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THE GASEOUS STANDARD ENTROPY $S^\circ_{298}(g)$ OF THE 3RD LAW OF THERMODYNAMICS CAN BE ESTIMATED FROM GAS-CHROMATOGRAPHIC RETENTION DATA

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Standard entropy $S^\circ_{298}(g)$ of the 3rd law of thermodynamics can be estimated by the regression analysis of log γ of gas-chromatography determined under non-polar conditions on $S^\circ_{298}(g)$. Results can be practically achieved by using the concept of the mean-square fluctuating electric field.

KEYWORDS——standard entropy; 3rd law of thermodynamics; retention ratio; gas chromatography; aliphatic hydrocarbon; regression analysis

Standard entropy $S^\circ_{298}(g)$ of the 3rd law of thermodynamics determined from the measurements of molar specific heat at 1 atm or molecular statistical thermodynamics using vibrational spectroscopy have been summarized in the literature.[1,2] In addition, empirical methods for the estimation of this parameter are also presented,[2,3] but they are tedious and time consuming. In fact, these parameters are limited in number and are insufficient for practical purposes, e.g. physical organic chemistry,[4] QSAR,[5] etc. This has prompted us to present an empirical method for determining the $S^\circ_{298}(g)$.

In this work, the authors focused their attention on the gas-chromatographic retention ratio determined in the non-polar mobile and stationary phases, and the results of regression analysis revealed that they are sufficient for the estimation of unknown $S^\circ_{298}(g)$.

For instance, the retention ratio γ determined at 298°K for a number of acyclic saturated alkanes[6] summarized in Table 1 gave the following result:

$$\log \gamma = 0.0496\ (\pm 0.0019)\ S^\circ_{298}(g) - 4.6043\ (\pm 0.1833), \qquad (1)$$
$$n=48, \quad r=0.992, \quad SD=0.099, \quad F=2891.68, \quad d=1.89,$$

where γ is defined as

$$\gamma = V_g(\mathrm{HC})/V_g(\mathrm{hexane}).^{7)} \qquad (2)$$

Eq. 1 demonstrates that the unknown $S^\circ_{298}(g)$ of acyclic saturated alkanes can be estimated from the regression equation.

Molecular theory supports this: Under non-polar conditions, e.g. if non-polar mobile and stationary phases are employed, V_g or γ can be expected, from the dispersion force between the solute and stationary phase, to be

$$E_{dis} = -\frac{3}{2}\frac{\alpha_A\alpha_B}{r^6_{AB}}\frac{I_AI_B}{I_A+I_B}, \qquad (3)^{8)}$$

Table 1. Retention Ratios γ and $S^\circ_{298}(g)$ [cal $mol^{-1}deg^{-1}$] of Acyclic Saturated Alkanes

		$S^\circ_{298}(g)$	γ			$S^\circ_{298}(g)$	γ
1	C_1	44.52	0.005	25	2,2-Me_2-C_6	103.06	3.49
2	C_2	54.85	0.01	26	2,5-Me_2-C_6	104.96	3.87
3	C_3	64.51	0.03	27	2,4-Me_2-C_6	106.51	3.93
4	C_4	74.12	0.11	28	3,3-Me_2-C_6	104.70	4.14
5	C_5	83.94	0.35	29	2,3-Me_2-C_6	106.11	5.09
6	C_6	92.83	1.00	30	3,4-Me_2-C_6	107.15	5.53
7	C_7	102.27	2.82	31	2,2-Me_2-C_7	113.07	9.16
8	C_8	111.55	7.66	32	2,2,3-Me_3-C_4	91.61	1.43
9	2-Me-C_3	70.42	0.07	33	2,2,4-Me_3-C_5	101.15	2.48
10	2-Me-C_4	82.12	0.26	34	2,2,3-Me_3-C_5	101.62	3.81
11	2-Me-C_5	90.95	0.72	35	2,3,4-Me_3-C_5	102.31	4.49
12	3-Me-C_5	90.97	0.84	36	2,3,3-Me_3-C_5	103.14	4.61
13	2-Me-C_6	100.38	2.02	37	2,2,5-Me_3-C_5	103.14	4.61
14	3-Me-C_6	101.37	2.19	38	2,2,4-Me_3-C_6	111.34	6.76
15	2-Me-C_7	108.81	5.46	39	2,4,4-Me_3-C_6	112.14	7.86
16	4-Me-C_7	108.35	5.53	40	2,3,5-Me_3-C_6	112.30	8.75
17	3-Me-C_7	110.32	5.85	41	2,2,3-Me_3-C_6	111.34	9.28
18	2,2-Me_2-C_3	73.23	0.13	42	3-Et-C_5	98.35	2.43
19	2,2-Me_2-C_4	85.62	0.51	43	3-Et-2-Me-C_5	105.43	5.09
20	2,3-Me_2-C_4	87.42	0.69	44	3-Et-3-Me-C_5	103.48	5.40
21	2,2-Me_2-C_5	93.90	1.28	45	3-Et-C_6	109.51	5.88
22	2,4-Me_2-C_5	94.80	1.37	46	3-Et-2,2-Me_2-C_5	109.96	8.91
23	3,3-Me_2-C_5	95.93	1.75	47	2,2,3-Me_4-C_5	108.23	8.49
24	2,3-Me_2-C_5	98.96	2.02	48	2,2,4,4-Me_4-C_5	101.13	5.53

C_n(n=1,8) is the number of carbon atoms of the linear alkanes.

where subscripts A and B denote the solute and stationary phase, respectively, and, α, I and r are the polarizability, ionization potential and the distance A---B. But, unfortunately, the estimation of r_{AB}, the distance between the solute and wall of the stationary phase, is difficult. Therefore, when both stationary and mobile phases are non-polar and I_B and α_B are constants, the energy E brought about by the interaction between the solute and the wall of the stationary phase can be given preferably by Eq. 4, based on the concept of the mean-square fluctuating electric field proposed by Raynes et al:⁹⁾

$$E \propto \frac{\alpha_A I_A}{r_A^6}, \qquad (4)$$

where r_A is the hard-sphere radius of hydrocarbon determined from the second virial coefficients.¹⁰⁾

As all values of ionization potential I of aliphatic hydrocarbons are found within 10-13 eV, so E depends mainly on α_A/r_A^6, where α_A¹¹⁾ and r_A^6 require the dimensions of $[L]^3$ and $[L]^6$ respectively, and become exponential against $S^\circ_{298}(g)$.¹²⁾ The details of this work will be published in due time.

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