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THERMODYNAMIC EVALUATION OF COAL REACTIVITY

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ABSTRACT. From empirical formulae for 10 Romanian coals and from their heating values, thermodynamic parameters are evaluated: enthalpies, entropies, heat capacities. With these values, the Gibbs free energies and equilibrium constants for some reactions during coal gasification (including reactions with carbon dioxide, steam, oxygen) are calculated, for temperatures in the 25...1000°C range. The temperature and pressure dependence of the equilibria is discussed by means of zero-affinity plots. Lignites present a much higher thermodynamic reactivity then graphite, that should be exploited in the choice of gasification conditions for coals.

INTRODUCTION

In the study of coal gasification, the reactivity of the coal is a key parameter. Both the kinetic and thermodynamic reactivity are important. Here we try to evaluate the reactivity by means of thermodynamic calculations, i.e., by the calculation of the Gibbs free energy of reaction.

We are concerned here with the reactivity of the *organic coal mass*, i.e., the mass of anhydrous coal less the mineral mass. This latter quantity differs from the ash mass, as a consequence of the processes during heating (water loss from hydrated silicates, the decomposition of carbonates, the combustion of pyrite, volatilization of chlorides). The parameters referred to the organic coal mass can be evaluated from the two phase model of coals [1]. In this way, from the processing of analytical data we determined the empirical formulae of the organic mass, considering the principal elements in their constitution: carbon, hydrogen and oxygen (with neglect of the nitrogen and sulfur content). The higher heating value Q_s^c for the organic mass could also be calculated. The formulae are written as CH_xO_y [2]. These indices are given in Table 1 for 10 coals, on the basis of mean values of the parameters, obtained from representative samples.

Symbols: C_p molar heat capacity under constant pressure; ΔG Gibbs free energy of reaction; H_{298}^o standard enthalpy; ΔH_{298}^o standard enthalpy of reaction;

ΔH_T^o enthalpy of reaction at temperature *T*, under normal pressure; ΔH_{298}^o standard entalphy; K_p equilibrium constant in partial pressures; K_x equilibrium constant in mole fractions; *M* molecular mass; *p* pressure; p_i partial pressure; Q_s^c higher heating value for the organic mass (of the carbonaceous matter); S_{298}^o standard entropy; ΔS_{298}^o standard entropy of reaction; ΔS_T^o entropy of reaction at temperature *T*, under normal pressure; *T* temperature; T_e temperature for zero affinity; *x*, *y* indices for H and O respectively, in the empirical formulae of coals; ν number of moles; $\Delta\nu$ variation of the number of moles .

EXPERIMENTAL

Starting with proximate and ultimate analysis data on coals from different Romanian coal deposits, in a wide range of incarbonisation degrees, ranging from lignites to bituminous coals (Table 1), we get the values for moisture, ash, volatiles, carbon, hydrogen, sulfur, nitrogen and oxygen contents, as well as the lower and higher heating values. These are the basis for our subsequent calculations. The higher heating values for the organic mass Q_s^c (in kJ.kg^{-1}) are given in Table 1.

RESULTS AND DISCUSSION

The calculation of thermodynamic parameters

In order to make thermodynamic calculations for the reactivity of coals, with respect to the reaction participants, the following parameters are used: standard enthalpies of formation, H_{298}^o, standard entropies, S_{298}^o and molar heat capacities under constant pressure C_p. For all the involved substances, other than coals, we used the CODATA Key Values [3]. For molar heat capacities we used the temperature dependence equations:

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

(for methane) and

$$C_p = a + bT + c'/T^2 \quad (2)$$

for all other compounds [4].

For coals, the *enthalpy of formation* corresponding to the empirical formula is calculated from the higher heating value. The standard enthalpy ΔH^o_{298} of the combustion reaction:

$$CH_xO_y + (1+0.25x-0.5y)O_2 = CO_2 + 0,5xH_2O \text{ (i)}$$

is related to the higher heating value of the organic mass Q_s^C by the well- known relation:

$$\Delta H^o_{298} = -MQ_s^c/1000 \quad (3)$$

where Q_s^c is obtained by extrapolation of the higher heating value of the anhydrous coal to zero ash content (instead to maceral phase ash content, since no data on SiO_2 content were available [5]). *M* is the molecular mass of the formula: M = 12+x+16y. These values are also given in Table 1. From the combustion reaction, we can calculate the molar enthalpy of formation for the coal:

$$H^o_{298}(c) = H^o_{298}(CO_2) + 0.5x\, H^o_{298}(H_2O,l) - H^o_{298} \quad (4)$$

We use the enthalpy of liquid water, since we deal with the upper heating value of coals. The calculated values are given in Table 1; for all the 10 coals the values are negative: the formation of the coals from elements is exothermal, but for bituminous coals the values are only slightly negative.

Table 1.

Composition and thermodynamic characteristics of some coals

No.	Coal	x= H/C	y= O/C	Q_s^C (kJ.kg^{-1})	H_{298}^o (kJ.mol^{-1})	H_{298}^o(c) (kJ. mol^{-1})	C_p (J. mol^{-1}K^{-1})	S_{298}^o(C) (J. mol^{-1}K^{-1})
1	Anina bituminous coal	0.66	0.09	34560	-487.29	-0.54	15.41	18.49
2	Lupeni bituminous coal	0.81	0.14	33660	-506.89	-2.38	17.69	21.23
3	Lonea soft coal	0.91	0.21	31800	-517.61	-5.96	19.82	23.79
4	Țebea brown coal	0.99	0.27	30460	-527.51	-7.49	21.60	25.92
5	Comăneşti brown coal	0.91	0.27	28640	-493.62	-29.95	20.83	25.00
6	Rovinari lignite	1.00	0.33	27500	-502.74	-33.69	22.70	27.24
7	Ceptura lignite	1.00	0.38	26200	-500.38	-36.05	23.54	28.25
8	Ojasca lignite	1.07	0.35	27030	-504.71	-41.72	23.71	28.45
9	Câmpulung lignite	0.96	0.30	27680	-491.78	-38.93	21.82	26.18
10	Căpeni-Vârghiş lignite	1.02	0.41	25620	-501.85	-37.44	24.24	29.09

The *standard entropy* S^o_{298} for the coals, as well as the *molar heat capacity* C_p cannot be exactly calculated for complex solid substances such as coal. Values for specific heats can be estimated from Neumann and Kopp-like formulas, such as that proposed by Szadeczky [6], with increments for solids [7-9]. For molar heat capacities (formula CH_xO_y), we find:

$$C_p = 7.56 + 9.6\,x + 16.8\,y\ [\text{J.mol}^{-1}\text{K}^{-1}] \tag{5}$$

The values calculated by this formula are given in Table 1.

The standard entropy can be estimated for organic solids from the Strelkov formula [10]:

$$S^o_{298} = 1.1\ C_p \tag{6}$$

We found it better to use a higher value for the proportionality factor, viz. 1.2 [8,9] and obtained the values given in Table 1. These values are a reasonable good approximation for the entropies, since the reactions that will be considered here show considerable entropy variations, mainly due to gas formation or consumption.

In order to calculate the free energy of reaction at different temperature, we have to calculate the enthalpies and the entropies at these temperatures for all the substances undergoing the reaction. For all the substances except the coals, enthalpies and entropies were exactly calculated:

$$H_T^0 = H_{298}^0 + \int_{298}^{T} C_p dT; \quad S_T^0 = S_{298}^0 + \int_{298}^{T} \frac{C_p}{T} dT; \qquad (7)$$

with the formulae given above for the temperature dependence of C_p. For the coals, the C_p values were assumed to be constant (Table 1).

The Gibbs free energy of reaction for coal gasification

Some basic reactions during coal gasification are:

- Complete combustion (i); its reaction enthalpy is of course negative, the volume variation being determined by the variation of the number of moles of gases, $\Delta\nu$. This is zero for graphite, but positive for coals:

$$\Delta\nu = 0.25x+0.5y \qquad (8)$$

and increasing with the hydrogen, and still more, with the oxygen content.

- The Boudouard reaction (gasification with carbon dioxide):

$$CH_xO_y(s) + (1\text{-}y)CO_2(g) = (2\text{-}y)CO(g) + 0.5x\ H_2(g) \quad (ii)$$

is endothermic under standard conditions and shows a positive volume variation: $\Delta\nu = 1 + 0.5\ x$

- A second Boudouard-like reaction could be written for coals:

$$CH_xO_y(s) + (1\text{-}y+0.5x)CO_2(g) = (2\text{-}y+0.5x)CO(g) + 0.5x\ H_2O(g) \quad (iii)$$

It is also endothermic at room temperature and with the same volume variation as the previous one.

- The gasification with steam to give H_2 and CO:

$$CH_xO_y(s) + (1\text{-}y)H_2O(g) = CO(g) + (1+0.5x\text{-}y)\ H_2(g) \quad (iv)$$

is also an endothermic reaction, with a volume increase: $\Delta\nu = 1 + 0.5\ x$

- The analogous reaction, yielding CO_2:

$$CH_xO_y(s) + (2\text{-}y)H_2O(g) = CO_2\{g) + (2+0.5x\text{-}y)\ H_2(g) \quad (v)$$

shows the same volume variation as the previous one and is also endothermic.

- The coal hydrogenation reaction, with the hydrogen resulted from other reactions:

$$CH_xO_y(s) + (2\text{-}0.5x+y)\ H_2(g) = CH_4(g) + y\ H_2O(g) \quad (vi)$$

is an exothermic reaction, usually with volume decrease: $\Delta\nu = -1+0.5x$.

- The homogeneous reaction of carbon oxide conversion:

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \quad (vii)$$

is slightly exothermic and without variation of volume ($\Delta\nu = 0$).

Of course, not all these reactions are independent; for instance, reaction (iii) is a linear combination of reactions (ii) and (vii) and reaction (v) is simply the sum of reaction (iv) with (vii).

We calculated the molar Gibbs free energies for all these reactions at standard temperature, as well as at temperatures in the range 100 ... 1000°C for the 10 coal types investigated and for graphite:

$$\Delta G_T^o = \Delta H_T^o - T\Delta S_T^o. \tag{9}$$

Since the "molar mass" for coals has a purely conventional meaning, it should be more significant to compare the ΔG-values by referring to the mass unity of coal.

Formulas of organic matter of coal per one carbon atom were successfully used by Stephens [11] to calculate equilibrium gas composition for Wyoming coal gasification as well as by Stephens and Miller [12], but the evaluation of indices for H and O was made in a conventional manner.

Table 2 presents these values for the total combustion of the coal. The ΔG-value for graphite is almost temperature independent (reaction with very little entropy variation, $\Delta\nu = 0$). The values for bituminous coals (1, 2) are more negative than for graphite: the hydrogen content in the fuel increases its heating value. For lignites, the thermal effect is lower than for graphite, a consequence of the higher oxygen content. For the coals, the ΔG value becomes more negative at higher temperatures.

For the Boudouard equilibrium (ii) the free energy is given in Table 3. The values are always lower for coals then for graphite and their temperature variation is less important for lower rank coals. The values for the organic mass of lignites for instance are 4...8 MJ/kg lower than for graphite at the same temperature. Therefore, the zero value of ΔG is reached by coals at significantly lower temperatures as by graphite (with 300...400^{O}C for bituminous coals and with 400-550^{o}C for brown coals and lignites), i.e. their thermodynamic reactivity is higher.

Table 2.

The Gibbs free reaction energy $-\Delta G_T^o$ (MJ.kg^{-1}) for coal combustion (i)

T(^{o}C)	C*	1	2	3	4	5	6	7	8	9	10
25	32.86	34.12	33.22	31.42	30.13	28.36	27.25	26.05	26.76	27.42	25.48
100	32.86	34.27	33.41	31.63	30.36	28.58	27.49	26.29	27.02	27.65	25.73
200	32.90	34.47	33.66	31.92	30.67	28.88	27.81	26.63	27.35	27.06	26.07
300	32.92	34.69	33.92	32.21	30.99	29.19	28.14	26.96	27.70	28.28	26.42
400	32.94	34,91	34.18	32.51	31.32	29.50	28.48	27.31	28.05	28.61	26.77
500	32.95	35,14	34.46	32.82	31.65	29.82	28.83	27.66	28.41	28.94	27.13
600	32.96	35.38	34.74	33.14	31.99	30.15	29.18	28.02	28.77	29.28	27.49
700	32.96	35.63	35.03	33.46	32.34	30.48	29.58	28.38	29.14	29.63	27.86
800	32.96	35.88	35.33	33.79	32.70	30.82	29.90	28.76	29.52	29.98	28.24
900	32.96	36.15	35.64	34.13	33.06	31.17	30.27	29.13	29.91	30.34	28.62
1000	32.96	36.42	35.96	34.48	33.43	31.53	30.65	29.51	30.30	30.71	29.01

C* - graphite

Table 3.

The Gibbs free reaction energy ΔG_T^o (MJ.kg^{-1}) for the Boudouard reaction (ii)

$T(^oC)$	C^*	1	2	3	4	5	6	7	8	9	10
25	10.01	6.08	4.72	3.27	2.11	3.50	2.50	1.78	2.52	3.38	1.36
100	8.90	4.96	3.64	2.25	1.13	2.54	1.57	0.89	1.59	2.43	0.49
200	7.42	3.46	2.17	0.86	-0.19	1.23	0.32	-0.31	0.34	1.15	-0.69
300	5.93	1.93	0.69	-0.54	-1.53	-0.09	-0.95	-1.52	-0.92	-0.14	-1.88
400	4.45	0.40	-0.80	-1.95	-2.89	-1.43	-2.24	-2.75	-2.20	-1.45	-3.08
500	2.97	-1.14	-2.30	-3.37	-4.25	-2.76	-3.53	-3.99	-3.48	-2.77	-4.28
600	1.50	-2.70	-3.82	-4.81	-5.62	-4.12	-4.83	-5.23	-4.78	-4.09	-5.50
700	0.04	-4.26	-5.34	-6.25	-7.00	-5.47	-6.13	-6.48	-6.08	-5.43	-6.72
800	-1.42	-5.83	-6.86	-7.69	-8.38	-6.84	-7.45	-7.74	-7.39	-6.77	-7.96
900	-2.86	-7.40	-8.40	-9.14	-9.77	-8.21	-8.77	-9.00	-8.70	-8.11	-9.19
1000	-4.31	-8.98	-9.93	-10.6	-11.2	-9.58	-10.1	-10.3	-10.0	-9.46	-10.4

C^* - graphite

For the other Boudouard-like reaction (iii), the calculated ΔG values are given in Table 4. Here the temperature dependance is greater than for the previous reaction, so the ΔG values are higher for low temperatures and lower for high temperatures. The higher reactivity of coals as compared with graphite is also clearly seen. At high temperatures, this reaction prevails over reaction (ii).

Table 4.

The Gibbs free reaction energy ΔG_T^o (MJ.kg^{-1}) for the Boudouard reaction (iii)

$T(^oC)$	C^*	1	2	3	4	5	6	7	8	9	10
25	10.01	6.75	5.49	4.07	2.93	4.26	3.28	2.53	3.34	4.16	2.11
100	8.90	5.56	4.32	2.96	1.86	3.21	2.27	1.56	2.32	3.12	1.15
200	7.42	3.96	2.75	1.47	0.42	1.80	0.90	0.25	0.96	1.73	-0.13
300	5.93	2.35	1.17	-0.04	-1.03	0.38	-0.47	-1.06	-0.41	0.33	-1.42
400	4.45	0.72	-0.43	-1.56	-2.49	-1.06	-1.86	-2.39	-1.80	-1.08	-2.71
500	2.97	-0,90	-2.02	-3.08	-3.95	-2.49	-3.24	-3.71	-3.18	-2.48	-4.01
600	1.50	-2.53	-3.63	-4.61	-5.42	-3.93	-4.63	-5.05	-4.57	-3.90	-5.32
700	0.04	-4.17	-5.23	-6.14	-6.89	-5.37	-6.03	-6.38	-5.97	-5.32	-6.62
800	-1.42	-5.82	-6.85	-7.68	-8.37	-6.82	-7.43	-7.72	-7.37	-6.75	-7.94
900	-2.86	-7.46	-8.46	-9.21	-9.84	-8.27	-8.83	-9.06	-8.77	-8.18	-9.25
1000	-4.31	-9.11	-10.1	-10.8	-11.3	-9.73	-10.2	-10.4	-10.2	-9.61	-10.6

C^* - graphite

The trends are analogous for coal gasification with steam (reaction iv), as shown in Table 5. The thermodynamic reactivity of coals versus steam is greater at low temperature in comparison with that versus CO_2; from 800^{o}C on, the trend is inverted. The equilibria (iv) are shifted towards coal gasification at temperatures as low as 100^{o}C for lignite (10) as compared to graphite (about 680^{o}C).

Table 5.

The Gibbs free reaction energy ΔG_T^o (MJ.kg^{-1}) for the reaction (iv)

T(^{o}C)	C*	1	2	3	4	5	6	7	8	9	10
25	7.62	4.23	3.08	1.89	0.91	2.29	1.45	0.85	1.52	2.26	0.50
100	6.78	3.32	2.18	1.01	0.06	1.46	0.64	0.07	0.71	1.43	-0.28
200	5.63	2.07	0.95	-0.18	-1.10	0.32	-0.47	-1.01	-0.40	0.31	-1.33
300	4.46	0.80	-0.32	-1.39	-2.28	-0.84	-1.60	-2.10	-1.54	-0.84	-2.41
400	3.28	-0.50	-1.60	-2.63	-3.47	-2.01	-2.75	-3.20	-2.68	-2.00	-3.50
500	2.10	-1,82	-2.90	-3.88	-4.69	-3.21	-3.91	-4.33	-3.85	-3.18	-4.60
600	0.92	-3.15	-4.22	-5.15	-5.92	-4.41	-5.08	-5.46	-5.02	-4.37	-5.71
700	-0.27	-4.50	-5.55	-6.43	-7.16	-5.63	-6.27	-6.60	-6.21	-5.57	-6.84
800	-1.46	-5.86	-6.89	-7.72	-8.41	-6.86	-7.47	-7.75	-7.40	-6.79	-7.97
900	-2.66	-7.24	-8.25	-9.02	-9.67	-8.10	-8.67	-8.92	-8.61	-8.01	-9.11
1000	-3.85	-8.62	-9.62	-10.3	-10.9	-9.35	-9.89	-10.1	-9.83	-9.24	-10.3

C* - graphite

The steam gasification with formation of CO_2, reaction (v) (Table 6) shows lower ΔG values than reaction (iv) for temperatures below 800^{o}C, i.e. the formation of CO_2 prevails over the formation of CO. The situation changes at higher temperatures. For almost all lignites, the Gibbs free energy of the reaction is negative already at room temperature, thus the reaction is possible from the thermodynamic point of view (although kinetically too slow to be important).

Table 6.

The Gibbs free reaction energy ΔG_T^o (MJ.kg^{-1}) for the reaction (v)

T(^{o}C)	C*	1	2	3	4	5	6	7	8	9	10
25	5.24	2.20	1.18	0.13	-0.74	0.63	-0.11	-0.65	-0.01	0.64	-0.96
100	4.65	1.51	0.49	-0.56	-1.41	-0.02	-0.76	-1.27	-0.66	-0.01	-1.58
200	3.83	0.55	-0.48	-1.50	-2.34	-0.93	-1.65	-2.13	-1.56	-0.90	-2.43
300	2.99	-0.46	-1.49	-2.48	-3.30	-1.86	-2.57	-3.02	-2.48	-1.83	-3.31
400	2.12	-1.50	-2.53	-3.49	-4.28	-2.83	-3.51	-3.94	-3.43	-2.79	-4.21
500	1.23	-2,56	-3.60	-4.53	-5.29	-3.82	-4.48	-4.87	-4.41	-3.77	-5.13
600	0.33	-3.66	-4.69	-5.58	-6.32	-4.82	-5.47	-5.83	-5.40	-4.77	-6.07
700	-0.59	-4.77	-5.80	-6.66	-7.37	-5.85	-6.48	-6.80	-6.41	-5.79	-7.03
800	-1.52	-5.91	-6.94	-7.76	-8.44	-6.90	-7.50	-7.79	-7.44	-6.82	-8.00
900	-2.45	-7.06	-8.09	-8.87	-9.52	-7.95	-8.54	-8.79	-8.48	-7.87	-8.99
1000	-3.39	-8.23	-9.25	-10.0	-10.6	-9.03	-9.59	-9.80	-9.53	-8.93	-9.98

C* - graphite

The coal hydrogenation to methane (vi) presents rather important negative ΔG-values at standard temperature (Table 7). They increase with temperature and become positive for graphite at round 550^{o}C; for coals the values are much lower and still negative at 1000^{o}C. The brown coal (4), followed by lignite (10), present the highest reactivity toward hydrogen.

For the equilibrium (vii), thermodynamic characteristics are known from literature. We considered also some reactions of incomplete combustion of coals, with formation of carbon monoxide and water:

$$CH_xO_y(s) + (0.5+0.25x-0.5y)O_2(g) = CO(g) + 0.5x\ H_2O(g) \quad \text{(viii)}$$

or of carbon monoxide and hydrogen:

$$CH_xO_y(s) + (0.5-0.5y)O_2(g) = CO(g) + 0.5x\ H_2(g) \quad \text{(ix)}$$

Both are reaction with a volume increase: $\Delta\nu$ = 0.5 + 0.25x + 0.5y (viii) and $\Delta\nu$ = 0.5 + 0.5x + 0.5y (ix) respectively. We compared their Gibbs free energies (ΔG) in Table 8 and 9 with those of carbon monoxide formation from elements:

$$C(graphite) + 0.5\ O_2(g) = CO(g)$$

Table 7.

The Gibbs free reaction energy ΔG_T^o (MJ.kg^{-1}) for coal hydrogenation (vi)

T(^{o}C)	C*	1	2	3	4	5	6	7	8	9	10
25	-4.23	-5.86	-6.37	-6.86	-7.31	-5.97	-6.33	-6.60	-6.10	-5.75	-6.77
100	-3.71	-5.60	-6.18	-6.72	-7.21	-5.84	-6.24	-6.53	-6.03	-5.65	-6.70
200	-2.95	-5.22	-5.89	-6.50	-7.04	-5.65	-6.10	-6.40	-5.91	-5.48	-6.59
300	-2.14	-4.82	-5.57	-6.26	-6.85	-5.43	-5.93	-6.25	-5.77	-5.29	-6.45
400	-1.29	-4.39	-5.25	-6.00	-6.64	-5.20	-5.75	-6.08	-5.62	-5.09	-6.30
500	-0.42	-3,96	-4.91	-5.74	-6.43	-4.96	-5.56	-5.91	-5.47	-4.88	-6.14
600	0.47	-3.53	-4.57	-5.48	-6.22	-4.72	-5.38	-5.74	-5.31	-4.67	-5.98
700	1.38	-3.10	-4.23	-5.21	-6.01	-4.48	-5.19	-5.56	-5.15	-4.46	-5.83
800	2.29	-2.67	-3.90	-4.95	-5.80	-4.25	-5.00	-5.39	-4.99	-4.25	-5.67
900	3.21	-2.25	-3.57	-4.70	-5.60	-4.01	-4.82	-5.23	-4.84	-4.05	-5.52
1000	4.13	-1.83	-3.25	-4.45	-5.40	-3.79	-4.65	-5.07	-4.70	-3.85	-5.37

C* - graphite

Both reactions are exothermal, with ΔG-values becoming more negative with increasing temperature. In the first reaction (viii), coals present more negative ΔG-values than graphite, especially bituminous and brown coals, while for lignites the values get near those for graphite. In the second reaction (ix) the standard ΔG-values are above those for graphite, and their temperature dependence is more pronounced, so that at high temperature, the values for bituminous coals go below those for graphite.

Table 8.

Gibbs free reaction energy -ΔG_T^o (MJ.kg^{-1}) for incomplete coal combustion (viii)

T(^{o}C)	C*	1	2	3	4	5	6	7	8	9	10
25	11.43	15.87	16.13	15.61	15.27	13.43	13.18	12.57	12.99	12.93	12.34
100	11.99	16.49	16.75	16.22	15.88	14.03	13.77	13.15	13.59	13.53	12.93
200	12.74	17.31	17.58	17.05	16.70	14.84	14.58	13.95	14.39	14.34	13.72
300	13.49	18.15	18.42	17.88	17.52	15.66	15.39	14.74	15.21	15.15	14.51
400	14.24	19,00	19.28	18.72	18.36	16.48	16.21	15.55	16.03	15.97	15.31
500	14.99	19,85	20.14	19.57	19.20	17.31	17.03	16.36	16.86	16.80	16.12
600	15.72	20.71	21.00	20.43	20.05	18.15	17.87	17.18	17.70	17.64	16.93
700	16.94	21.58	21.88	21.29	20.90	18.99	18.70	18.00	18.54	18.48	17.75
800	17.19	22.46	22.75	22.16	21.76	19.84	19.54	18.83	19.38	19.32	18.57
900	17.91	23.34	23.64	23.03	22.62	20.69	20.39	19.66	20.23	20.17	19.40
1000	18.63	24.23	24.53	23.91	23.49	21.55	21.24	20.50	21.09	21.03	20.23

C* - graphite

Table 9.

The Gibbs free reaction energy -ΔG_T^o (MJ.kg^{-1}) for incomplete coal combustion (ix)

T(^{o}C)	C*	1	2	3	4	5	6	7	8	9	10
25	11.43	10.52	9.98	9.21	8.73	7.39	6.92	6.57	6.44	6.75	6.39
100	11.99	11.22	19.69	9.92	9.44	8.08	7.61	7.25	7.13	7.45	7.06
200	12.74	12.15	11.65	10.88	10.39	9.02	8.55	8.17	8.08	8.38	7.97
300	13.49	13.11	12.63	11.85	11.36	9.97	9.50	9.10	9.04	9.33	8.90
400	14.24	14,08	13.62	12.84	12.34	10.92	10.46	10.04	10.01	10.29	9.83
500	14.99	15,05	14.62	13.84	13.33	11.89	11.43	10.99	10.99	11.26	19.78
600	15.72	16.04	15.63	14.84	14.34	12.87	12.40	11.95	11.97	12.24	11.73
700	16.94	17.04	16.65	15.86	15.35	13.86	13.39	12.91	12.97	13.23	12.69
800	17.19	18.04	17.68	16.88	16.36	14.85	14.38	13.89	13.97	14.22	13.66
900	17.91	19.06	18.71	17.91	17.39	15.86	15.38	14.87	14.99	15.23	14.63
1000	18.63	20.08	19.76	18.95	18.42	16.86	16.39	15.85	16.00	16.24	15.61

C* - graphite

Equilibrium constants for some reactions of coal gasification

The equilibrium constant in partial pressures K_p is calculated from ΔG-values:

$$K_p = \exp\left(\frac{-\Delta G_T^0}{RT}\right) \tag{10}$$

and the K_x constant is obtained by:

$$K_x = K_p \cdot p^{-\Delta\nu} \qquad (11)$$

($\Delta\nu$ - the variation in the number of gases moles).

For reactions with strongly negative ΔG-values (for instance the combustion reactions (i), (viii) or (ix)) the value of the equilibrium constant is enormous and its calculation is of no interest; the reactions are virtually complete. The same is true for the hydrogenation reactions of coals (inasmuch the temperatures are not too high), except the graphite hydrogenation, where over 550°C the equilibrium constant becomes less than 1). It is worth to calculate the equilibrium constants for ΔG values near to zero, when the conversion (obtained from these constants) is neither 1 (as for ΔG << 0), nor 0 (as for ΔG >> 0).

For the homogeneous equilibrium (vii), the equilibrium constants decrease rapidly with increasing temperature. The values K_p for the gasification with CO_2 and hydrogen formation (ii):

$$K_p = \frac{p_{CO}^{2-y} \cdot p_{H_2}^{0.5x}}{p_{CO_2}^{1-y}} \qquad (12)$$

and for the reaction (iii):

$$K_p = \frac{p_{CO}^{2-y+0.5x} \cdot p_{H_2O}^{0.5x}}{p_{CO_2}^{1-y+0,5x}} \qquad (13)$$

show a very large range of the values: from 10^{-22} to 10^{8}; they highlight the same regularities concerning the reactivity of coals in the two reactions as the ΔG values.

The equilibrium constants for the reactions of coals with steam (iv) are given by:

$$K_p = \frac{p_{CO} \cdot p_{H_2}^{1+0.5x-y}}{p_{H_2O}^{1-y}} \qquad (14)$$

For the other reaction with steam (v) the equilibrium constants are the product of the K_p-values for reaction (iv) and the corresponding ones for reaction (vii).

Zero-affinity plots for reactions of the coal gasification

For characterizing the thermodynamic reactivity of coal as a function of both temperature and *pressure*, the *zero-affinity plots* were proposed [4,8,13-15]. These curves are plotted in *T* - lg *p* coordinates, and represent the points of zero Gibbs free energy of the reaction, $\Delta G_T^p = 0$, i.e., where the equilibrium constant $K_x = 1$. These plots divide the surface in two areas: one for $\Delta G_T^p > 0$ ($K_x < 1$), the other for $\Delta G_T^p < 0$ and $K_x > 1$; the latter is the domain where reactions go with good conversion. From the thermodynamic point of view, we can use reactions in the domain near the zero-affinity plot on both sides of it.

The pressure for zero affinity depends upon temperature according to the equation:

$$\ln p = \frac{-\Delta G_T^0}{\Delta\nu RT} \qquad (15)$$

In the case of reactions with $\Delta\nu = 0$, only the temperature affects the equilibrium, and there is a constant temperature for zero-affinity:

$$T_z = H_T^o / S_T^o. \qquad (16)$$

A reaction of this kind is (vii), with T_z (as mentioned above) about 800°C; the domain $\Delta G < 0$ is the area on the left of the line $T = T_z$ for any pressure. The gasification reactions of coals with carbon dioxide (ii, iii), steam (v, vii) and oxygen (viii, ix) proceed all with an increase of the number of gas moles $\Delta\nu > 0$. For the reactions (ii), (iii) and (v), the pressures for $K_x = 1$ were calculated; their logarithms are given in Tables 10, 11 and 12 respectively.

Table 10.

Equilibrium pressures lg p ($K_x = 1$) for the Boudouard reaction (ii)

T(°C)	C*	1	2	3	4	5	6	7	8	9	10
25	-21.0	-11.3	-8.85	-6.41	-4.29	-7.27	-5.34	-3.97	-5.36	-7.11	-3.09
100	-14.9	-7.36	-5.45	-3.52	-1.84	-4.20	-2.68	-1.59	-2.71	-4.09	-0.89
200	-9.82	-4.05	-2.57	-1.07	0.24	-1.61	-0.43	0.43	-0.46	-1.53	0.98
300	-6.49	-1.87	-0.68	0.55	1.62	0.10	1.06	1.77	1.02	0.16	2.22
400	-4.14	-0.33	0.67	1.69	2.59	1.31	2.12	2.72	2.08	1.35	3.10
500	-2.41	0,82	1.67	2.55	3.32	2.21	2.90	3.43	2.86	2.24	3.75
600	-1.08	1.71	2.45	3.22	3.89	2.92	3.52	3.98	3.48	2.94	4.27
700	-0.03	2.42	3.07	3.75	4.35	3.48	4.01	4.42	3.97	3.49	4.68
800	0.83	3.01	3.58	4.19	4.72	3.94	4.42	4.79	4.37	3.95	5.02
900	1.53	3.49	4.00	4.55	5.04	4.33	4.76	5.10	4.71	4.33	5.31
1000	2.12	3.91	4.37	4.86	5.31	4.65	5.05	5.36	5.00	4.66	5.55

C* - graphite

Table 11.

Equilibrium pressures lg p ($K_x = 1$) for the Boudouard reaction (iii)

T(°C)	C*	1	2	3	4	5	6	7	8	9	10
25	-21.0	-12.5	-10.3	-7.98	-5.95	-8.83	-7.01	-5.64	-7.11	-8.74	-4.78
100	-14.9	-8.24	-6.48	-4.63	-3.01	-5.32	-3.87	-2.77	-3.95	-5.24	-2.09
200	-9.82	-4.64	-3.25	-1.81	-0.54	-2.35	-1.22	-0.36	-1.29	-2.30	0.18
300	-6.49	-2.27	-1.14	0.04	1.08	-0.41	0.52	1.23	0.46	-0.37	1.67
400	-4.14	-0.59	0.36	1.36	2.24	0.97	1.76	2.36	1.45	1.00	2.73
500	-2.41	0,64	1.46	2.33	3.09	1.99	2.67	3.19	2.61	2.01	3.51
600	-1.08	1.61	2.32	3.08	3.75	2.78	3.38	3.84	3.33	2.80	4.12
700	-0.03	2.37	3.01	3.68	4.28	3.41	3.94	4.36	3.90	3.43	4.61
800	0.83	3.00	3.57	4.18	4.71	3.93	4.41	4.78	4.36	3.94	5.01
900	1.53	3.52	4.04	4.59	5.07	4.36	4.79	5.13	4.75	4.37	5.34
1000	2.12	3.96	4.43	4.94	5.38	4.73	5.12	5.43	5.08	4.73	5.62

C* - graphite

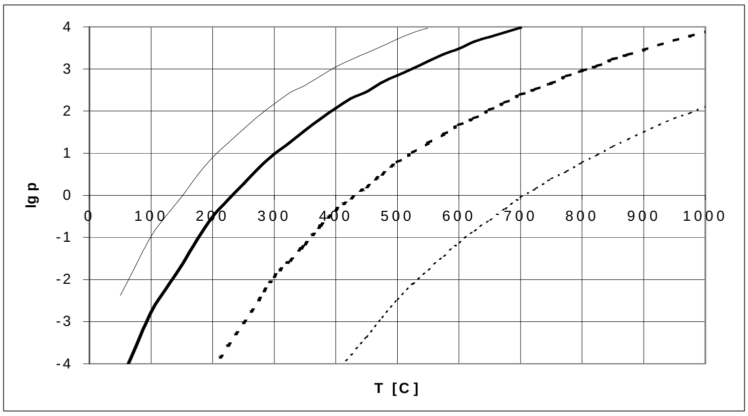

Fig. 1 Zero affinity plots for the Boudouard reaction (ii)

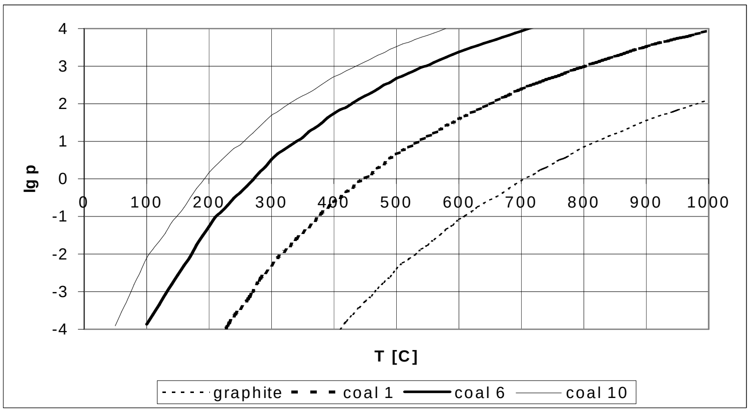

Fig. 2 Zero affinity plots for the Boudouard reaction (iii)

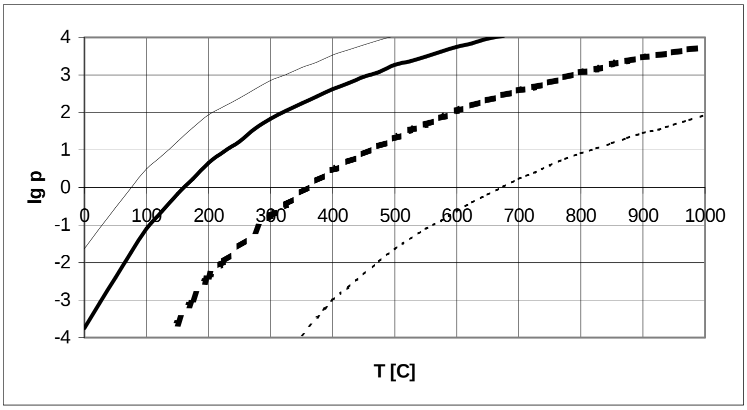

Fig. 3 Zero affinity plots for the steam gasification (iv)

Table 12.

Equilibrium pressures lg p ($K_x = 1$) for coal reactions with steam (iv)

T(^{o}C)	C*	1	2	3	4	5	6	7	8	9	10
25	-16.0	-7.86	-5.79	-3.70	-1.85	-4.76	-3.11	-1.90	-3.25	-4.75	-1.13
100	-11.4	-4.93	-3.27	-1.59	-0.10	-2.42	-1.09	-0.12	-1.20	-2.40	0.50
200	-7.46	-2.43	-1.12	0.22	1.40	-0.42	1.63	1.41	0.54	-0.41	1.91
300	-4.88	-0.77	0.31	1.42	2.40	0.90	1.78	2.43	1.70	0.92	2.84
400	-3.06	0.41	1.33	2.28	3.12	1.85	2.60	3.16	2.53	1.86	3.52
500	-1.70	1,30	2.10	2.93	3.67	2.57	3.22	3.72	3.16	2.58	4.03
600	-0.66	2.00	2.70	3.44	4.10	3.13	3.71	4.15	3.65	3.14	4.43
700	0.18	2.56	3.19	3.86	4.45	3.58	4.10	4.51	4.05	3.59	4.76
800	0.86	3.03	3.60	4.20	4.74	3.95	4.43	4.80	4.38	3.96	5.03
900	1.42	3.42	3.94	4.49	4.98	4.27	4.71	5.05	4.66	4.28	5.26
1000	1.89	3.75	4.23	4.74	5.20	4.54	4.94	5.26	4.90	4.55	5.46

C* - graphite

For the two reactions with CO_2: (ii) and (iii), and that with steam (iv) the zero-affinity curves are plotted in Figures 1-3 respectively for graphite, a bituminous coal (1) and two lignites: (6) and (10), in the pressure domain from 10^{-4} to 10^4 bar. The $\Delta G < 0$ area is situated at the right and under the plots. This domain is shifted to the left (lower temperatures) for coals in comparison to graphite, and for lignites as compared to bituminous coals. These reactions are less pressure dependent for lignites in comparison to bituminous coals and graphite: the plots are steeper and only for very high pressures the equilibrium temperature is substantially increased.

CONCLUSIONS

During the first stage of coals gasification in ordinary technical conditions, a thermal decomposition takes place, with loss of volatile components and production of semi-coke. The proper gasification reactions are then reactions of this coke, especially for lignites, meaning an important loss of reactivity, though even the coke has a higher thermodynamic reactivity as graphite [8]. One should take advantage of the high thermodynamic reactivity of lignites, by designing gasogens for low temperature gasification, with the use of the own moisture of the coal, as suggested and experimented by Franke et al. [16] and Block [17], for Rhine-Basin lignite and calculated for Romanian lignites by Niac and Pop [18]. On the other hand, small quantities of inorganic impurities and/or additives can act as catalysts and enhance the reaction rate. For high-rank coals however, this would be of little help, since their equilibrium temperatures are much higher.

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