

THERMODYNAMIC PROPERTIES OF HYDRAZINE

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ABSTRACT

The thermodynamic properties—entropy and enthalpy—of hydrazine have been computed for the temperature range 273.16 to 1500°K and for the pressure range 0.00352 to 600 atm. A temperature-entropy diagram based on the data is presented.

The common thermodynamic properties of hydrazine are not available in literature. In the present study volume, entropy and enthalpy of hydrazine (mol. wt. 32.048) have been computed for the saturated vapour, saturated liquid, and superheated gaseous regions.

Compressibility Data: Giguere and Roundie¹ determined the saturated gas volume of hydrazine in the temperature range 363.16 to 404.16°K and pressure range 0.35 to 1.0 atm. Hows and Harden² reported the constants of the Martin-Hou equation of state.

As no other data are available for the gaseous region, the modified Martin-Hou³ equation of state was used for evaluating 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 gaseous region with an average deviation of 1.6 per cent.

Specific Heat of Superheated Gas: The specific heat of hydrazine at constant pressure has been determined by Hows and Harden², Scott *et al*⁴, and Kobe and Harrison⁵. Hows and Harden² proposed an empirical equation for specific heat. In the present study, the specific heat of real gaseous hydrazine at a constant pressure of 0.00352 — the vapour pressure at 273.16°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 using the smoothed data^{2,4} for specific heat for ideal gaseous hydrazine, by the method of least squares. Thus, the specific heat values used in the present study follow the relationship,

$$C_p \text{ at } P=0.00352 = 4.0547 + 0.0353T - 2.2886 \times 10^{-5} T^2 \\ + 5.9869 \times 10^{-9} T^3 + 1.826 \times 10^5 T^{-8}$$

which fits the corrected smoothened data^{2,4} with an average deviation of 0.62 per cent.

Vapour Pressure: Scott *et al.*⁴, Giguere and Rundle¹ and Audrieth and Ogg⁶ reported vapour pressure in the temperature ranges 273.16 to 343.16° K, 363.16 to 404.16° K and 273.16 to critical temperature respectively. The International Critical Tables⁷ give the vapour pressure data for the temperature range 388.66 to critical temperature. Hows and Harden² and Audrieth and Ogg⁶ suggested empirical equations for vapour pressure for different ranges of temperatures. In the present study, the smoothened values reported by Audrieth and Ogg⁶ have been used and fitted to an empirical equation

$$\ln P = 58.7582 - \frac{0.707 \times 10^4}{T} - 7.088 \ln T + 0.457 \times 10^{-2} T$$

with an average deviation of 0.44 per cent.

Latent Heat of Vaporization: Scott *et al.*⁴ and Hughes *et al.*⁸ reported latent heat of vaporization at 298.16° K. Audrieth and Ogg⁶ reported the latent heat of vaporization for the temperature range 298.16 to 388.16° K. In the present work 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. The values thus obtained and the available data^{4,6,8} were smoothened and used.

Normal boiling point and critical constants: From the values reported by various authors^{2,6,7} the following have been accepted for the present study:

Normal boiling point	=	386.66° K
Critical temperature	=	653.16° K
Critical pressure	=	145 atm.
Critical volume	=	0.1389 litres/mole.

Specific volume of saturated liquid and vapour phase in equilibrium: Experimental vapour volumes have been reported by Giguere and Rundle¹ (363.6 to 404.16° K). Audrieth and Ogg⁶ (273.16 to 323.16° K), Ahlert *et al.*⁹ (273.16 to 449.83° K) and Hows and Harden² (273.16 to critical temperature), reported liquid density. In the present study the saturated vapour volumes were calculated using modified Martin-Hou³ equation of state. The calculated and the reported values^{1,2,6,9} 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: The real gaseous entropy at 298.16° K was reported by Scott *et al.*⁴ The real gaseous enthalpy at 298.16° K was calculated¹⁰ from the ideal

heat content⁶ and the heat of formation at 0° K⁴ after applying the Bertelot correction. The values thus obtained for entropy and enthalpy at 298.16° K and 0.0189 atm, the vapour pressure at 298.16° K, are 64.86 cal./mole °K and 28870.98 cal./mole, respectively.

The entropy and enthalpy values at 0.0189 atm. isobar were calculated following the same mathematical treatment as in the case of n-butane¹¹.

The modified Martin and Hou equation³ is,

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

The values of the constants are as follows:

$b = 0.0597$	$K = 5.475$	
$A_2 = -8.5158$	$B_2 = 0.126 \times 10^{-2}$	$C_2 = -0.5988 \times 10^2$
$A_3 = 0.5312$	$B_3 = 0.6045 \times 10^{-4}$	$C_3 = 4.8052$
$A_4 = -0.0221$	$B_5 = 0.5100 \times 10^{-6}$	$C_5 = -0.4003 \times 10^{-3}$

The entropy and enthalpy values for the saturated vapour and liquid, calculated as in the case of n-octane¹² are given in Table 1.

Discussion: The thermodynamic properties of hydrazine calculated for the pressure range 0.00352 to 600 atm. and the temperature range 273.16 to 1500° K are given in Tables 1 to 4*. The temperature-entropy diagram is shown in Fig. 1. As the modified Martin and Hou³ 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 PVT data calculated in the present study for the saturated vapour region with the experimental data of other authors⁵ 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 2, 3 and 4 to be internally consistent.

*Complete tabular material can be obtained from the authors

HYDRAZINE

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
273.16	0.00352	0.03126	6367.0	27.33	39.78	68.11	17695.3	10866.3	28561.6
280.00	0.00577	0.03143	3981.3	27.82	38.61	66.43	17834.0	10810.8	28644.8
290.00	0.0113	0.03169	2105.3	28.53	37.00	65.53	18038.5	10730.0	28768.5
300.00	0.0211	0.03197	1166.2	29.23	35.49	64.72	18247.3	10647.0	28894.3
310.00	0.0375	0.03227	677.9	29.95	34.05	64.00	18466.8	10555.5	29022.3
320.00	0.0638	0.03257	411.2	30.62	32.74	63.36	18675.5	10476.8	29152.3
330.00	0.1047	0.03287	258.2	31.26	31.52	62.78	18882.7	10401.6	29284.3
340.00	0.1661	0.03319	167.5	31.92	30.34	62.26	19102.4	10315.6	29418.0
350.00	0.2558	0.03351	111.9	32.53	29.27	61.80	19308.8	10244.5	29553.3
360.00	0.3831	0.03384	76.79	33.14	28.25	61.39	19520.2	10170.0	29700.2
370.00	0.5597	0.03417	53.95	33.74	27.28	61.02	19734.8	10093.6	29858.4
380.00	0.7966	0.03454	38.86	34.34	26.35	60.69	19954.8	10013.0	29967.8
385.66	1.0000	0.03478	31.46	34.74	25.75	60.49	20104.5	9956.5	30061.0
390.00	1.112	0.03494	28.51	34.93	25.47	60.40	20174.4	9933.3	30098.1
400.00	1.547	0.03534	20.96	35.53	24.57	60.10	20420.7	9828.0	30246.7
410.00	2.101	0.03580	15.77	36.11	23.74	59.85	20656.5	9733.4	30399.9
420.00	2.803	0.03629	12.07	36.74	22.89	59.63	20917.5	9613.8	30551.3
430.00	3.681	0.03684	9.37	37.35	22.05	59.43	21191.2	9481.5	30722.7
440.00	4.765	0.03747	7.37	38.02	21.24	59.26	21488.2	9345.6	30813.8
450.00	6.055	0.03815	5.87	38.65	20.45	59.10	21752.0	9202.5	30934.5

TABLE I—(concl'd.)

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
450.00	7.679	0.05890	4.72	39.31	19.66	58.97	22050.7	9043.6	31094.3
470.00	9.568	0.03977	3.84	39.94	18.91	58.85	22345.5	8847.7	31233.2
480.00	11.80	0.04083	3.16	40.52	18.22	58.74	22625.1	8745.6	31370.7
490.00	14.41	0.04233	2.62	41.14	17.51	58.65	22926.7	8579.9	31506.6
500.00	17.43	0.04372	2.18	41.80	16.76	58.56	23250.6	8380.0	31640.6
510.00	20.89	0.04526	1.84	42.37	16.12	58.49	23551.2	8221.2	31772.4
520.00	24.86	0.04670	1.55	43.07	15.36	58.43	23914.0	7987.2	31901.2
530.00	29.36	0.04820	1.32	43.67	14.70	58.37	24235.7	7791.0	32026.7
540.00	34.42	0.04994	1.13	44.30	14.02	58.32	24577.6	7570.8	32148.4
550.00	40.11	0.05190	0.973	44.89	13.38	58.27	24906.3	7359.0	32265.3
560.00	46.41	0.05420	0.839	45.55	12.67	58.22	25282.0	7095.2	32377.2
570.00	53.46	0.05640	0.726	46.19	11.68	58.17	25653.1	6828.6	32481.7
580.00	61.22	0.05910	0.629	46.88	11.24	58.12	26059.1	6519.2	32578.3
590.00	69.77	0.06200	0.546	47.57	10.49	58.06	26475.4	6189.1	32664.5
600.00	79.16	0.06560	0.473	48.31	9.68	57.99	26929.2	5808.0	32737.2
610.00	89.91	0.0696	0.405	49.07	8.80	57.87	27414.4	5368.0	32782.4
620.00	100.6	0.0746	0.352	49.95	7.83	57.78	27966.6	4854.6	32821.2
600.00	112.8	0.0812	0.299	50.92	6.68	57.60	28600.9	4208.4	32809.3
640.00	126.0	0.0916	0.249	52.09	5.24	57.33	29368.5	3353.6	32722.7
650.00	140.3	0.1135	0.189	53.98	2.72	56.70	30621.8	1768.0	32389.8

Thermodynamic Properties of Hydrazine

HYDRAZINE

TABLE II
Volume (litres/mole)

Pressure atm.	Temp. °K.									
	280.0	320.0	360.0	400.0	440.0	480.0	520.0	560.0	600.0	620.0
0.005	4594.5	5251.1	5907.6	6564.3	7220.8	7877.2	8533.6	9190.0	9846.5	10174.7
0.01		2625.3	2953.6	3281.9	3610.2	3938.6	4266.8	4595.0	4923.2	5087.3
0.05		524.7	590.5	656.2	721.9	787.5	853.2	918.9	984.5	1017.4
0.10			295.1	328.0	360.8	393.7	426.5	459.4	492.2	508.6
0.5				65.4	72.0	78.6	85.2	91.8	98.4	101.6
1.0				32.6	35.9	39.2	42.5	45.8	49.1	50.8
2.0					17.8	19.5	21.2	22.9	24.5	25.3
3.0					11.8	13.0	14.1	15.2	16.3	16.9
5.0						7.70	8.39	9.07	9.74	10.1
10.0							3.76	4.12	4.47	4.99
15							2.69	2.93	3.17	3.29
20							1.98	2.17	2.35	2.44
30								1.39	1.52	1.59
40								1.00	1.11	1.16
60									0.683	0.727
100										
200										0.359
300										
400										
500										
600										

TABLE II (concl'd.)

Pressure atm.	640.0	650.0	660.0	680.0	Temp. °K. 700.0	800.0	900.0	1000.0	1200.0	1500.0
0.005	10502.9	10667.0	10831.1	11159.3	11487.6	13138.6	14769.7	16410.8	19693.0	24616.2
0.01	5251.5	5333.5	5415.6	5579.7	5743.8	6564.3	7384.9	8205.4	9846.5	12308.1
0.05	1050.2	1066.6	1083.0	1115.9	1148.7	1312.9	1477.0	1641.1	1969.3	2461.6
0.10	525.1	533.3	541.5	557.9	574.3	656.4	738.4	820.5	984.6	1230.8
0.50	104.9	106.6	108.2	111.5	114.8	131.2	147.7	164.1	196.9	246.2
1.00	52.4	53.2	54.1	55.7	57.4	65.6	73.8	82.0	98.5	123.1
2.00	26.2	26.6	27.0	27.8	28.6	32.8	36.9	41.0	49.2	61.5
3.00	17.4	17.7	18.0	18.5	19.1	21.8	24.6	27.3	32.8	41.0
5.00	10.4	10.6	10.7	11.1	11.4	13.1	14.7	16.4	19.7	24.6
10.0	5.16	5.24	5.33	5.50	5.66	6.51	7.34	8.18	9.84	12.3
15.0	3.40	3.46	3.52	3.64	3.75	4.32	4.88	5.44	6.55	8.21
20.0	2.53	2.57	2.62	2.71	2.79	3.23	3.65	4.07	4.91	6.16
30.0	1.65	1.68	1.71	1.77	1.83	2.13	2.42	2.71	3.27	4.11
40.0	1.21	1.23	1.26	1.31	1.35	1.58	1.80	2.02	2.45	3.08
60.0	0.765	0.783	0.801	0.837	0.871	1.03	1.19	1.34	1.63	2.06
100.0	0.393	0.409	0.424	0.452	0.478	0.593	0.695	0.791	0.975	1.24
140.0		0.193	0.232	0.272	0.300	0.402	0.484	0.557	0.694	0.888
200.0					0.154	0.259	0.3.6	0.383	0.485	0.626
300.0						0.161	0.209	0.251	0.325	0.424
400.0						0.133	0.163	0.193	0.248	0.324
500.0						0.121	0.142	0.163	0.206	0.267
600.0						0.115	0.131	0.147	0.180	0.230

Thermodynamic Properties of Hydrazine

HYDRAZINE

TABLE III

Entropy (cal./mole °K)

Pressure atm.	Temp. K ^o									
	280.0	320.0	360.0	400.0	440.0	480.0	520.0	560.0	600.0	620.0
0.005	66.72	68.42	70.02	71.55	73.00	74.39	75.73	77.02	78.26	78.86
0.01		67.04	68.64	70.17	71.62	73.02	74.35	75.64	76.88	77.49
0.05		63.84	65.45	66.97	68.43	69.82	71.16	72.44	73.68	74.29
0.10			64.07	65.59	67.05	68.44	69.78	71.07	72.31	72.91
0.5				62.38	63.84	65.24	66.58	67.86	69.11	69.71
1.0				60.99	62.45	63.85	65.19	66.48	67.72	68.33
2.0					61.05	62.46	63.80	65.09	66.34	66.94
3.0					60.22	61.63	62.98	64.28	65.52	66.13
5.0						60.38	61.94	63.24	64.49	65.10
10.0						59.11	60.49	61.81	63.07	63.68
15.0							59.60	60.94	62.21	62.83
20.0							58.95	60.30	61.59	62.21
30.0								59.36	60.65	61.51
40.0								58.64	59.90	60.63
60.0									58.61	59.59
100.0										57.51
140.0										
200.0										
300.0										
400.0										
500.0										
600.0										

TABLE III (concl'd)

Pressure atm.	640.0	650.0	660.0	680.0	Temp. °K 700.0	800.0	900.0	1000.0	1200.0	1500.0
0.005	79.45	79.75	80.04	80.61	81.17	83.86	86.35	88.67	92.88	98.38
0.01	78.08	78.37	78.66	79.23	79.80	82.48	84.98	87.30	91.50	97.01
0.05	74.88	75.17	75.46	76.04	76.60	79.29	81.78	84.10	88.31	93.81
0.10	73.50	73.79	74.09	74.66	75.22	77.91	80.40	82.72	86.93	92.43
0.50	70.30	70.60	70.89	71.46	72.02	74.71	77.20	79.52	83.73	89.23
1.00	68.92	69.22	69.51	70.08	70.64	73.33	75.83	78.15	82.36	87.86
2.0	67.54	67.83	68.12	68.70	69.26	71.95	74.45	76.77	80.98	86.48
3.0	66.72	67.02	67.31	67.88	68.45	71.14	73.64	75.96	80.17	85.67
5.0	65.70	65.99	66.28	66.86	67.42	70.12	72.62	74.94	79.15	84.66
10.0	64.28	64.58	64.87	65.45	66.02	68.72	71.22	73.55	77.77	83.27
15.0	63.43	63.73	64.03	64.61	65.18	67.89	70.40	72.73	76.95	82.46
20.0	62.82	63.12	63.42	64.00	64.58	67.30	69.81	72.15	76.37	81.81
30.0	61.93	62.23	62.53	63.13	63.71	66.45	68.97	71.32	75.55	81.07
40.0	61.26	61.57	61.88	62.48	63.07	65.83	68.37	70.72	74.96	80.49
60.0	60.25	60.57	60.89	61.51	62.11	64.93	67.49	69.86	74.12	79.66
100.0	58.63	59.01	59.37	60.06	60.72	63.69	66.32	68.73	73.03	78.60
140.0		56.76	57.67	58.70	59.51	62.77	65.49	67.94	72.29	77.89
200.0					57.27	61.59	64.51	67.04	71.47	77.14
300.0						60.00	63.24	65.92	70.48	76.20
400.0						59.08	62.34	65.10	69.75	75.54
500.0						58.50	61.73	64.48	69.17	75.00
600.0						58.08	61.27	64.03	68.72	74.58

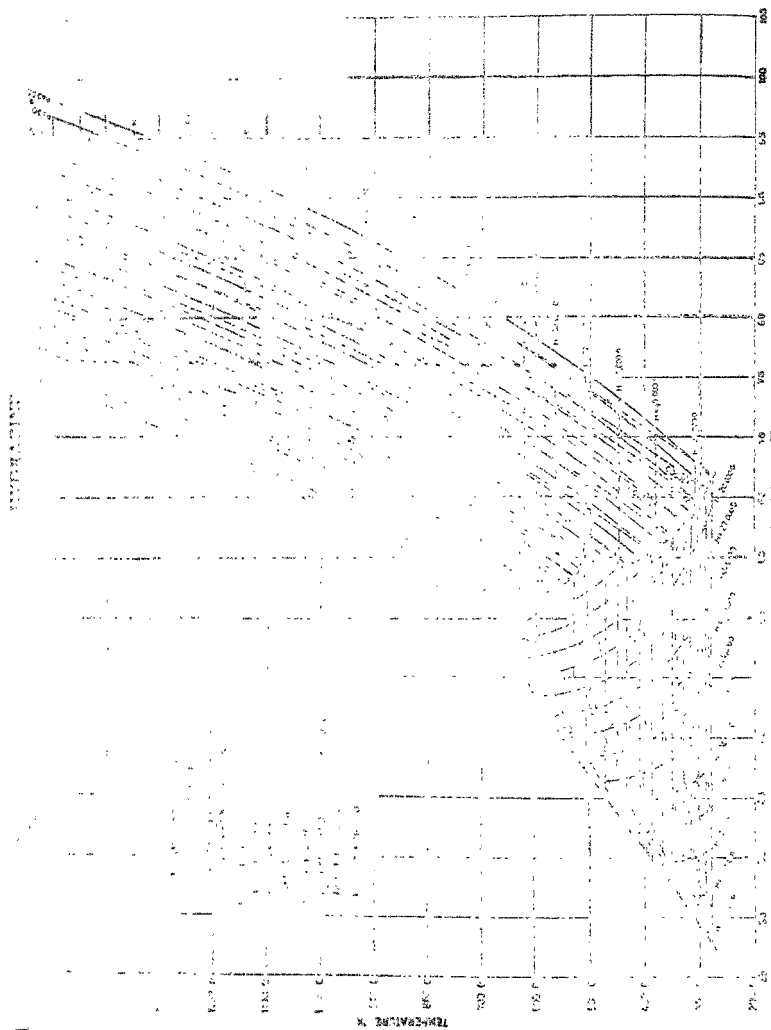
Thermodynamic Properties of Hydrochloric

TABLE IV (concl'd.)

Pressure atm.	640.0	650.0	660.0	680.0	Temp. °K 700.0	800.0	900.0	1010.0	1200.0	1500.0
0.005	34353.1	34541.9	34732.0	35116.1	35505.2	37519.5	39635.5	41838.0	46459.1	53864.6
0.01	34353.0	34541.9	34732.0	35116.1	35505.2	37519.5	39635.5	41838.0	46459.1	53864.6
0.05	34352.7	34541.6	34731.7	35115.8	35504.9	37519.4	39635.4	41837.8	46459.0	53864.5
0.10	34352.4	34541.2	34731.4	35115.5	35504.6	37519.1	39635.2	41837.7	46458.9	53864.4
0.50	34349.6	34538.5	34728.7	35113.0	35502.2	37517.2	39633.6	41836.3	46457.9	53863.8
1.00	34346.1	34535.1	34725.4	35109.9	35499.3	37514.8	39631.7	41834.7	46456.7	53862.9
2.0	34339.0	34528.3	34718.8	35103.6	35493.3	37510.1	39627.8	41831.5	46454.4	53861.5
3.0	34332.0	34521.4	34712.1	35097.3	35487.3	37505.4	39623.9	41828.2	46452.0	53860.0
5.0	34317.8	34507.6	34698.7	35084.6	35475.3	37495.9	39616.1	41821.7	46447.2	53857.0
10.0	34281.6	34472.5	34664.6	35052.4	35444.9	37472.0	39596.5	41805.3	46435.3	53849.3
15.0	34244.4	34436.5	34629.8	35019.6	35413.8	37447.7	39576.8	41788.7	46423.3	53841.6
20.0	34206.3	34399.7	34594.1	34986.0	35382.1	37423.1	39556.9	41772.0	46411.3	53834.0
40.0	34126.8	34322.9	34519.9	34916.5	35316.8	37373.0	39516.5	41738.7	46387.3	53818.7
40.0	34042.5	34241.7	34441.7	34843.6	35248.6	37321.4	39475.3	41704.8	46363.1	53803.5
60.0	33855.3	34062.9	34270.4	34685.7	35102.0	37213.8	39310.8	41635.9	46314.4	53773.2
100.0	33352.0	33596.1	33834.3	34398.9	34753.5	36977.8	39212.1	41493.3	46216.5	53713.1
140.0		32429.1	33026.4	33712.6	34275.0	36708.3	39020.3	41345.0	46117.9	53654.4
200.0					33021.3	36231.2	38710.7	41115.0	45970.8	53569.3
300.0						35448.3	38192.9	40738.7	45737.9	53439.2
400.0						35061.0	37828.0	40439.0	45544.0	53335.0
500.0						34902.8	37643.0	40253.3	45397.0	53247.5
600.0						34549.0	37562.6	40175.0	45319.0	53192.0

Thermodynamic Properties of Hydrazine

Fig. 1
Temperature-Entropy diagram for Hydrazine



NOMENCLATURE

A , B , C and D = sp. 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 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 $^\circ\text{K}$.

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

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

T_c = critical temp. $^\circ\text{K}$.

V = volume, litres/mole.

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