 4491.4
87.359	86.908	86.082	85.490	84.643	83.542
59.170	47.271	31.409	23.477	15.543	9.1949
- 3391.6	- 3404.9	- 3417.8	- 3431.0	- 3497.6	- 3511.6
89.090	88.640	87.819	87.232	86.394	85.313
63.320	50.601	33.645	25.165	16.686	9.9008
- 2431.3	- 2435.8	- 2447.0	- 2458.3	- 2481.0	- 2527.2
90.684	90.235	89.417	88.833	88.002	86.934
67.462	53.922	35.870	26.845	17.819	10.597
- 1454.2	- 1458.1	- 1468.0	- 1477.8	- 1497.6	- 1537.5
92.211	91.763	90.947	90.365	89.538	88.480
71.597	57.237	38.091	28.517	18.946	11.287
- 469.78	- 473.27	- 482.00	- 490.77	- 508.23	- 543.53
93.659	93.212	92.398	91.817	90.994	89.943
76.759	61.374	40.860	30.600	20.347	12.142
769.13	766.08	758.43	750.77	735.49	704.69
95.368	94.922	94.109	93.530	92.710	91.665

TABLE  
 Properties of Superheated

T°K	P, Atms.	Properties of Superheated			
		8.0	10.0	15.0	20.0
440.0	V	3.799			
	H	-7139.7			
	S	77.254			
460.0	V	4.0979	3.1305		
	H	-6616.4	-6744.3		
	S	78.417	77.762		
480.0	V	4.3769	3.3763	2.0110	
	H	-6203.4	-6310.5	-6622.4	
	S	79.508	78.898	78.033	
500.0	V	4.6420	3.6052	2.2036	1.4702
	H	-5596.7	-5688.5	-5945.5	-6265.5
	S	80.543	79.963	79.119	77.691
540.0	V	5.1437	4.0303	2.5370	1.7785
	H	-4593.2	-4664.0	-4854.2	-50.681
	S	82.473	81.934	81.114	79.996
580.0	V	5.6210	4.4280	2.8332	2.0304
	H	-3595.0	-3652.4	-3802.8	-3964.8
	S	84.276	83.762	82.956	81.988
620.0	V	6.0827	4.8091	3.1087	2.2561
	H	-2597.5	-2645.5	-2769.8	-2900.3
	S	85.919	85.420	84.469	83.743
660.0	V	6.5341	5.1793	3.3712	2.4668
	H	-1598.4	-1639.7	-1745.4	-1854.8
	S	87.480	86.922	86.070	85.377
700.0	V	6.9582	5.5419	3.6262	2.6679
	H	-597.13	-633.2	-725.2	-819.5
	S	88.953	88.473	87.571	86.900
750.0	V	7.5262	5.8876	3.9361	2.9104
	H	658.13	626.84	547.74	467.40
	S	90.685	90.211	89.327	88.676

III

Carbon Tetrachloride

30.0	50.0	80.0	100.0	150.0	200.0
0.97867					
- 5624.3					
78.369					
1.2135	0.48778				
- 4336.1	- 5530.2				
80.693	77.962				
1.3974	0.69213	0.25201			
- 3184.3	- 3884.9	- 5629.6			
82.594	80.692	77.355			
1.5593	0.82729	0.41049	0.26894		
- 2086.2	- 2608.4	- 3570.6	- 4356.0		
84.310	82.688	80.585	79.149		
1.7088	0.94010	0.50925	0.36877	0.19325	
- 1015.1	- 1437.1	- 2143.7	- 2649.4	- 3933.8	
85.886	84.412	82.686	81.664	79.375	
1.8848	1.0654	0.60839	0.45924	0.2643	0.19084
302.96	- 39.791	- 581.06	- 949.78	- 1891.9	- 2561.7
87.705	86.340	84.843	84.011	82.192	80.947

where  $C_s$  and  $C_H$  are integration constants.

The basic reference point was taken to be the absolute zero temperature with  $H = 0$  and  $S + R \ln P = 0$  for elements.

The entropy at  $298.16^\circ K$  is given by Hildenbrand and McDonald<sup>10</sup> to be 77.65 calories/mole. The enthalpy at  $298.16^\circ K$  was calculated to be  $-9699.61$  calories/mole.

Using the values of entropy and enthalpy at  $298.16^\circ K$ , in Equations (7) and (8), the integration constants  $C_s$  and  $C_H$  were evaluated.

The entropy and enthalpy of carbon tetrachloride were evaluated at various temperatures and pressures using Equations (7) and (8).

*Entropy and Enthalpy of Saturated Vapour.* These were evaluated by substituting the experimental vapour pressures, volumes and temperatures in the Equations (7) and (8).

*Entropy and Enthalpy of Saturated Liquid.* — These were evaluated using the relations,

$$S_1 = S_g - \Delta S_V \quad (9)$$

$$H_1 = H_g - \Delta H_V \quad (10)$$

where  $\Delta S_V$  and  $\Delta H_V$  are the entropy of vaporization and heats of vaporization, respectively.

*Superheated Carbon Tetrachloride.* The volume of superheated vapour was calculated using Equation (3), by substituting the values of pressure and by making use of Newton-Raphson iterative method.

The entropy and enthalpy of superheated vapour were calculated by substituting the calculated volume of superheated vapour in Equations (7) and (8). The properties of saturated liquid and vapour are presented in Table II and the properties of superheated vapour are presented in Table III\*. These values are presented in graphical form as Figure I†. Table III has been checked for internal consistency using the usual relations, and found to be internally consistent.

#### NOMENCLATURE

$a, b, c, d$	= constants in Equation [1.b]
$a', b', c'$	= constants in Equation [1.a]
$A, B, C, D$	= constants in Equation [6]
$A', B', C', D'$	= constants in Equation [2]
$b_1, A_2, A_3, A_4 \dots$	= constants of Martin and Hou Equation of State
$C_p$	= Ideal gas specific heat at constant pressure, Calories/gram mole $^\circ K$

\* Complete tabular material can be obtained from the authors.

† 80 cm  $\times$  75 cm diagram can be obtained from the authors.

$C_v$	= Ideal gas specific heat at constant volume, Calories/gram mole °K
$H$	= Enthalpy, Calories/gram mole
$P$	= Pressure, Atmospheres
$S$	= Entropy, Calories/gram mole °K
$T$	= Temperature, °K
$V$	= Specific volume, Litres/gram mole
$\Delta H_v$	= Enthalpy of vaporization, Calories/gram mole
$\Delta S_v$	= Entropy of vaporization, Calories/gram mole °K

Subscripts :

- l refers to liquid
- g refers to gas vapour
- c refers to the Critical Point.

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TEMPERATURE - ENTROPY  
DIAGRAM FOR  
**CARBON TETRACHLORIDE**

PREPARED BY D. N. SESHADRI, D. S. VISWANATH,  
AND N. R. KULOR

P • PRESSURE, ATMOSPHERES —————  
H • ENTHALPY, CALORIES/GRAM MOLE ————  
V • VOLUME, LITRES/GRAM MOLE - - - - -

REFERENCE STATE:—  
C (GRAPHITE) AND Cl<sub>2</sub> (GAS)  
AT 0°K AND ZERO PRESSURE  
H = 0, AND  $S = R \ln P = 0$

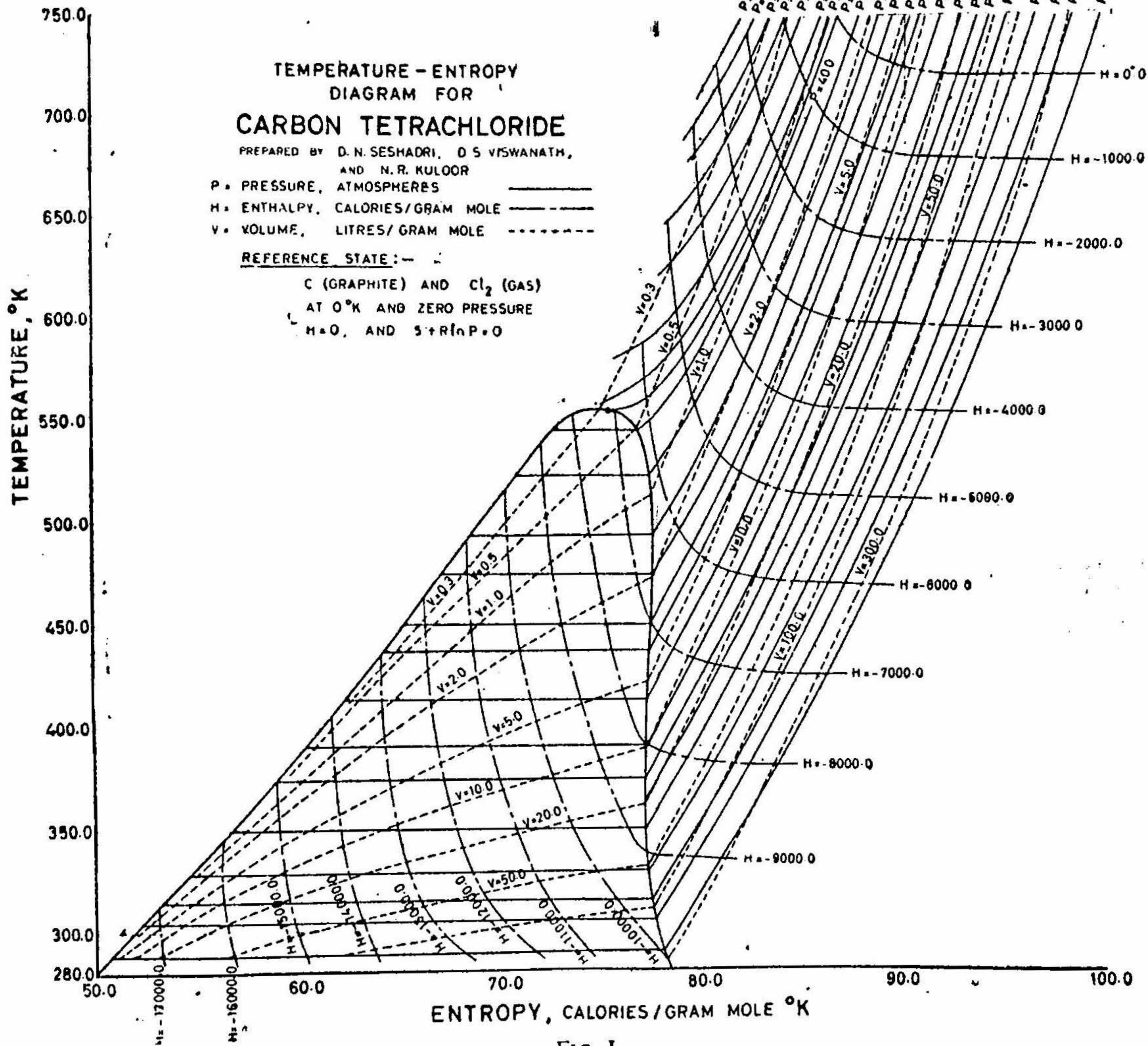


FIG. I