

## EVALUATION OF THE CHEMICAL EXERGY OF FUELS AND PETROLEUM FRACTIONS

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### Abstract

A correlation formula to estimate chemical exergies of oil fractions and fuel mixtures from enthalpy of combustion and atomic composition is developed. Heat capacity of a mixture of 10 hydrocarbons was measured in the range 5–290 K. It was shown that contribution of entropy of mixing to exergy of typical oil fractions is about –0.11% in the approximation of ideal solution, and about –0.18% for a real solution.

**Keywords:** chemical exergy of fuels, chemical exergy of petroleum fractions

### Introduction

Chemical exergy of a substance is the maximal possible useful work that may be produced by process of physical and chemical equilibration of the substance with the ambient. Chemical exergy at  $P=P_0$  is expressed through thermodynamic characteristics of devaluation process [1] as

$$E_0 = -\Delta_{\text{deval}} H^0 + T_0 \Delta_{\text{deval}} S^0 \quad (1)$$

To evaluate the chemical exergy of a mixture, the knowledge of its enthalpy of combustion, elemental composition and absolute entropy is necessary. When some of these data are absent, the methods of estimation of energy are used.

If the heat of combustion only is known, the Rant's equation [2] gives

$$E_0 = -0.975 \Delta_c H^0 \quad (2)$$

If the elemental composition is also known, the Szargut's correlation formula [3] can be applied:

$$-E_0 / \Delta_c H^0 = a + b[H]/[C] + c[O]/[C] + \dots \quad (3)$$

where  $[A]/[B]$  are atomic ratios of different chemical elements in the mixture.

If the molecular composition is available, the chemical energy of a mixture can be calculated basing on thermodynamic functions of individual components in the approximation of the ideal solution.

The aim of the present study is

1. To re-evaluate the parameters  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$  of Eq. (3),
2. To estimate the magnitude of the ideal-solution mixing term in exergies of fuels, and
3. To estimate the influence of non-ideality of hydrocarbon mixtures on their chemical exergy.

### Correlation formula

We have restricted our investigations by C, H, O, N, S elements which are the most important for fuel mixtures. Formula (3) was taken in form

$$-E_0/\Delta_c H^0 = a + b[H]/[C] + c[O]/[C] + d[N]/[C] + e[S]/[C] \quad (4)$$

The entropy of mixing was neglected in this consideration. Thus, the exergy of a mixture was assumed to be a sum of the exergies of the pure components. Exergies of individual substances were calculated basing on their enthalpies of formation and absolute entropies and parameters of the 'standard thermochemical ambient' [4]. Thermodynamic data for 1176 liquid substances, including 485 hydrocarbons, 510 oxygen compounds, 51 nitrogen compounds, 7 N,O-compounds, and 123 sulfur compounds [5, 6] were used to derive coefficients of Eq. (4). Chemical energies of those compounds are stored in a special computer database developed in our Laboratory. Resulting values of the parameters  $a$  to  $e$  are given in Table 1.

Deviations of the chemical exergy values estimated by Eq. (4) from exergies of individual substances and mixtures neglecting mixing do not exceed 0.8 in general and 0.1% for hydrocarbons.

**Table 1** Parameters of correlation formula (4)

Parameter	Value [3]	Value (this work)
$a$	1.0374	1.02034
$b$	0.0159	-0.01381
$c$	0.0567	0.03374
$d$	-	0.02593
$e$	-	-0.08408

### Ideal-solution mixing term

Molecular compositions of fractions of Belarussian oils from Retchitza and Ostashkovitchi boiling in the range (28–50°C) are known [7] (Table 2). Basing on their compositions, we have calculated the entropies of those fractions in the approximation of ideal solution. Contributions of the entropies of mixing to the chemical exergies (ideal-solution mixing terms, IMT) for each fraction have been evaluated, as well.

The ideal-solution mixing term constitutes  $-0.11 \pm 0.02\%$  of the total value of the chemical energy in case of the selected fractions.

**Table 2** Chemical composition (mass%) and chemical exergies of (28–50°C) fractions from Belarussian oils [7]

	Retchitza		Ostashkovitchi	
	Well 36	Well 42	Well 2	Well 30
<i>i</i> -Butane	1.02	0.12	0.72	0.68
<i>n</i> -Butane	3.82	1.54	3.54	4.75
<i>i</i> -Pentane	32.81	26.91	21.03	37.21
<i>n</i> -Pentane	47.21	41.54	29.47	41.83
2,2-Dimethylbutane	0.02	0.60	0.70	0.08
2,3-Dimethylbutane	3.72	2.57	2.61	4.62
Cyclopentane	4.36	2.95	2.23	5.38
2-Methylpentane	6.02	14.13	15.86	5.01
3-Methylpentane	0.42	5.21	7.18	0.35
<i>n</i> -Hexane	0.08	4.43	16.95	0.09
$\sum x_i E_i / \text{kJ mol}^{-1}$	3460.33	3480.87	3476.50	3476.54
<i>IMT</i> / $\text{kJ mol}^{-1}$	-3.33	-3.81	-4.43	-3.44
$E_0$ (ideal mixture) / $\text{kJ mol}^{-1}$	3457.00	3477.06	3472.07	3473.10

### Influence of non-ideality

To study the influence of non-ideality on chemical exergies of hydrocarbon mixtures, a model mixture has been prepared according to Table 3. The average molar mass of the model mixture is  $102.7287 \text{ g mol}^{-1}$ .

**Table 3** Composition of the model hydrocarbon mixture

Compound	Mass/g	<i>n</i> /mol	Mole fraction
Hexane	0.57503	0.006673	0.105300
Cyclohexane	0.70466	0.008373	0.132128
Benzene	0.83355	0.010671	0.168397
Toluene	0.72522	0.007871	0.124208
Heptane	0.64411	0.006428	0.101439
<i>i</i> -Octane	0.58369	0.005110	0.080636
Octane	0.56761	0.004969	0.078414
Nonane	0.62566	0.004878	0.076981
Decane	0.63111	0.004436	0.069996
Undecane	0.61909	0.003961	0.062502

The entropy of that mixture was derived from experimental values of heat capacity. The heat capacity of the mixture was measured with an adiabatic calorimeter [8, 9] in the temperature range 5–300 K. Uncertainty of the measurements is about 2% at the temperature of liquid helium, about 1% in the range 10–20 K and less than 0.4% above 40 K. The experimental values of the heat capacity are given in Table 4. To explore deviation of the studied mixture from ideal solution behavior we calculated its heat capacity in the ‘ideal solution – pure crystals’ approximation. In the calculation we assumed that the components do not form solid solutions, and the liquid phase is an ideal solution. The heat capacity of the system was derived by numeric differentiation of its enthalpy:

$$C_p = [H(T_2) - H(T_1)] / \Delta T \quad (5)$$

where  $\Delta T$  was 0.2 K. Enthalpy of the system was calculated basing on thermodynamic functions of individual components [5] according to the accepted approximation:

$$H(T) = \sum n_i(\text{cr}) H_i(\text{cr}) + \sum n_i(\text{liq}) H_i(\text{liq}) \quad (6)$$

where  $n_i(\text{cr})$  and  $n_i(\text{liq})$  are amounts of  $i$ -th component of the mixture in the crystal and liquid phases, respectively, at temperature  $T$ .  $H_i(\text{cr})$  and  $H_i(\text{liq})$  are enthalpies of  $i$ -th component in the crystal and liquid state at temperature  $T$ . Composition of the liquid phase in the heterogeneous region was determined by a well known expression for solubility of crystalline substances in the ideal solution:

$$\ln(x_i) = [G_i^0(\text{cr}) - G_i^0(\text{liq})] / RT \quad (7)$$

The liquid phase appeared at the lowest temperature where sum of solubilities of all 10 components reached 1. The amount of the liquid phase was determined by a following algorithm. Ratios of total amounts  $n_i$  to solubilities  $x_i$  were calculated for all the components. A component with the lowest ratio  $n_i/x_i$  dissolved completely at a considered temperature. Amounts of all other components in the liquid phase were calculated basing on the total amount of the dissolved component in the mixture  $n_{\min}$  and solubilities in the ideal mixture:

$$n_i(\text{liq}) = n_{\min} x_i / (1 - \sum x_{i \neq \min}) \quad (8)$$

After that it was checked whether amount of any dissolved compound  $n_i(\text{liq})$  exceeds a total amount  $n_i$ . If so, the according component was completely dissolved at the given temperature. In that case amounts of partially dissolved substances were re-calculated taking into account the amounts of the completely dissolved compounds  $n_m$ :

$$n_i(\text{liq}) = \sum n_m x_i / (1 - \sum x_{i \neq m}) \quad (9)$$

and the checking procedure was repeated. Negative result of the checking showed that the final result is achieved.

Experimental values of the heat capacity of the mixture are compared to the calculated ones in Fig. 1. In spite of different numbers of peaks in the heterogeneous re-

**Table 4** Experimental values of the heat capacity of the hydrocarbon mixture

<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$
Series 1			Series 2			Series 3		
4.73	2.837	0.2915	100.12	929.6	95.49	90.71	840.4	86.33
5.11	4.847	0.4979	102.36	936.8	96.23	93.15	867.6	89.13
5.51	6.112	0.6279	104.56	952.5	97.85	95.52	884.9	90.90
5.87	7.106	0.7300	106.72	989.0	101.6	97.83	909.6	93.44
6.25	8.541	0.8774	108.84	1015	104.2	100.09	931.8	95.72
6.66	10.14	1.041	110.94	1037	106.5	102.34	933.8	95.93
7.02	11.95	1.227	113.01	1081	111.0	104.56	956.2	98.23
7.35	13.40	1.376	115.09	1104	113.4	106.73	984.6	101.1
7.66	14.90	1.530	117.17	1110	114.0	108.87	1012	103.9
8.04	17.35	1.782	121.34	1095	112.5	110.98	1048	107.7
8.50	19.80	2.034	123.46	1116	114.6	113.06	1092	112.1
8.91	22.35	2.296	125.53	1154	118.6	115.16	1084	111.4
9.39	25.69	2.639	127.56	1192	122.4	117.27	1090	112.0
9.94	29.78	3.059	129.61	1210	124.3	119.39	1091	112.1
10.44	33.18	3.408	131.82	1067	109.6	121.52	1091	112.1
11.02	38.45	3.950	134.07	1044	107.2	123.63	1104	113.4
11.68	44.67	4.589	136.04	1199	123.2	125.70	1162	119.4
12.27	49.82	5.118	137.84	1329	136.5	127.79	1227	126.0
13.03	55.79	5.731	139.53	1566	160.9	129.82	1189	122.2
13.76	62.75	6.446	141.08	2089	214.6	132.05	1053	108.1
14.42	70.29	7.221	142.35	3383	347.5	134.30	1098	112.8

**Table 4** Continued

<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$
Series 1			Series 2			Series 3		
15.03	76.15	7.823	143.29	5907	606.8	136.23	1208	124.1
15.68	83.74	8.603	144.06	7186	738.2	138.03	1346	138.3
16.39	91.69	9.420	144.95	3697	379.7	139.71	1615	166.0
17.14	101.0	10.38	146.06	3008	309.0	141.25	2183	224.2
18.08	111.2	11.42	147.19	3405	349.8	142.48	3620	371.8
19.09	123.8	12.72	148.24	3775	387.8	143.16	3598	369.6
20.00	136.4	14.01	149.22	4190	430.5	143.41	4242	435.8
21.07	149.3	15.34	150.13	4504	462.7	143.65	4543	466.7
22.29	165.6	17.01	151.00	4579	470.4	143.88	5271	541.5
23.40	179.6	18.45	151.86	4479	460.1	144.08	6013	617.7
24.84	198.0	20.34	152.75	4340	445.8	144.26	6850	703.7
26.58	218.4	22.43	153.67	4117	422.9	144.43	7381	758.3
28.13	238.4	24.49	154.65	3368	346.0	144.59	7523	772.9
29.79	261.9	26.91	155.78	2402	246.8	144.76	6531	670.9
31.89	289.3	29.72	157.00	2443	251.0	144.98	3542	363.9
34.06	313.5	32.20	158.21	2516	258.4	145.16	2351	241.6
36.03	339.1	34.84	159.56	2606	267.7	145.24	2421	248.7
37.82	358.2	36.80	161.12	2270	233.2	145.33	2337	240.1
39.48	376.3	38.65	162.76	2150	220.9	145.42	2031	208.6
41.24	394.5	40.52	164.40	2258	231.9	145.50	2392	245.7
43.11	415.6	42.69	166.02	2350	241.4	145.58	2580	265.0

**Table 4** Continued

<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	<i>T</i> /K	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$
Series 1			Series 2			Series 3		
45.31	437.4	44.93	167.59	2477	254.5	145.77	2683	275.6
47.81	462.7	47.53	169.12	2590	266.0	146.07	2797	287.3
50.10	486.0	49.92	170.62	2735	280.9	146.58	3048	313.1
52.24	506.2	52.00	172.07	2873	295.2	147.47	3411	350.4
54.67	528.3	54.27	173.47	2986	306.8	148.48	3817	392.1
57.38	555.2	57.04	174.84	3067	315.0	149.42	4252	436.8
59.91	579.0	59.48	176.20	3122	320.7	150.31	4544	466.8
62.30	599.1	61.55	177.54	3139	322.4	151.17	4569	469.4
64.79	617.6	63.44	178.88	3137	322.3	151.91	4429	455.0
67.36	638.7	65.62	180.40	3017	309.9	152.56	4327	444.5
69.82	658.0	67.60	182.20	2669	274.2	153.34	4248	436.4
72.17	675.8	69.43	184.08	2588	265.9	154.28	3734	383.6
74.43	694.7	71.37	185.97	2643	271.5	155.34	2566	263.6
79.30	729.1	74.90	187.82	2756	283.1	156.55	2423	248.9
82.16	749.1	76.95	189.62	2920	299.9	157.76	2488	255.6
84.91	771.0	79.20	191.38	3063	314.7	158.96	2561	263.1
87.56	795.8	81.75	193.09	3243	333.2	160.14	2569	263.9
90.10	837.3	86.02	194.71	3465	355.9	161.36	2153	221.1
92.56	869.0	89.28	196.27	3689	379.0	162.65	2139	219.7
94.95	888.6	91.29	197.78	3939	404.6	163.93	2212	227.2
97.61	913.6	93.85	199.23	4205	432.0	165.31	2289	235.2
100.54	938.4	96.40	200.63	4473	459.5	166.71	2393	245.9

**Table 4** Continued

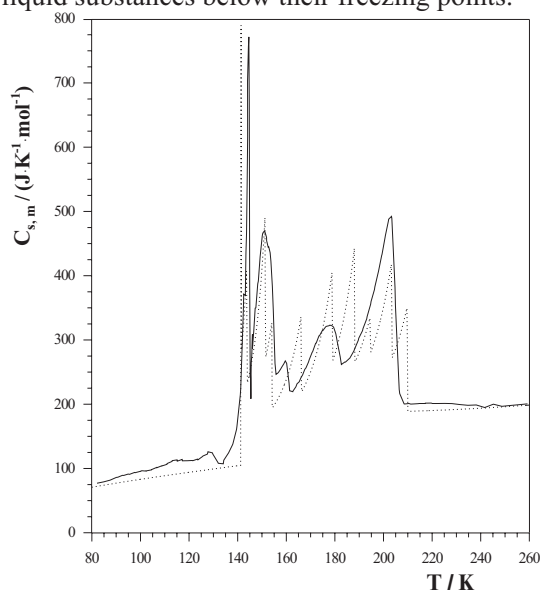
<i>T</i> /K	$C_s/$ J K <sup>-1</sup> kg <sup>-1</sup>	$C_s/$ J K <sup>-1</sup> mol <sup>-1</sup>	<i>T</i> /K	$C_s/$ J K <sup>-1</sup> kg <sup>-1</sup>	$C_s/$ J K <sup>-1</sup> mol <sup>-1</sup>	<i>T</i> /K	$C_s/$ J K <sup>-1</sup> kg <sup>-1</sup>	$C_s/$ J K <sup>-1</sup> mol <sup>-1</sup>
Series 1			Series 2			Series 3		
			201.98	4724	485.3	168.09	2500	256.8
			203.30	4798	492.9	169.43	2624	269.6
			204.73	3720	382.2	170.83	2745	282.0
			206.45	2172	223.1	172.27	2874	295.3
			208.44	1954	200.7	173.67	2987	306.9
			210.46	1959	201.2	175.04	3065	314.9
			212.48	1953	200.6	176.47	3129	321.5
			214.72	1959	201.2	177.98	3148	323.4
			217.17	1965	201.8	179.48	3118	320.3
			219.62	1966	202.0	181.02	2887	296.6
			222.30	1959	201.2	182.69	2552	262.1
			225.22	1961	201.4	184.38	2587	265.8
			228.12	1957	201.1	186.17	2648	272.0
			231.28	1944	199.7	188.04	2781	285.7
			234.71	1932	198.4	189.83	2949	302.9
			238.13	1937	199.0	191.57	3098	318.2
			241.63	1898	195.0	193.26	3280	336.9
			245.17	1949	200.2	194.87	3507	360.3
			248.67	1916	196.9	196.43	3727	382.9
			252.18	1929	198.2	197.92	3966	407.4
			255.70	1941	199.4	199.37	4221	433.6



**Table 4** Continued

$T/K$	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	$T/K$	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$	$T/K$	$C_s/$ $J K^{-1} kg^{-1}$	$C_s/$ $J K^{-1} mol^{-1}$
Series 1			Series 2			Series 3		
			259.20	1954	200.7	200.77	4504	462.7
			262.76	1966	202.0	202.11	4756	488.6
			266.25	1971	202.5	203.44	4767	489.7
			269.73	1989	204.3	204.91	3444	353.8
			273.22	1996	205.1	206.68	2110	216.8
			276.40	1989	204.3	208.68	1951	200.5
			279.85	2021	207.6	211.20	1950	200.3
			283.27	2038	209.4	214.18	1956	201.0
			286.67	2049	210.4	217.15	1959	201.3
			290.45	2066	212.2	220.11	1960	201.3

gion, the experimental (142–205 K) and calculated (141.3–209.8 K) temperature ranges of melting of the mixture between fusion of the eutectics and dissolving of the last portion of the crystal are in reasonable accordance. Anomalies of heat capacity of the solid phase at 110 and 130 K indicate probable presence of solid solutions that may cause existence of the residual entropy at  $T=0$  K. However, the fact of a restricted mutual solubility in the solid state even of hydrocarbons with a close molecular structure [10] allows to suppose that the value of  $S(0\text{ K})$  for our system is small. Deviation of the experimental heat capacity of the liquid from the calculated one in the range 210–240 K may be caused by non-ideality or by error in extrapolation of heat capacities of liquid substances below their freezing points.



**Fig. 1** Heat capacity of the hydrocarbon mixture; — experimental data; ..... calculated

The entropy of the model mixture at  $T=298.15$  K was calculated assuming zero residual entropy at  $T=0$  K. It constitutes  $321.9 \pm 1.6 \text{ J K}^{-1} \text{ mol}^{-1}$ , whereas the entropy of ideal solution should be  $310.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . The entropy of mixing at  $T=298.15$  K is  $30.1 \text{ J K}^{-1} \text{ mol}^{-1}$  from which  $11.3 \text{ J K}^{-1} \text{ mol}^{-1}$  is the excess entropy of the mixture.

The chemical energy of the model mixture with different approximations has been calculated basing on the enthalpies of combustion of the individual components (Table 5).

**Table 5** Chemical energy of the studied mixture at  $T=298.15$  K in different approximations

Approximation	$E_0/\text{kJ mol}^{-1}$	$E_0/\text{kJ kg}^{-1}$
Neglecting of mixing	4728.2	46026
With IMT	4722.5	45971
Based on the experimental entropy	4719.1	45938

In a case of the model hydrocarbon mixture the excess entropy contribution to the chemical energy is about 60% of the ideal mixing term, or  $-0.07\%$  of the total chemical energy.

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