A comparison of some thermodynamic quantities for hydrocarbons and mercaptans

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Empirical equations were derived for determining the dependency of formation enthalpy, entropy and heat capacity on the number of carbon atoms present in the molecule for hydrocarbons and mercaptans. It was shown that particular care should be taken to calculations of enthalpy and entropy values at respective temperatures, especially when Gibbs energy and equilibrium constant values are calculated, because the formation enthalpy values of organic sulfur compounds suddenly decrease in the 700–800 K temperature interval.

Key words: enthalpy, entropy, heat capacity, hydrocarbons, mercaptans

INTRODUCTION

Investigation of thermodynamic properties for organic sulfur compounds started in the year 1886 [1], however, more detail investigations were not conducted until 1932, because more and more attention was being paid to hydrocarbons having a larger economic impact and probably due to the fact that sulfur compounds have an obnoxious odour [2]. At that time Gibbs energy values were determined for only two sulfur compounds, (carbon disulfide and carbonyl sulfide [3]) and in 1949 for seven more sulfur compounds [4].

After World War II thermodynamic properties of organic sulfur compounds were intensively studied at Bartlesville (USA) Crude Oil Scientific Center and Thermochemical Laboratory at Lund University (Sweden). Some thermodynamic values are given in references [5–9]. Unfortunately, in all these literature sources we cannot find heat capacity values for mercaptans, but a rule is proposed to calculate it from hydrocarbon heat capacity values by introducing a correction in the compound molecular formula, i.e. by replacing the $-CH_3$ group by the $-SH$ group.

In addition, there ae no data on changes in heat capacity, entropy and enthalpy values that accompany changes in the number of carbon atoms present in the molecule and on the role of temperature in changes of these functions. On the other hand, it is necessary to investigate the conditions at which toxic materials are emitted into the atmosphere when mercaptans are heated and decompose. That is why we need to know the thermodynamic function values for mercaptan formation at various temperatures.

We aimed to assess the values of entropy, enthalpy and heat capacity for the formation of the saturated and unsaturated hydrocarbons as well as mercaptans and to determine their dependency on the number of carbon atoms present in the molecule and on temperature. This would allow to regulate sulfur compound concentrations in power unit flue gases.

PROCEDURES

Compound formation enthalpy, entropy and heat capacity values were calculated using reference data [2]. Molar heat capacity variation with temperature was expressed by a conventional equation:

$$C_p = a + bT + cT^2. \qquad (1)$$

The values of the empirical constants *a, b, c* were calculated by using equations given in reference [2]:

$$c = \frac{C_{P1}}{(T_2 - T_1)(T_3 - T_1)} - \frac{C_{P2}}{(T_2 - T_1)(T_3 - T_2)} + \frac{C_{P3}}{(T_3 - T_2)(T_3 - T_1)} \qquad (2)$$

$$b = \frac{C_{P2} - C_{P1}}{T_2 - T_1} - (T_1 + T_2) \cdot c \qquad (3)$$

$$a = C_{P1} - bT_1 - cT_1^2 \qquad (4)$$

where $C_{P1,}$ $C_{P2,}$ C_{P3} are molar heat capacity values at there different temperatures (T_1, T_2, T_3).

RESULTS AND DISCUSSION

1. Comparison of entropy values for hydrocarbons and mercaptans. Various references [2–9] give very close values of many thermodynamic functions for saturated and unsaturated hydrocarbons and for mercaptans. Their entropy values under normal ideal gas conditions obtained using reference [2] data are given in Table 1. It is evident from Table 1 that the entropy of saturated and unsaturated hydrocarbons containing the same number of carbon atoms differs only slightly: by approximetaly 4.0 J/(mol · K). A slightly larger deviation from this value was obtained for hydrocarbons with 2–5 carbon atoms present in the molecule. The average difference between saturated hydrocarbons and the correspounding mercaptan entropy values was 65.5–65.6, while between unsaturated hydrocarbon and mercaptan this difference was about 69.7 J/(mol · K).

As can be seen from Table 1, an increase in the number of carbon atoms present in the molecule causes an increase in entropy values; furthermore, both hydrocarbon and mercaptan formation entropy dependencies on the number of carbon atoms present in the molecule are almost linear.

These linear dependencies employing the values of the least-squares fitted parameters can be expressed by equations, when n ≥ 5: for saturated hydrocarbons

$$(S^0_{298})_1 = 154.84 + 38.98\,n\,, \tag{5}$$

for unsaturated hydrocarbons

$$(S^0_{298})_2 = 151.08 + 38.97\,n, \tag{6}$$

and for mercaptans

$$(S^0_{298\,3}) = 220.77 + 38.97\,n\,. \tag{7}$$

We noted that angle coefficients in all these equations were equal in magnitude, so the straight lines are parallel. Here, only the free member differs. This regularity clarifies why we can calculate the mercaptan entropy value as given in references [5, 6, 9] knowing only the entropy value of hydrocarbon. The latter reference gives the entropy correction factor when the $-CH_3$ group is replaced by $-SH$, leading to a decrease in the number of carbon atoms. From equations (5) and (6) it follows that the difference between the entropy value for hydrocarbons containing *n* carbon atoms in the molecule and for mercaptan containing *n–1* carbon atoms is equal approximately to 26.73. References give this

Table 1. **Entropy values of saturated and unsaturated hydrocarbons and mercaptans under standard ideal gas conditions, J/(mol · K)**

Saturated hydrocarbons		Unsaturated hydrocarbons		Mercaptans		Differences	
Formula	$(S^0_{298})_1$ [1]	Formula	$(S^0_{298})_2$ [2]	Formula	$(S^0_{298})_3$ [2]	$(S_{298})_3$–$(S_{298})_1$	$(S_{298})_3$–$(S_{298})_2$
CH_4	186.40	–	–	CH_4S	255.23	+68.83	–
C_2H_6	229.65	C_2H_4	219.60	C_2H_6S	296.30	+66.65	+76.70
C_3H_8	270.55	C_3H_6	267.12	C_3H_8S	336.62	+66.07	+69.50
C_4H_{10}	310.33	C_4H_8	305,80	$C_4H_{10}S$	375.47	+65.14	+69.67
C_5H_{12}	349.18	C_5H_{10}	346.04	$C_5H_{12}S$	415.67	+66.49	+69.63
C_6H_{14}	388.66	C_6H_{12}	384.89	$C_6H_{14}S$	454.60	+65.94	+69.71
C_7H_{16}	428.18	C_7H_{14}	423.87	$C_7H_{16}S$	493.58	+65.40	+69.71
C_8H_{18}	467.04	C_8H_{16}	462.85	$C_8H_{18}S$	532.56	+65.52	+69.71
C_9H_{20}	506.02	C_9H_{18}	501.83	$C_9H_{20}S$	571.54	+65.52	+69.71
$C_{10}H_{22}$	545.00	$C_{10}H_{20}$	540.81	$C_{10}H_{22}S$	610.52	+65.52	+69.71
$C_{11}H_{24}$	583.97	$C_{11}H_{22}$	579.79	$C_{11}H_{24}S$	649.50	+65.53	+69.71
$C_{12}H_{26}$	622.91	$C_{12}H_{24}$	618.73	$C_{12}H_{26}S$	688.48	+65.57	+69.75
$C_{13}H_{28}$	661.89	$C_{13}H_{26}$	657.70	$C_{13}H_{28}S$	727.46	+65.57	+69.76
$C_{14}H_{30}$	700.87	$C_{14}H_{28}$	696.68	$C_{14}H_{30}S$	766.44	+65.57	+69.76
$C_{15}H_{32}$	739.43	$C_{15}H_{30}$	735.66	$C_{15}H_{32}S$	805.41	+65.98	+69.75
$C_{16}H_{34}$	778.83	$C_{16}H_{32}$	774.64	$C_{16}H_{34}S$	844.35	+65.52	+69.71
$C_{17}H_{36}$	817.81	$C_{17}H_{34}$	813.62	$C_{17}H_{36}S$	883.33	+65.52	+69.71
$C_{18}H_{38}$	856.79	$C_{18}H_{36}$	852.60	$C_{18}H_{38}S$	922.31	+65.52	+69.71
$C_{19}H_{40}$	895.75	$C_{19}H_{38}$	891.58	$C_{19}H_{40}S$	961.29	+65.54	+69.71
$C_{20}H_{42}$	934.74	$C_{20}H_{40}$	930.56	$C_{20}H_{42}S$	1000.27	+65.53	+69.71

correction factor to be equal to 21.77 J/(mol · K). This may be due to an inaccurate entropy value determination.

2. Comparison of formation enthalpy values for hydrocarbons and mercaptans. Various references [2, 9] give approximately close hydrocarbon formation enthalpy values. Enthalpy values represented in Table 2 were obtained by using reference [2]. Here, all the enthalpy values for hydrocarbon and mercaptan are negative, with the exception of that for ethylene and propylene. An increase in the number of carbon atoms in the molecule decreases consecutively the enthalpy values. The difference between the enthalpy values for hydrocarbons and mercaptans is rather constant. This difference is slightly higher only in the cases for methane-methyl mercaptan and ethylene-ethyl mercaptan, hydrocarbon enthalpy values are lower than for corresponding mercaptans, while for unsaturated hydrocarbons they are higher. The enthalpy value dependency on the number of carbon atoms present in the molecule can be expressed by the equations:

for saturated hydrocarbons,

$$(\Delta H^0_{298})_1 = -43.51 - 20.63\,n\,, \tag{8}$$

for unsaturated hydrocarbons

$$(\Delta H^0_{298})_2 = 82.09 - 20.63\,n \tag{9}$$

and for mercaptans

$$(\Delta H^0_{298})_3 = -5.35 - 20.62\,n\,. \tag{10}$$

All the there angle coefficient values are rougly equal, meaning that the straight lines are parallel. The difference between the enthalpy of saturated hydrocarbons is equal to 38.16, while of unsaturated hydrocarbons and mercaptans 87.44 kJ/mol.

Taking into consideration that the replacement of $-CH_3$ group by –SH group causes a decrease in the number of carbon atoms, the correction factor arising from equations 8 and 10 should be equal to 58.93 kJ/mol.

This correction factor given in references is slightly higher (66.1 kJ/mol), most likely due to an incorrect mercaptan enthalpy determination.

3. Comparison of values of heat capacity for hydrocarbons and mercaptans. The values of molar heat capacity (Table 3) for all the saturated and unsaturated hydrocarbons and mercaptans increase with an increase in the number of carbon atoms present in the molecule, and the dependency of molar heat capacity for these compounds on the number of carbon atoms (n) present in the molecule can be expressed by linear equations:

Table 2. **Saturated and unsaturated hydrocarbons and mercaptans enthalpy values at standard ideal gas conditions, J/(mol · K)**

Saturated hydrocarbons		Unsaturated hydrocarbons		Mercaptans		Differences	
Formula	$(\Delta H^0_{298})_1$ [2]	Formula	$(\Delta H^0_{298})_2$ [2]	Formula	$(\Delta H^0_{298})_3$ [2]	$(\Delta H^0_{298})_3-(\Delta H^0_{298})_1$	$(\Delta H^0_{298})_3-(\Delta H^0_{298})_2$
CH_4	–74.90	–	–	CH_4S	–22.99	51.91	–
C_2H_6	–84.74	C_2H_4	+52.335	C_2H_6S	–46.14	38.60	–98.475
C_3H_8	–103.92	C_3H_6	+20.43	C_3H_8S	–67.91	36.01	–88.34
C_4H_{10}	–126.23	C_4H_8	–1.256	$C_4H_{10}S$	–88.13	38.10	–86.874
C_5H_{12}	–146.54	C_5H_{10}	–20.93	$C_5H_{12}S$	–108.48	38.06	–87.55
C_6H_{14}	–167.30	C_6H_{12}	–41.70	$C_6H_{14}S$	–129.08	38.22	–87.38
C_7H_{16}	–187.90	C_7H_{14}	–62.34	$C_7H_{16}S$	–149.72	38.18	–87.38
C_8H_{18}	–208.59	C_8H_{16}	–82.98	$C_8H_{18}S$	–170.32	38.27	–87.34
C_9H_{20}	–229.19	C_9H_{18}	–103.58	$C_9H_{20}S$	–190.96	38.23	–87.38
$C_{10}H_{22}$	–249.83	$C_{10}H_{20}$	–124.22	$C_{10}H_{22}S$	–211.60	38.23	–87.38
$C_{11}H_{24}$	–270.47	$C_{11}H_{22}$	–144.86	$C_{11}H_{24}S$	–232.20	38.27	–87.34
$C_{12}H_{26}$	–291.07	$C_{12}H_{24}$	–165.46	$C_{12}H_{26}S$	–252.84	38.23	–87.38
$C_{13}H_{28}$	–311.71	$C_{13}H_{26}$	–186.10	$C_{13}H_{28}S$	–273.44	38.27	–87.34
$C_{14}H_{30}$	–332.35	$C_{14}H_{28}$	–206.66	$C_{14}H_{30}S$	–294.08	38.27	–87.42
$C_{15}H_{32}$	–352.99	$C_{15}H_{30}$	–227.39	$C_{15}H_{32}S$	–314.72	38.27	–87.33
$C_{16}H_{34}$	–373.59	$C_{16}H_{32}$	–247.98	$C_{16}H_{34}S$	–335.32	38.27	–87.34
$C_{17}H_{36}$	–394.19	$C_{17}H_{34}$	–268.58	$C_{17}H_{36}S$	–355.96	38.23	–87.38
$C_{18}H_{38}$	–414.83	$C_{18}H_{36}$	–289.22	$C_{18}H_{38}S$	–376.56	38.27	–87.34
$C_{19}H_{40}$	–435.43	$C_{19}H_{38}$	–309.82	$C_{19}H_{40}S$	–397.20	38.23	–87.38
$C_{20}H_{42}$	–456.07	$C_{20}H_{40}$	–330.46	$C_{20}H_{42}S$	–417.84	38.23	–87.38

Table 3. **Molar heat capacity for saturated and unsaturated hydrocarbons and mercaptans under standard ideal gas conditions, J/(mol · K)**

Saturated hydrocarbons		Unsaturated hydrocarbons		Mercaptans		Differences	
Formula	$(C^0_{P298})_1$ [2]	Formula	$(C^0_{P298})_2$ [2]	Formula	$(C^0_{P298})_3$ [2]	$(C^0_{P298})_3-(C^0_{P298})_1$	$(C^0_{P298})_3-(C^0_{P298})_2$
CH_4	35.76	–	–	CH_4S	50.28	14.52	–
C_2H_6	52.67	C_2H_4	43.58	C_2H_6S	72.72	20.05	29.14
C_3H_8	73.56	C_3H_6	63.93	C_3H_8S	94.83	21.27	30.90
C_4H_{10}	97.51	C_4H_8	85.70	$C_4H_{10}S$	118.24	20.73	32.54
C_5H_{12}	120.29	C_5H_{10}	109.65	$C_5H_{12}S$	141.30	21.01	31.65
C_6H_{14}	143.19	C_6H_{12}	132.45	$C_6H_{14}S$	164.16	20.97	31.71
C_7H_{16}	166.09	C_7H_{14}	155.33	$C_7H_{16}S$	187.07	20.98	31.74
C_8H_{18}	188.99	C_8H_{16}	178.19	$C_8H_{18}S$	209.93	20.94	31.74
C_9H_{20}	211.85	C_9H_{18}	201.09	$C_9H_{20}S$	232.83	20.98	31.74
$C_{10}H_{22}$	234.75	$C_{10}H_{20}$	223.95	$C_{10}H_{22}S$	255.73	20.98	31.78
$C_{11}H_{24}$	257.61	$C_{11}H_{22}$	246.85	$C_{11}H_{24}S$	278.59	20.93	31.74
$C_{12}H_{26}$	280.52	$C_{12}H_{24}$	269.76	$C_{12}H_{26}S$	301.49	20.97	31.73
$C_{13}H_{28}$	303.42	$C_{13}H_{26}$	292.62	$C_{13}H_{28}S$	324.35	20.93	31.73
$C_{14}H_{30}$	326.28	$C_{14}H_{28}$	315.52	$C_{14}H_{30}S$	347.25	20.97	31.73
$C_{15}H_{32}$	349.18	$C_{15}H_{30}$	338.38	$C_{15}H_{32}S$	370.15	20.97	31.77
$C_{16}H_{34}$	372.04	$C_{16}H_{32}$	361.28	$C_{16}H_{34}S$	393.01	20.97	31.73
$C_{17}H_{36}$	394.94	$C_{17}H_{34}$	384.18	$C_{17}H_{36}S$	415.92	20.98	31.74
$C_{18}H_{38}$	417.84	$C_{18}H_{36}$	407.04	$C_{18}H_{38}S$	438.78	20.94	31.74
$C_{19}H_{40}$	440.70	$C_{19}H_{38}$	429.34	$C_{19}H_{40}S$	462.10	21.40	32.16
$C_{20}H_{42}$	463.60	$C_{20}H_{40}$	452.80	$C_{20}H_{42}S$	484.58	20.98	31.78

for saturated hydrocarbons,

$$(Cp)_1 = 5.88 + 22.89\, n \tag{11}$$

for unsaturated hydrocarbons

$$(Cp)_2 = 4.73 + 22.87\, n \tag{12}$$

and for mercaptans

$$(Cp)_2 = 26.77 + 22.89\, n \tag{13}$$

Thus, the dependence of heat capacity for hydrocarbons as well as for mercaptans on the number of carbon atoms present in the molecule are displayed by straight lines and the latter are parallel because the angle coefficients are equal.

As is evident from equations (11)–(13), the difference between the molar heat capacity of saturated hydrocarbons and the corresponding mercaptans possessing the same number of carbon atoms is equal to 19.95, while for unsaturated hydrocarbons and mercaptans 31.69 J/(mol · K).

The dependency of molar heat capacity on temperature is often described by different equations [2]. Calculating the reaction equilibrium constant for different temperatures it is necessary to know the values of heat capacity constants for all reacting materials and reaction products. The heat capacity constant values for organic sulfur compounds were not available in the references we used. However, only correction factors ***a***, ***b*** and ***c*** were given when the $-CH_3$ group was replaced by the –SH group in the compounds [5, 6].

To calculate the values of the heat capacity constants ***a***, ***b*** and ***c*** for saturated hydrocarbons, unsaturated hydrocarbons and mercaptans (Table 4), we used refernce [2] data, equations (1)–(3) and heat capacity values at three different temperatures: 300, 400 and 500 K. The dependency of these constants on the number of carbon atoms present in the molecule are given in Table 4 and Fig. 1. As one can see from Fig. 1, beginning with compounds with 5 carbon atoms, the values of coefficient ***a*** increase according to a linear dependency. The equations for these lines are as follows:

for saturated hydrocarbons,

$$a_1 = 3.08 + 1.229\, n \tag{14}$$

for usaturated hydrocarbons

$$a_2 = 1.51 + 1.271\, n \tag{15}$$

and for mercaptans

Table 4. **Constants of molar heat capacity for saturated and unsaturated hydrocarbons and mercaptans calculated by single heat capacity values given in reference [2] for 300, 400 and 500 K, J/(mol · K)**

Saturated hydrocarbons				Unsaturated hydrocarbons				Mercaptans			
Formula	a	b · 10^3	c · 10^6	Formula	a	b · 10^3	c · 10^6	Formula	a	b · 10^3	c · 10^6
CH_4	27.51	11.93	52.34	–	–	–	–	CH_4S	22.44	100.30	–25.12
C_2H_6	13.23	136.07	–12.56	C_2H_4	8.21	130.42	–39.77	C_2H_6S	18.25	205.15	–75.36
C_3H_8	2.60	262.93	–83.74	C_3H_6	10.97	192.59	–50.24	C_3H_8S	20.76	274.03	–85.83
C_4H_{10}	8.54	326.99	–96.30	C_4H_8	–1.34	332.85	–142.35	$C_4H_{10}S$	24.58	342.90	–96.30
C_5H_{12}	9.34	410.10	–127.70	C_5H_{10}	8.29	381.00	–138.16	$C_5H_{12}S$	26.42	422.24	–123.51
C_6H_{14}	11.01	489.44	–154.91	C_6H_{12}	9.09	464.11	–169.57	$C_6H_{14}S$	27.42	504.93	–154.91
C_7H_{16}	11.39	575.48	–190.50	C_7H_{14}	10.34	545.33	–198.87	$C_7H_{16}S$	29.10	584.27	–182.13
C_8H_{18}	12.64	656.70	–219.81	C_8H_{16}	11.76	626.14	–228.18	$C_8H_{18}S$	30.10	666.96	–213.53
C_9H_{20}	14.07	737.50	–249.11	C_9H_{18}	13.02	707.36	–257.49	$C_9H_{20}S$	31.78	746.30	–240.74
$C_{10}H_{22}$	15.92	818.73	–278.42	$C_{10}H_{20}$	14.44	788.17	–286.80	$C_{10}H_{22}S$	33.03	827.52	–270.05
$C_{11}H_{24}$	16.75	899.53	–307.73	$C_{11}H_{22}$	15.07	872.74	–320.29	$C_{11}H_{24}S$	34.46	908.33	–299.36
$C_{12}H_{26}$	17.38	984.11	–341.22	$C_{12}H_{24}$	16.33	953.96	–349.60	$C_{12}H_{26}S$	35.71	989.55	–328.66
$C_{13}H_{28}$	18.63	1065.33	–370.53	$C_{13}H_{26}$	17.75	1034.77	–378.91	$C_{13}H_{28}S$	37.14	1070.36	–357.97
$C_{14}H_{30}$	20.05	1146.14	–399.84	$C_{14}H_{28}$	19.01	1115.99	–408.21	$C_{14}H_{30}S$	38.39	1151.58	–387.28
$C_{15}H_{32}$	21.31	1227.36	–429.15	$C_{15}H_{30}$	20.43	1196.80	–437.52	$C_{15}H_{32}S$	39.44	1234.27	–418.68
$C_{16}H_{34}$	22.73	1308.17	–458.45	$C_{16}H_{32}$	23.01	1278.02	–466.83	$C_{16}H_{34}S$	40.44	1314.66	–450.08
$C_{17}H_{36}$	23.99	1389.40	–487.76	$C_{17}H_{34}$	22.94	1359.24	–496.14	$C_{17}H_{36}S$	42.12	1396.30	–477.30
$C_{18}H_{38}$	25.25	1470.61	–517.07	$C_{18}H_{36}$	24.37	1440.05	–525.44	$C_{18}H_{38}S$	43.12	1478.99	–508.70
$C_{19}H_{40}$	26.67	1551.42	–546.38	$C_{19}H_{38}$	25.62	1521.27	–554.75	$C_{19}H_{40}S$	44.80	1558.33	–535.91
$C_{20}H_{42}$	27.93	1632.64	–575.69	$C_{20}H_{40}$	27.05	1602.08	–584.06	$C_{20}H_{42}S$	46.05	1639.55	–565.22

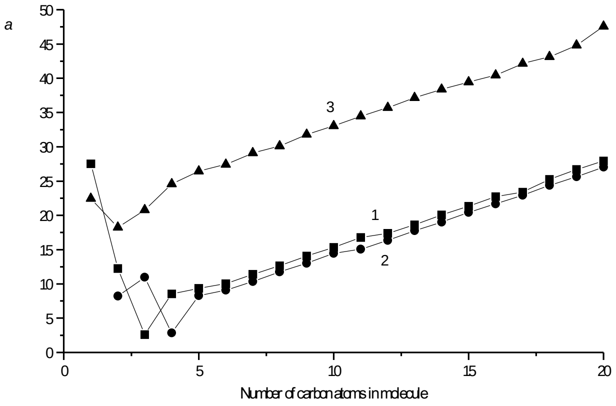

Fig. 1. Dependency of heat capacity constant *a* on the number of carbon atoms present in the molecule: *1* – for saturated hydrocarbons, *2* – for unsaturated hydrocarbons, *3* – for mercaptans

$$a_3 = 19.88 + 1.307\, n. \qquad (16)$$

The angle coefficients of these equations differ only by one hundredth parts, so we can assume that these straight lines are parallel to each other. A comparison of differences between free members of equations (14)–(15) obtained for saturated and unsaturated hydrocarbons shows that they are insignificant. The values of constant ***a*** for mercaptans are significantly higher. If we would calculate the constant ***a*** value when the $–CH_3$ group is replaced by –SH, then the number of carbon atoms present in the mercaptan molecule would decrease and the difference between the constant ***a*** values for mercaptans and saturated hydrocarbons would be on the average equal to 16.67 J/(mol · K).

References give a slightly higher correction coefficient – 17.04 J/(mol · · K). As follows from Table 4, such a recalculation coefficient is improper for mercaptans containing less than four carbon atoms; *e.g.*, the difference between constant ***a*** for methane and methyl mercaptan is equal to 9.21 J/(mol · K).

The value of constant ***b*** increases for all the compounds studied with an increase in the number of carbon atoms according to a linear relationship. All the lines are practically parallel and can be expressed for ***n*** ≥ 5 by equations:

for saturated hydrocarbons

$$b_1 = (-3.79 + 81.667\, n) \cdot 10^{-3}, \qquad (17)$$

for unsaturated hydrocarbons

$$b_2 = (-24.48 + 81.393\, n) \cdot 10^{-3}. \qquad (18)$$

for mercaptans

$$b_3 = (16.50 + 81.151\ n) \cdot 10^{-3}. \qquad (19)$$

As follows from data given in Table 4, beginning with hydrocarbons with 8 carbon atoms, the difference between constant ***b*** for hydrocarbons and mercaptans would be equal to 72.43 · 10^{-3} J/(mol · K), if we would replace $-CH_3$ by –SH. The correction factor given in references is somewhat higher – 104.43 · 10^{-3} J/(mol · K).

This difference is much lower for the first methane homologs; *e.g.*, when ethane is converted to methyl mercaptan this difference is equal to 35.77 · · 10^{-3} J/(mol · K).

The values of heat capacity constant ***c*** decrease in consecutive order with an increase in the number of carbon atoms present in the compounds investigated (Table 5). Only up to the number of 5 carbon atoms do the values not coincide. The values of heat capacity constant ***c*** for compounds having more than 5 carbon atoms can be expressed by the following linear equations:

For saturated hydrocarbons,

$$c_1 = (20.46–29.91\ n) \cdot 10^{-6}, \qquad (20)$$

for unsaturated hydrocarbons

$$c_2 = (8.99–29.72\ n) \cdot 10^{-6}, \qquad (21)$$

and for mercaptans

$$c_3 = (28.29–29.83\ n) \cdot 10^{-6}. \qquad (22)$$

As the negative equation angle coefficient shows, the values of the heat capacity constant *c* decrease with an increase in the number of carbon atoms present in the molecule.

The close values are a proof that the dependency lines are almost parallel. In addition, the free coefficient values differ also very little. The difference in heat capacity of saturated hydrocarbons and mercaptans when $-CH_3$ group is replaced by –SH group increases the ***c*** value on the average by 38.79 · 10^{-6} J/(mol · K).

As may be inferred from the data presented in reference [2], the values of heat capacity for mercaptans increase rather considerably with temperature, and it is believed that the simple equation (1) is apparently lacking sufficient accuracy over a more wider temperature interval. Hence, we made some attempts to calculate the heat capacity constants ***a***, ***b*** and ***c*** for mercaptans at various temperature intervals. The data of these calculations are presented in Table 5.

As follows from Table 5, actually constants of heat capacity differ substantially. Consenquently, when calculations of heat capacity are preformed at given temperatures, it is essential that the heat capacity constant be chosen for an appropriate, rather narrow temperature interval.

Table 5. **Constants of molar heat capacity expressed by equation $C_p = a + bT + cT^2$ calculated for mercaptans at various temperature intervals, J/(mol · K)**

Formula	a	b · 10^3	c · 10^6	Temperature interval
CH_4S	22.46	100.8	–25.0	300–500
	18.66	117.9	–44.0	400–600
	19.26	115.7	–42.0	500–700
	22.20	106.6	–35	600–800
	23.88	102.1	–32	700–900
	28.92	90.2	–25	800–1000
C_2H_6S	18.17	205.67	–76.1	300–500
	33.34	173.3	–90	400–600
	18.49	206.75	–79.5	500–700
	23.95	189.85	–66.5	600–800
	29.27	175.6	–57	700–900
	38.63	153.5	–44	800–1000
C_3H_8S	31.29	238.85	–85.5	300–500
	15.32	298.5	–113	400–600
	17.12	291.9	–107	500–700
	25.1	267.0	–88	600–800
	32.38	247.7	–75	700–900
	36.7	237.5	–69	800–1000
$C_4H_{10}S$	36.13	304.45	–96.5	300–500
	16.65	378.6	–136	400–600
	17.4	375.85	–133.5	500–700
	27.48	344.65	–109.5	600–800
$C_5H_{12}S$	26.41	422.25	–123.5	300–500
	14.71	474.9	–182	400–600
	19.51	457.3	–166	600–800
	29.57	426.1	–142	600–800
	45.83	382.6	–113	700–900
	42.95	389.4	–117	800–1000
$C_6H_{14}S$	50.01	403.3	–42	300–500
	13.61	567.1	–224	400–600
	20.51	541.8	–201	500–700
	32.9	503.45	–171.5	600–800
	52.78	450.2	–136	700–900
	52.42	451.05	–136.5	800–1000
$C_7H_{16}S$	29.05	584.55	–182.5	300–500
	11.65	662.85	–269.5	400–600
	22.60	622.50	–233	500–700
	35.41	583.05	–202.5	600–800
	59.49	518.55	–159.5	700–900
	61.65	513.45	–156.5	800–1000

4. Changes of entropy and enthalpy with temperature

Some materials transform from solid to liquid or gaseous state with an increase in temperature, also a solid material allotropy modification can occur. The thermodynamic parameters of materials can change due to that. It is necessary to take this into account [10] when any thermodynamic function changes are calculated for different temperatures. As can be seen from Table 1 and Fig. 2, the entropy values increase in consecutive order with an increase in temperature and number present in the molecule. In addition, for all hydrocarbons and mercaptans the higher is the number of carbon atoms present in the molecule, the more rapid is the increase of entropy value with increase in temperature.

Other dependencies were noted when changes in hydrocarbon and mercaptan ethalpy values were investigated.

As can be seen from Fig. 3, the formation enthalpy values for saturated hydrocarbons increase regularly with an increase in temperature. However, this value for mercaptans suddenly decreases in a 700–800 K temperature interval. For methyl mercaptan this loop ranges up to about 57.4 kJ/mol and is greater the higher is the mercaptan molecular mass. The difference for mercaptans with 20 carbon atoms reaches 64.5 kJ/mol.

Besides, the mercaptan enthalpy values almost do not change in the 800–1000 K temperature interval. This phenomenon can be attributed to the use of different sulfur standard states for calculation of formation enthalpy in a 700–800 K temperature interval.

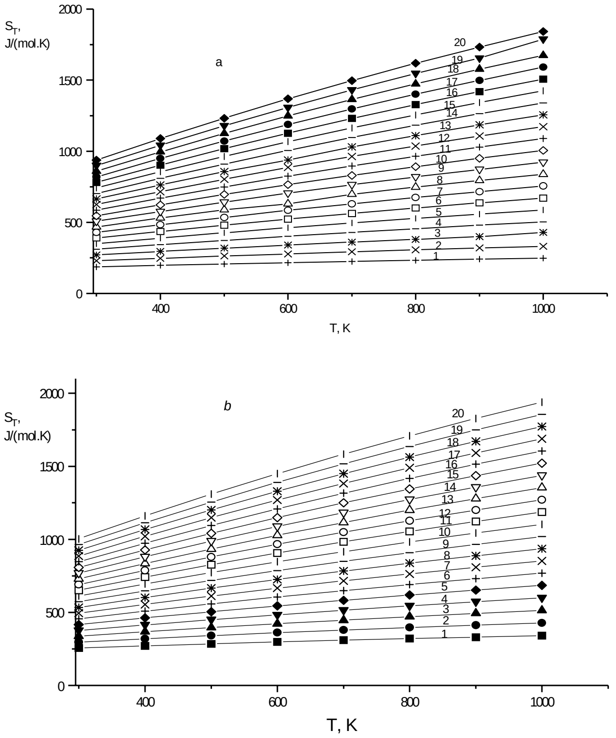

Fig. 2. The entropy dependency on temperature for saturated aliphatic hydrocarbons (*a*) and mercaptans (*b*). The line numeration corresponds to the number of carbon atoms present in the molecule

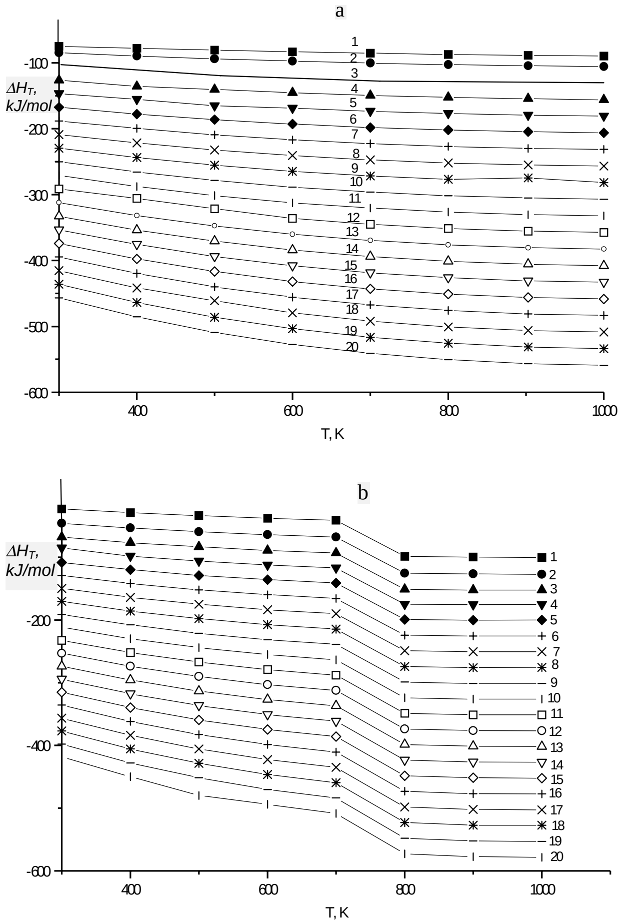

Fig. 3. Dependency of formation ethalpy on temperature for saturated hydrocarbons (*a*) and mercaptans (*b*). The curve numeration corresponds to the number of carbon atoms present in the molecule

Such a sudden decrease of formation enthalpy was also observed for hydrogen sulfide and a number of other sulfur compounds: SCO, CS, SO_2Cl_2, S_2Cl_2 [2]. Such a drop in enthalpy values is also characteristic of other organic sulfides [2]. Therefore, calculations of the Gibbs energy or equilibrium constant for systems with mercaptans should be performed with particular care, especially when selecting a proper temperature interval for enthalpy determination. Unfortunately, no data were found in literature on this conclusion.

CONCLUSIONS

1. A comparison of formation enthalpy, entropy and molar heat capacity dependency on temperature and on the number of carbon atoms present in the molecule for saturated and unsaturated hydrocarbons as well as for mercaptans was conducted using reference data.

2. It was determined that the standard entropy values for all these compounds increased linearly

with an increase in the number of carbon atoms present in the molecule and an increase of one carbon atom in the molecule causes an increase in entropy values on the average by 39.97 J/(mol · K).

3. It was found that formation enthalpy values for saturated and unsaturated hydrocarbons as well as mercaptan decrease linearly with an increase in the number of carbon atoms present in the molecule. This dependency can be expressed by parallel curves and an increase by one carbon atom decreases the compound enthalpy values by 20.6 kJ/mol.

4. It was determined that the values of the molar heat capacity for saturated and unsaturated hydrocarbons as well as mercaptans increase linearly with an increase in the number of carbon atoms present in the molecule. The linear dependences of constants of heat capacity a, b and c on the number of carbon atoms present in the molecule were also determined.

5. It was shown that suitable constants of heat capacity a, b and c must be used in an appropriate narrow temperature interval.

6. It was demonstrated that the formation enthalpy of mercaptans suddenly decreased in a 700–800 K temperature interval. Therefore, we propose that particular care should be taken to use proper temperature intervals when thermodynamic properties are determined, especially when reactions with sulfur compounds are investigated.

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ANGLIAVANDENILIŲ IR TIOLIŲ TERMODINAMINIŲ FUNKCIJŲ VERČIŲ PALYGINIMAS

Santrauka

Pateiktos angliavandenilių bei tiolių susidarymo entalpijų, entropijų, molinės šilumos ir molinės šilumos koeficientų verčių priklausomybės nuo anglies atomų skaičiaus molekulėje empirinės formulės. Parodyta, kad literatūroje pateikta formulė molinės šilumos koeficientų vertėms, esant skirtingoms temperatūroms, apskaičiuoti priklauso nuo pasirinktos temperatūros verčių. Kadangi sieros vandenilio ir organinių sieros junginių susidarymo entalpijų vertės staigiai sumažėja 700–800 K temperatūrų intervale, apskaičiuojant reakcijų, kuriose dalyvauja šie junginiai, Gibso energiją ir pusiausvyros konstantų vertes, būtina naudotis iš anksto nustatytomis šių junginių entalpijų ir entropijų vertėmis esant atitinkamoms temperatūroms.