

## Saturated-liquid heat capacity calculation of alkanes

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*Abstract:* An empirical model for the calculation of the heat capacity of alkanes is recommended. This model was tested and compared to known models (Luria–Benson and Ružička–Domalski) using 68 sets with 1155 literature experimental heat capacity data of 39 alkanes. The obtained results indicate that the new model is slightly better than the existing models, especially near the critical point.

*Keywords:* heat capacity, prediction, alkanes, calculation, saturated-liquid.

### INTRODUCTION

The heat capacity is an important thermodynamic property for design applications. Experimental saturated-liquid heat capacity data are available for many substances, particularly for alkanes, but the temperature regions are not always sufficiently wide. Many of the experimental data cover a range from the melting point up to the normal boiling temperature.

### MODELS

The previous models (Luria and Benson<sup>1</sup>, Ružička and Domalski<sup>2,3</sup>) use group additivity for the calculation of the saturated-liquid heat capacity. Luria–Benson model can be expressed as:

$$c_{ps} = A + BT + CT^2 + DT^3 \quad (1)$$

The parameters  $A$ ,  $B$ ,  $C$  and  $D$  are obtained from the equations:

$$A = \sum_{i=1}^k n_i a_i; B = \sum_{i=1}^k n_i b_i; C = \sum_{i=1}^k n_i c_i; D = \sum_{i=1}^k n_i d_i \quad (2)$$

The parameters  $a_i$ ,  $b_i$ ,  $c_i$  and  $d_i$  are listed in Table I. Ružička–Domalski model can be expressed by

$$c_{ps}/R = A + B(T/100) + D(T/100)^2 \quad (3)$$

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The parameters  $A$ ,  $B$  and  $D$  are obtained from

$$A = \sum_{i=1}^k n_i a_i; \quad B = \sum_{i=1}^k n_i b_i; \quad D = \sum_{i=1}^k n_i d_i \quad (4)$$

Parameters  $a_i$ ,  $b_i$  and  $d_i$  are listed in Tables.<sup>2,3</sup>

In our previous correlation model for saturated liquid heat capacity<sup>4</sup>

$$\ln(c_{ps}) = A + B/(1 - T/T_c) + C \ln(1 - T/T_c) + D(1 - T/T_c)^{1.2} \quad (5)$$

when  $T \rightarrow T_c$ , then  $T/T_c \rightarrow 1$ , and fraction  $1/(1 - T/T_c) \rightarrow \infty$ . During correlation of experimental data which do not reach the critical point, parameter  $B$  may become negative. For temperatures outside of the experimental range, in the vicinity of the critical point, the negative value of  $B/(1 - T/T_c)$  results in rapid decrease of the heat capacity values. Therefore, this model is not suitable for extrapolation of data in the vicinity of the critical point, as is shown in Fig. 1.

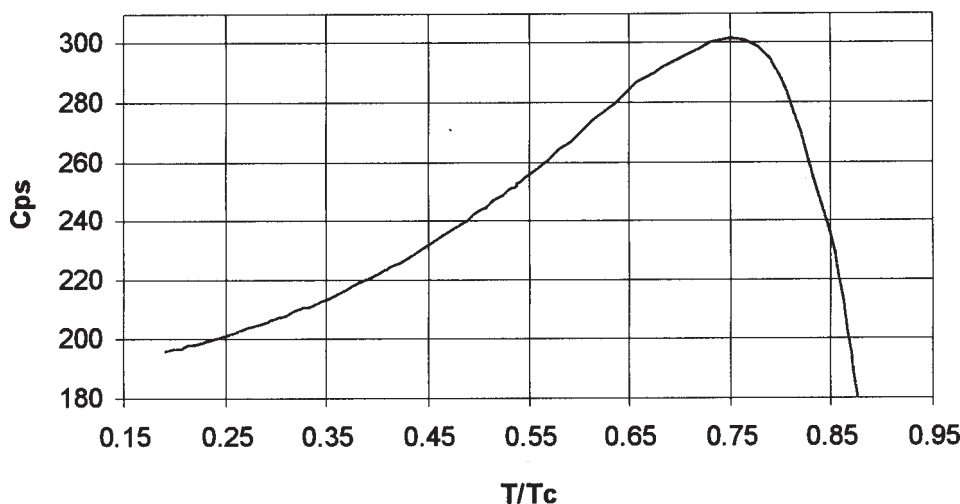


Fig. 1. Heat capacity curve of 3-methylheptane, Eq. (5).

This paper presents a new correlation model which allows extrapolation of data up to the critical point

$$\ln(c_{ps}) = A + B \ln(1 - T/T_c) + CT_c^{1.16} + D(T_c - T)^{0.7} \quad (6)$$

Application of this model onto experimental data from Table I for  $n$ -alkanes and  $i$ -alkanes results in the following generalized parameters

$$A = 3.1731; \quad B = -0.081614; \quad C = 0.0017578; \quad D = -0.0090872 \quad (7)$$

Therefore, the simple empirical model (6) with parameters (7) allows for the calculation of heat capacities for  $n$ -alkanes and  $i$ -alkanes over broad temperature range, varying from the melting up to the critical temperature.

TABLE I. The literature experimental data and quality of the calculation

Compounds	$m$	$\Delta T/K$	$T_c/K$	Ref.	Eq. (1)		Eq. (3)		Eq. (6)	
					$p_{av}/\%$	$p_{max}/\%$	$p_{av}/\%$	$p_{max}/\%$	$p_{av}/\%$	$p_{max}/\%$
Ethane	50	96.77 – 294.85	305.30	5	9.45	46.80	14.43	44.43	3.56	15.55
Ethane	29	91.59 – 180.88	305.30	6	2.44	6.37	10.60	11.12	3.56	6.73
Propane	22	89.67 – 229.76	369.80	7	1.40	2.79	1.36	3.41	2.88	5.07
Propane	7	91.06 – 104.78	369.80	8	0.83	1.56	0.89	1.32	2.29	2.82
Butane	20	142.22 – 268.14	425.20	9	0.99	2.43	2.12	3.17	1.76	3.16
Butane	8	139.70 – 261.80	425.20	10	1.14	2.83	1.68	2.39	1.97	3.41
2-Methylpropane	25	116.94 – 257.02	408.20	11	3.99	7.16	3.38	4.74	1.77	3.22
2,2-Dimethylpropane	29	143.75 – 278.92	433.80	12	9.20	17.91	8.79	14.11	7.46	12.89
2-Methylbutane	13	120.00 – 290.00	460.40	13	1.69	7.03	1.44	5.11	0.87	5.02
2-Methylbutane	14	120.50 – 275.80	460.40	14	1.40	2.42	0.86	1.42	0.26	0.60
2-Methylbutane	83	115.67 – 297.81	460.40	15	1.28	3.04	1.07	1.66	0.39	0.96
Pentane	19	151.32 – 286.41	469.80	16	1.50	4.16	1.39	2.88	1.56	4.48
Pentane	14	149.90 – 290.00	469.80	17	1.37	4.23	0.98	2.86	2.15	4.47
2,2-Dimethylbutane	15	180.00 – 320.00	489.00	18	2.13	3.70	1.81	3.06	2.44	5.82
2,2-Dimethylbutane	12	178.73 – 279.57	489.00	19	1.59	2.13	0.43	0.95	1.45	3.41
2,2-Dimethylbutane	17	177.25 – 296.10	489.00	20	1.50	2.07	1.77	1.95	1.36	3.42
2,3-Dimethylbutane	19	140.00 – 320.00	500.00	18	4.48	8.02	4.67	7.65	1.54	3.35
2,3-Dimethylbutane	38	149.37 – 306.46	500.00	20	1.72	2.50	1.49	2.78	3.36	4.95
2-Methylpentane	21	120.00 – 320.00	497.70	18	3.32	4.97	3.00	4.36	3.83	6.13
2-Methylpentane	27	121.16 – 303.27	497.70	20	0.90	2.18	0.23	0.59	0.86	2.72
3-Methylpentane	24	119.05 – 327.33	504.60	21	0.73	1.67	0.94	1.48	2.77	3.80
3-Methylpentane	17	160.00 – 320.00	504.60	18	2.35	4.56	2.72	4.83	1.70	3.60
3-Methylpentane	16	157.04 – 302.14	504.60	20	0.91	1.45	1.05	1.31	3.18	3.80

TABLE I. Continued

Compounds	$m$	$\Delta T/K$	$T_c/K$	Ref.	Eq. (1)		Eq. (3)		Eq. (6)	
					$p_{av}/\%$	$p_{max}/\%$	$p_{av}/\%$	$p_{max}/\%$	$p_{av}/\%$	$p_{max}/\%$
Hexane	5	188.80 – 293.50	507.90	10	0.75	1.57	0.58	1.91	0.59	2.14
Hexane	33	180.60 – 301.43	507.90	22	1.18	2.58	0.86	3.36	0.98	3.84
Hexane	8	183.50 – 295.10	507.90	14	1.60	3.02	1.04	1.85	1.61	2.12
Hexane	15	180.00 – 320.00	507.90	18	3.16	8.88	4.18	10.16	4.06	9.44
Hexane	24	180.42 – 300.98	507.90	20	1.01	1.93	0.78	2.70	0.88	3.19
2,2,3-Trimethylbutane	6	253.20 – 293.90	531.10	23	0.73	1.57	1.05	1.76	3.83	4.76
2,2-Dimethylpentane	13	153.20 – 294.10	520.50	23	0.57	1.68	1.35	2.68	2.96	5.43
2,3-Dimethylpentane	8	160.30 – 291.30	537.50	23	0.78	1.16	0.89	1.95	4.81	6.42
2,4-Dimethylpentane	15	160.20 – 294.40	519.80	23	1.73	2.76	0.61	1.02	3.67	7.27
3,3-Dimethylpentane	14	145.70 – 292.90	536.40	23	1.28	2.38	0.83	1.08	6.47	8.57
2-Methylhexane	12	160.20 – 292.40	530.40	14	0.45	1.31	0.50	0.82	2.02	3.37
3-Ethylpentane	11	161.40 – 294.80	540.60	23	1.76	2.30	1.88	2.26	4.50	6.23
3-Methylhexane	10	106.30 – 289.20	535.20	23	2.38	6.31	1.40	2.37	1.93	2.93
Heptane	6	194.60 – 317.65	540.10	24	0.90	2.22	1.32	3.67	1.46	3.99
Heptane	96	185.03 – 300.99	540.10	22	1.45	4.47	1.25	5.29	1.28	5.81
Heptane	35	190.00 – 520.00	540.10	25	2.27	8.92	0.93	8.65	1.28	5.07
Heptane	14	188.00 – 299.20	540.10	14	1.81	3.39	1.20	4.43	1.19	4.89
2,2,3,3-Tetramethylbutane	3	375.41 – 377.90	567.80	26	2.56	2.70	1.83	1.90	1.72	1.81
2,2,4-Trimethylpentane	8	171.15 – 317.34	543.80	14	1.15	2.38	1.52	2.47	2.82	5.59
2,2,4-Trimethylpentane	15	169.60 – 295.20	543.80	24	1.99	3.87	2.35	3.67	1.98	3.13
2,3,4-Trimethylpentane	14	172.76 – 323.59	566.40	27	2.39	3.10	0.58	0.95	5.38	10.43
3-Methylheptane	32	107.25 – 376.00	563.60	18	1.75	10.32	0.97	2.21	1.09	2.77
Octane	5	227.00 – 298.30	568.80	10	2.24	3.20	1.02	1.24	0.79	0.97

TABLE I. Continued

Compounds	$m$	$\Delta T/K$	$T_c/K$	Ref.	Eq. (1)		Eq. (3)		Eq. (6)	
					$p_{av}/\%$	$p_{max}/\%$	$p_{av}/\%$	$p_{max}/\%$	$p_{av}/\%$	$p_{max}/\%$
Octane	18	222.61 – 297.58	568.80	28	1.19	1.74	0.77	2.36	0.78	2.18
Octane	8	223.00 – 293.70	568.80	14	2.69	3.36	1.26	2.02	1.09	1.60
Nonane	22	225.03 – 313.88	594.60	28	1.00	1.47	0.95	3.84	0.88	3.23
Nonane	8	224.50 – 299.10	594.60	14	2.20	2.83	0.99	2.07	0.87	1.45
Nonane	8	228.30 – 297.90	594.60	10	1.68	2.32	1.02	2.58	0.75	1.97
2,7-Dimethyloctane	8	223.20 – 295.00	602.90	14	1.06	1.81	1.28	2.31	2.48	3.21
2-Methylnonane	11	200.00 – 298.00	610.30	29	0.97	3.81	1.37	4.63	2.51	4.36
3-Methylnonane	12	190.00 – 298.00	613.40	29	1.66	2.59	0.76	1.14	1.13	1.79
4-Methylnonane	13	180.00 – 298.00	610.50	29	0.85	2.53	0.98	2.15	1.78	4.40
5-Methylnonane	12	190.00 – 298.00	609.60	29	0.94	1.64	0.33	1.02	1.59	3.90
Decane	17	247.02 – 318.62	617.60	28	0.88	1.29	0.99	2.37	0.71	1.53
Decane	6	242.30 – 295.50	617.60	14	2.83	3.80	0.83	1.16	1.18	1.91
Decane	6	251.20 – 297.70	617.60	10	1.86	2.01	0.50	1.02	0.32	0.52
Undecane	5	258.50 – 298.00	638.70	10	1.24	1.46	0.72	1.86	0.33	0.68
Undecane	12	251.74 – 298.92	638.70	28	0.70	1.00	1.40	3.10	0.64	1.80
Dodecane	4	275.10 – 297.70	658.30	10	1.49	1.84	0.57	0.99	0.81	1.27
Dodecane	11	266.69 – 317.41	658.30	28	0.52	0.70	1.09	2.40	0.17	0.73
Tridecane	8	271.66 – 306.38	676.20	28	0.36	0.55	1.58	2.71	0.29	0.57
Tetradecane	7	282.71 – 302.77	693.00	28	0.25	0.83	1.73	2.57	0.55	0.78
Pentadecane	7	285.51 – 312.78	706.80	28	0.15	0.42	1.69	2.52	0.22	0.39
Hexadecane	9	295.41 – 320.28	720.60	28	0.11	0.29	1.35	2.02	0.33	0.45
Hexadecane	2	290.00 – 300.00	720.60	30	0.75	0.87	2.50	2.84	0.37	0.51
Overall percent error	$P_{av}/\%$				2.11		2.33		1.99	

## RESULTS AND DISCUSSION

All the presented models were tested using 68 sets of literature experimental data, with 1155 experimental points of 39 pure alkanes. The results are presented in Table I. The number of experimental points per set ( $m$ ), the temperature range ( $\Delta T$ ), the critical temperature ( $T_c$ ), the literature reference (Ref.), the percentage average error ( $p_{av}$ ), and the maximum percentage error ( $p_{max}$ ) per set are presented in this Table.

The overall percent errors, also included in the Table, were calculated as follows:

$$P_{av} = \sum_{i=1}^N m_i p_{av,i} / \sum_{i=1}^N m_i; \quad p_{av} = 100 \sum_{i=1}^m [|c_{ps,exp,i} - c_{ps,cal,i}| / c_{ps,exp,i}] \quad (8)$$

The obtained overall percent error (1.99 %) of the recommended model indicates that it is slightly better than the existing models. In addition, the recommended model is more suitable for application near the critical point ( $T \rightarrow T_c$ , hence  $c_{ps} \rightarrow \infty$ ) than the existing models. Moreover, the recommended model is simpler than the other two.

## CONCLUSION

Three models were used to test their predictive ability for the saturated-liquid heat capacities. The obtained results indicate that the accuracy of the predictions are similar, except near the critical point. Therefore, it may be concluded that the recommended model gave better results.

## NOTATIONS

$c_{ps}$	– Saturated-liquid heat capacity, J mol <sup>-1</sup> K <sup>-1</sup>
$T_c$	– Critical temperature, K
$T$	– Temperature, K
$A, B, C, D$	– Adjustable parameters of the models
$p_{av}$	– Percentage average error per set, %
$p_{max}$	– Maximal percentage error per set, %
$P_{av}$	– Overall percent error per model, %
$m$	– Number of experimental data points per set
$n$	– Number of groups of the same type in a molecule
$k$	– Total number of different kinds of groups in a molecule
$N$	– Number of sets
$\Delta T$	– Temperature range, K
$R$	– Gas constant, 8.31451 J mol <sup>-1</sup> K <sup>-1</sup>

*Subscripts*

exp	– Experimental value
cal	– Calculated value

## ИЗВОД

ПРЕДСКАЗИВАЊЕ ТОПЛОТНОГ КАПАЦИТЕТА ЗАСИЋЕНЕ ТЕЧНОСТИ  
АЛКАНА

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У овом раду је препоручен нов емпиријски модел за предсказивање вредности топлотног капацитета засићене течности алкана. Модел је тестиран и упоређен са познатим моделима коришћењем 68 сетова са 1155 експерименталних података из литературе за 39 алкана. Добијени резултати указују да је нов модел бољи од постојећих, нарочито у околини критичне тачке.

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## REFERENCES

1. M. Luria, S. W. Benson, *J. Chem. Eng. Data* **22** (1977) 90
2. V. Růžička, E. S. Domalski, *J. Phys. Chem. Ref. Data* **22** (1993a) 597
3. V. Růžička, E. S. Domalski, *J. Phys. Chem. Ref. Data* **22** (1993b) 619
4. J. D. Jovanović, D. K. Grozdanić, *J. Serb. Chem. Soc.* **69** (2004) 233
5. R. Wiebbe, K. H. Hubbard, M. J. Brevoort, *J. Am. Chem. Soc.* **52** (1930) 611
6. R. K. Witt, J. D. Kemp, *J. Am. Chem. Soc.* **59** (1937) 273
7. J. D. Kemp, C. J. Egan, *J. Am. Chem. Soc.* **60** (1938) 1521
8. A. J. B. Cutler, J. A. Morrison, *Trans. Farad. Soc.* **61** (1965) 429
9. J. G. Aston, G. H. Messerly, *J. Am. Chem. Soc.* **62** (1940) 1917
10. H. M. Huffman, G. S. Parks, M. Barmore, *J. Am. Chem. Soc.* **53** (1931) 3876
11. J. G. Aston, R. M. Kennedy, S. C. Schumann, *J. Am. Chem. Soc.* **62** (1940) 2059
12. J. G. Aston, G. H. Messerly, *J. Am. Chem. Soc.* **58** (1936) 2354
13. S. C. Schumann, J. G. Aston, M. Sagenkahn, *J. Am. Chem. Soc.* **64** (1942) 1039
14. G. S. Parks, H. M. Huffman, S. B. Thomas, *J. Am. Chem. Soc.* **52** (1930) 1032
15. G. B. Jr. Guthrie, H. M. Huffman, *J. Am. Chem. Soc.* **65** (1943) 1139
16. G. H. Messerly, R. M. Kennedy, *J. Am. Chem. Soc.* **62** (1940) 2988
17. G. S. Parks, H. M. Huffman, *J. Am. Chem. Soc.* **52** (1930) 4381
18. D. R. Stull, *J. Am. Chem. Soc.* **59** (1937) 2726
19. J. E. Kilpatrick, K. S. Pitzer, *J. Am. Chem. Soc.* **68** (1946) 1066
20. D. R. Douslin, H. M. Huffman, *J. Am. Chem. Soc.* **68** (1946) 1704
21. H. L. Finke, J. F. Messerly, *J. Chem. Thermodynamics* **5** (1973) 247
22. B. Kalinowska, J. Jedlinska., W. Woycicki, J. Stecki, *J. Chem. Thermodynamics* **12** (1980) 891
23. H. M. Huffman, G. S. Parks, S. B. Thomas, *J. Am. Chem. Soc.* **52** (1930) 3241
24. K. S. Pitzer, *J. Am. Chem. Soc.* **62** (1940) 1224
25. D. C. Ginnings, G. T. Furukawa, *J. Am. Chem. Soc.* **75** (1953) 522
26. D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver, H. M. Huffman, *J. Am. Chem. Soc.* **74** (1952) 883
27. K. S. Pitzer, D. W. Scott, *J. Am. Chem. Soc.* **63** (1941) 2419
28. H. L. Finke, M. E. Gross, G. Waddington, H. M. Huffman, *J. Am. Chem. Soc.* **76** (1954) 333
29. G. S. Parks, T. J. West, G. E. Moore, *J. Am. Chem. Soc.* **63** (1941) 1133
30. G. S. Parks, G. E. Moore, M. L. Renquist, B. F. Naylor, L. A. McClaine, P. S. Fujii, J. A. Hatton, *J. Am. Chem. Soc.* **71** (1949) 3386.