SATURATED LIQUID ENTROPIES OF HYDROCARBONS

T. R. Das, S. H. Ibrahim and N. R. Kuloor

(Department of Chemical Engineering, Indian Institute of Science, Bangalore 12, India)

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Abstract

Prediction method has been given for saturated liquid entropies of hydrocarbons. This involves using Argon as the reference substance. It is possible to predict saturated liquid entropies of hydrocarbons within an average error of 1.0%.

Argon is non polar, non reactive and devoid of any quantum mechanical effects and hence it is suitable to be used as a reference substance for prediction of thermodynamic properties of organic and inorganic compounds. Using argon as the reference substance prediction methods have been given earlier for entropy of vaporisation of hydrocarbons[1] and inorganic gasses[2] and for the saturated liquid densities[3]. In this work a similar approach is followed to predict saturated liquid entropy.

No known methods are available to predict entropy in the saturated liquid range, except the theoretical method involving entropy of vaporisation and the entropy in the saturated vapour range. A similar method using less number of input data is desirable.

Saturated liquid entropy for argon and various hydrocarbons from the literature[4-17] were plotted against temperatures individually, from which the smoothed values of S_A and S_S at the required reduced temperatures were obtained. The reduced temperatures for the substances considered generally vary between 0.60 and 1.0. When these values of saturated liquid entropy of argon were plotted against the values of saturated liquid entropy of hydrocarbons, straight line relationships were obtained. Both saturated and unsaturated hydrocarbons gave the linear relationships. The slopes and intercepts of these straight lines varied from substance to substance.

To arrive at a generalised equation to predict S_S for all hydrocarbons and for all temperature range attempts were made to correlate these slopes and intercepts with some easily assessible physical properties of these substances Earlier either molecular weight or the normal boiling point were found to correlate the slopes and intercepts for the case of entropy of vaporisation of hydrocarbons and inorganic gases and the saturated liquid density.

When the slopes and intercepts were plotted against normal boiling point of these substances they gave good linear relationship. In another case when they were plotted against molecular weight, they gave linear relationship. Although both of them gave good linear relationship the normal boiling point was found to be a better correlating parameter. From these plots the following general equation can be obtained.

$$S_S = mS_A + C \qquad [1]$$

where S_S = saturated liquid entropy of the hydrocarbons and S_A is the saturated liquid entropy of Argon m is the slope and C is the intercept.

Introducing the values of m and C, equation [1] becomes as follows for normal boiling point as the correlating parameter.

$$S_S = [0.596 \exp (5.456 \times 10^{-3} T_b)] S_A + [9.16 \times 10^{-2} T_b - 9.16] \qquad [2]$$

and for the case of molecular weight as the correlating parameter, one obtains

$$S_S = [1.386 \exp (11.46 \times 10^{-3} M)] S_A + [0.240 M - 1.50] \qquad [3]$$

The calculated values using equation 2 and 3 and the smoothed experimental values along with average percentage error are given in Table 1. Except methane, which being the first member of the series behave anamolously, all others are correlated well by these equations.

Equation [2] gives 1.0% overall average error and equation [3] gives 4% overall average error. To predict saturated liquid entropy, equation [2] is recommended.

TABLE I

Calculated and Experimental values of Saturated Liquid Entropy

	Tr.	Saturated Liquid Entropy Cal/mole °k				
		Exp.	Cal Eqn (2)	% Div.	Cal Eqn (3)	% Div.
Methane	0.96	26.57	22.53	15.21	34.91	31 39
(4)	0.94	26.09	22.11	15.25	34.28	31.39
	0.92	25.67	21.72	15 39	33.68	31.20
	0.88	24.86	20.88	16.01	32.41	30.37
	0.84	24.08	20.13	16.42	31.26	29.82
	0.80	23.33	19.41	16.80	30.18	29.36
	0.76	22.53	18.69	17.04	29.08	29.07
	0.72	21.78	17.91	17.77	27.90	28.10
	0.68	20.98	17.15	18.26	26.75	27.50
	0.64	20.14	16.40	18.57	25.60	27.11
	0.60	19.32	15.62	19.15	24.42	26.40
				Av. 16.90		Av. 29.25
Ethane	0.96	39.92	39.65	0.68	43.97	10.15
(5)	0.94	39 24	39.03	0.54	43.23	10.17
	0.92	38.71	38.45	0.67	42.52	9.84
	0.88	37.16	37.21	0.13	41.04	10.44
	0.84	36.62	36.08	1.47	39.69	8,38
	0.80	35.63	35.02	1.71	38.41	7.80
	0.76	34.61	33.94	1.93	37.12	7.25
	0.72	33.59	32.79	2.38	35.74	6.40
	0.68	32.54	31.66	2.70	34.39	5.69
	0.64	31.44	30 53	2.89	33.04	5.09
	0.60	30.32	29.38	3.10	31.65	4.39
				Av. 1.65		Av. 7.78

TABLE 1 – (*contd.*)

	Tr.	Saturated Liquid Entropy Cal/mole °k				
		Exp.	Cal Eqn (2)	% Div.	Cal Eqn (3)	% Div.
Propane	0.96	52.77	53.10	0.62	54.03	2.39
(6)	0.94	51.88	52.30	0.81	53.16	2.47
	0.92	51.12	51.55	0.84	52.33	2.37
	0.88	49.65	49.95	0.60	50.58	1.87
	0.84	48.27	48.50	0.48	49.00	1.51
	0.80	46.83	47.13	0.53	47.50	1.32
	0.76	45.56	45.75	0.42	45.99	0.94
	0.72	44.19	44 25	0.14	44.36	0.38
	0.68	42.83	42.80	0.07	42.77	0.14
	0.64	41.38	41.35	0.07	41.19	0.46
	0.60	39.87	39 86	0.08	39.55	0 80
				Av. 0.42		Av. 1.33
n-butane	0.96	67.69	67.42	0 40	65.20	3.68
(7)	0 94	66.56	66.42	0.21	64.18	3.58
	0.92	65.58	65.47	0.17	63.21	3.61
	0 88	63.61	63.47	0.22	61.16	3.85
	0.84	61.73	61.65	0.13	59.30	3.94
	0.80	59.94	59 93	0.02	57.54	4.00
	0.76	58.12	58.19	0.12	55.76	4.06
	0.72	56.25	56.32	0.12	53.85	4.27
	0.68	54.33	54.50	0.31	51.99	4.31
	0.64	52.18	52.68	0.96	50.13	3.93
				Av. 0.27		Av. 3.92.

TABLE 1 – (*contd.*)

	Tr.	Saturated Liquid Entropy Cal/mole °k				
		Exp.	Cal Eqn (2)	% Div.	Cal Eqn (3)	% Div.
isobutane	0.96	63.16	63.33	0.27	65.20	3.23
(8)	0.94	62.05	62.39	0.55	64.18	3.43
	0.92	61.02	61.49	0.77	63.21	3.59
	0.88	59.06	59.61	0.93	61.16	3.56
	0.84	57.23	57.90	1.17	59.30	3.62
	0.80	55.42	56.28	1.55	57.54	3.83
	0.76	53.56	54.64	2.02	55.76	4.11
	0.72	51.73	52.88	2.22	53 85	4 10
	0.68	49.83	51.17	2.69	51.99	4.33
	0.64	47.90	49.46	3.26	50 13	4.66
				Av. 1.54		Av. 3.85
isopentane	0.96	80.78	78.65	2.64	77.82	3.66
(9)	0.94	79.48	77.48	2.52	76.61	3.61
	0.92	78.16	76.37	2.29	75.47	3.44
	0.88	75.72	74.03	2.29	73.06	3.51
	0.84	73.66	71.90	2.39	70.87	3.79
	0.80	71.12	69.90	1.72	68.81	3.25
	0.76	68.87	67.87	1.45	66.72	3.12
	0.72	66.66	65.68	1.47	64.47	3.29
	0.68	64.28	63.56	1.12	62.28	3.11
				Av. 1.99		Av. 3.42

TABLE 1 – (*contd.*)

	Tr.	Saturated Liquid Entropy Cal/mole °*k*				
		Exp.	Cal Eqn (2)	°/₀ Div.	Cal Eqn (3)	°/₀ Div.
n-hexane	0.96	99.22	97.46	1.77	91.97	7.31
(10)	0.94	97.78	95.99	1.83	90.56	7.38
	0.92	96.18	94.61	1.63	89.22	7.24
	0.88	93.06	91.68	1.48	86.39	7.14
	0.84	90.03	89.02	1.12	83.82	6.90
	0.80	87.06	86.52	0.62	81.40	6.50
	0.76	83.83	83.98	0.18	78.95	5.82
	0.72	80.60	81.25	0.81	76.30	5.33
	0.68	77.46	78.59	1.46	73.74	4.80
				Av. 1.21		Av. 6.49
n octane	0.96	130.58	130.08	0.38	126·28	3.29
	0.94	128 64	128.08	0.44	124.33	3.35
	0.92	126.77	126.19	0.46	122.48	3 38
	0.88	123 02	122.20	0.67	118.58	3.61
	0.84	119.31	118.58	0.61	115.04	3.58
	0.80	115.47	115.17	0.26	111.70	3.26
	0.76	111.45	111.70	0.22	108.32	2.81
	0.72	107.54	107.97	0.40	104.67	2.67
	0.68	103.43	104.35	0.89	101.13	2.22
	0.64	99.24	100.73	1.50	97.59	1.66
				Av. 0.58		Av. 2.98

TABLE 1 – (*contd.*)

	Tr.	Saturated Liquid Entropy Cal/mole °k				
		Exp.	Cal Eqn (2)	% Div.	Cal Eqn (3)	% Div.
n-nonane	0.96	147.58	147.42	0.11	147.16	0.28
(12)	0.94	145.56	145.13	0.30	144.87	0.47
	0.92	143.53	142.96	0.40	142.70	0.58
	0.88	139.32	138.39	0.67	138.12	0.86
	0.84	134.86	134.23	0.47	133.96	0.67
	0.80	130.46	130.32	0.11	130.04	0.32
	0.76	125.95	126.35	0.32	126.06	0.09
	0.72	121.62	122.08	0.38	121.78	0.13
	0.68	117.15	117.92	0.66	117.63	0.41
				Av. 0.38		Av. 0.42
n decane	0.96	165.21	165.64	0.26	171.07	3.55
(13)	0.94	162.95	163.04	0.06	168.38	3.33
	0.92	160.73	160.58	0.09	165.84	3.18
	0.88	155.96	155.38	0.37	160.46	2.89
	0.84	150.82	150.66	0.11	155.57	3.15
	0.80	145.71	146.21	0.34	150.97	3.61
	0.76	140.53	141.69	0.83	146.30	4.10
	0.72	135.49	136.84	1.00	141.28	4.27
	0.68	130.21	132.12	1.47	136.40	4.75
				Av. 0.50		Av. 3.65

TABLE 1 – (*contd.*)

	Tr.	Saturated Liquid Entropy Cal/mole °K				
		Exp.	Cal Eqn (2)	% Div.	Cal Eqn (3)	% Div.
Ethylene	0.96	37.25	35.75	4.03	42.62	14.42
(14)	0.94	36.49	35.18	3.59	41.89	14.80
	0.92	35.93	34.64	3.59	41.20	14.67
	0.88	34.92	33.50	4.07	39.75	13.83
	0.84	34.00	32.46	4.53	38.43	13.03
	0.80	33.16	31.48	5.07	37.19	12.15
	0.76	32.36	30.49	5.78	35.93	11.03
	0.72	31.38	29.43	6.21	34.57	10.17
	0.68	30.37	28.39	6.52	33.25	9.48
	0.64	29.27	27.35	6.56	31.93	9.09
				Av. 5.00		Av. 12.27
Propylene	0.96	51.77	51.39	0.73	52.49	1.39
(15)	0.94	50 94	50.61	0.65	51.64	1.37
	0.92	50.17	49 88	0.58	50.83	1.32
	0.88	48.91	48.33	1.19	49.12	0.43
	0.84	47.56	46.92	1.35	47.58	0.04
	0.80	46.23	45.59	1.38	46.12	0.24
	0.76	44.93	44.25	1.51	44.64	0.65
	0.72	43.58	42.80	1.79	43.04	1.24
	0.68	42.29	41.39	2.13	41.50	1.87
	0.64	40.95	39.98	2.37	39.95	2.44
				Av. 1.37		Av. 1.10

TABLE 1 – (*concld*)

	Tr.	Saturated Liquid Entropy Cal/mole °k				
		Exp.	Cal Eqn (2)	% Div.	Cal Eqn (3)	% Div.
1-butene	0.96	64.90	65.29	0.60	63.53	2.11
(16)	0.94	63.76	64.32	0 88	62 53	1.93
	0.92	62.80	63.40	0.96	61.58	1.94
	0.88	60.95	61.46	0.84	59.57	2.26
	0.84	59.36	59.69	0.55	57.75	2.71
	0.80	57.83	58.03	0.35	56.04	3.10
	0.76	56.18	56.34	0.28	54.30	3.35
	0.72	54.50	54.53	0.06	52.43	3.80
	0.68	52.82	52.76	0.11	50.61	4.18
	0.64	51.24	51.00	0.47	48.79	4.78
				Av. 0.51		Av. 3.02
1-pentene	0.96	79 82	79 59	0.29	75.90	4.91
(17)	0.94	78.63	78.40	0.29	74 72	4 97
	0.92	77.45	77.28	0.22	73.60	4.97
	0.88	75.26	74.91	0.47	71.25	5.33
	0.84	73.14	72.76	0.52	69.11	5.51
	0.80	71.03	70.73	0.42	67.10	5.53
	0.76	68.90	68.68	0.32	65.06	5.57
	0.72	66.70	66.46	0.36	62.86	5.76
	0.68	64.51	64.31	0.31	60.72	5.88
				Av. 0.35		Av. 5.38

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