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Dedicated to Professor Valer Fărcăşan
at his 85th anniversary

REACTIVITY OF A COAL IN GASIFICATION REACTIONS. A THERMODYNAMIC CASE STUDY

GAVRIL NIAC[a], OSSI HOROVITZ [b], ELENA MARIA PICĂ[a]

[a] Department of Chemistry, Technical University Cluj-Napoca, Romania
[b]Department of Physical Chemistry, "Babeş-Bolyai" University, Cluj-Napoca, Romania

ABSTRACT. Gibbs free energies, and equilibrium constants were calculated and zero-affinity plots were drawn based on average maceral phase composition, obtained by extrapolation of elemental content and higher heating value, to the ash content of the maceral phase, according to the two phase model of coals. Elements bound to the organic mass of coal (S, Al, Fe, Ca) were also considered. Their presence contributes to lowering the Gibbs free energy of gasification reactions. Zero-affinity plots show a much higher thermodynamic reactivity of the studied coal, as compared to graphite. Equilibrium constants (K_x) of gasification reactions for coal (Illinois No.6) approach the value 1 (ΔG_T^P=0) at temperatures 200-300℃ lower than the respective values for graphite.

Keywords: Gasification; Coal; Thermodynamic parameters; Illinois No.6 coal

INTRODUCTION

The concept of coal "reactivity" refers to a specific reactant and comprises two components: the *thermodynamic reactivity*, measured by the Gibbs free energy and the *kinetic reactivity*, expressed by rate constants or activation energies of the involved reactions. The classical way to calculate thermodynamic data (free energies, equilibrium constants) of coal gasification reactions with specific gasification agents, starts with the reactions of graphite and corrections are made for the other elements in coal. Calculations with the coal formula on a per carbon atom basis [1] is a better alternative [2, 3]. The problem is how to calculate the coefficients of such a formula, and how to express most conveniently the respective thermodynamic properties, especially the thermodynamic reactivity of the coal, as to allow comparison among coals differing in nature.

While minerals do not contribute to the thermodynamic properties of coal, ions bound ionically or covalently to organic matter, in the so called "maceral phase", participate to the reactions of gasification and should contribute to the Gibbs free energy of those reactions.

On the other hand, elemental composition (carbon content, hydrogen content, sulfur content) results from the organic as well as from the mineral part of the coal, therefore a per carbon atom formula can not be based upon elemental analysis data and averaging for several samples (having usually different ash contents), as practiced by several authors [2, 3]. Taking advantage of the *two* *phase model of coals* [4-7], the composition of the maceral phase (the true carbonaceous matter) can be evaluated extrapolating the elemental composition (including some components of ash), for several samples from the same coal deposit, differing in ash content, to the ash content of the pure maceral phase. This is the average of the amount of ash produced by 100 g pure macerals. The maceral ash content may be found by extrapolation of SiO_2-content (considered to be a component of the mineral phase only) to the ash axis.

In order to get a synthetic view on thermodynamic properties of a reaction, *zero affinity curves* and *iso-conversion curves* were proposed, and a large number of reactions were studied [8-12]. Zero affinity curves are plots of *pressure, p* (more conveniently log *p*), vs. *temperature, T,* for $\Delta G_T^p = 0$, or $K_x = 1$ (K_x being the equilibrium constant written with mol fractions and ΔG_T^p the Gibbs free energy for the reaction at temperature *T* and pressure *p*). Such a curve divides the (log *p)* xT surface into two domains, on the one side $\Delta G < 0$ or $K_x > 1$, on the other $\Delta G > 0$ or $K_x < 1$. At pressures and temperatures lying within the first domain the reaction is thermodynamically favored, while the second domain is unfavorable to the reaction. Such a *zero affinity curve* has the advantage to be independent on how the reaction is written, *i.e.* amplifying the equation does not change the curve.

The goal of this paper is to:

- establish the per carbon atom formula of the maceral phase,
- calculate Gibbs free energies for reactions of the maceral phase, both considering and neglecting metal ions,
- draw log *p* vs. *T* plots for $\Delta G^p_T = 0$ or $K_x(p) = 1$ (zero affinity plots), characteristic for the thermodynamic reactivity of coal in gasification reactions,
- compare these plots with those of graphite.

As a specific example Illinois No.6 coal was chosen, for which the necessary data were published in the final technical report on the Project entitled *Illinois Basin Coal Sample Program*, supported by the State of Illinois [13].

Analytical Properties of Illinois No.6 Coal

The analytical data taken from Chaven [13] are summarized in Table 1 and 2. The composition of the maceral phase, calculated as described in an other paper is given in Table 3 [14]. Other elements were neglected, since their concentration in the macerals is practically zero.

Table 1.

Analytical properties of Illinois No. 6 coal

No.	A(mf) %	V(mf) %	Q, MJ/kg	C(mf) %	H(mf) %	S(mf) %	N(mf) %
1	10.4	41.10	29.33	69.4	5.1	4.4	1.2
2	38.3	28.50	19.85	46.9	3.4	4.1	0.9
3	18.7	37.00	26.88	63.8	4.5	4.5	1.2
4	11.5	40.10	28.44	68.1	4.8	3.8	1.2
5	8.3	35.10	31.01	75	4.9	1.2	1.7
6	10.9	35.90	30.36	72.8	5	2.8	1.6

A – ash content; V – volatile matter; Q – heating value; mf – moisture free;

Table 2.

Ash components in moisture free Illinois No. 6 coal

Ash, %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	B_2O_3	ZnO	Na_2O	BaO	MnO
10.4	4.6	1.6	1.7	0.5	0.1	0.2	0.1	0.621	0.046	0.106	0.036	0.040
38.3	22.1	6.5	3.8	1.4	0.5	1	0.3	1.021	0.050	0.64	0.15	0.14
18.7	8.2	2.9	3.4	1.2	0.2	0.3	0.2	0.254	0.0093	0.151	0.082	0.092
11.5	6.1	2.3	1.4	0.6	0.1	0.3	0.1	0.328	0.0007	0.085	0.062	0.054
8.3	4	2	0.9	0.2	0.1	0.2	0.1	0.206	0.0006	0.085	0.039	0.019
10.9	5.5	2.2	1.7	0.4	0.1	0.3	0.1	0.129	0.028	0.108	0.05	0.044

Table 3.

Elemental composition of Illinois coal maceral phase

Element	C	H	S	N	Al	Fe	Ca	O (by diff.)
% in the maceral phase	78.33	5.38	2.79	1.58	0.38	0.62	0.14	10.78

Gibbs free energies of some gasification reactions of Illinois No.6 Coal

Based on analytical properties, the composition of Illinois coal maceral phase can be defined, on a per-carbon-atom basis [1] as follows:

$$CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0,0021}Fe_{0.0017}Ca_{0.0005} \qquad (1)$$

In the following calculations, both the complete above formula and a simplified formula, neglecting the metals content, were used.

In order to make thermodynamic calculations regarding the reactivity of coals, the following parameters were used for the reaction participants: standard enthalpies of formation, H_{298}^o, standard entropies, S_{298}^o and molar heat capacities under constant pressure C_p. For all the substances implied, other than coals, the values from usual thermodynamic tables, where available the CODATA Key Values [15], were used. The temperature dependence of molar heat capacities was calculated as: $C_p = a + bT + cT^2$ (for methane) and $C_p = a + bT + c'/T^2$ for all other compounds [10]. If necessary, the enthalpies of fusion and of vaporization were taken into consideration.

For the maceral part of coals, the *enthalpy of formation* corresponding to the formula was calculated from the higher heating value. As the standard enthalpy ΔH^o_{298} of the combustion reaction:

$$\begin{aligned} &CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0,0021}Fe_{0.0017}Ca_{0.0005} + 1.168\ O_2 = \\ &= CO_2 + 0.412\ H_2O + 0.013\ SO_2 + 0.0085\ N_2 + 0.00105\ Al_2O_3 + \\ &+\ 0.00085\ Fe_2O_3 + 0.0005\ CaO \qquad (2) \end{aligned}$$

refers to a mole, it is related to the higher heating value per kg of the maceral mass Q_s^c by the obvious relation:

$$\Delta H_{298}^o = -MQ_s^c/1000$$

where Q_s^c was obtained by extrapolation of the upper heating value of the anhydrous coal to 2.4% maceral ash content. M is the molecular mass of the formula (1). From the combustion reaction, the molar enthalpy of formation for the coal was calculated. The enthalpy of liquid water was used, since the upper heating value is concerned. The calculated value was -18.58 kJ/mol; while neglecting the metals in the formula, -21.42 kJ/mol was found. Since here the "molar mass" for coals has a purely conventional meaning, it should be more significant to compare the enthalpy values by referring to the unity mass of coal; these are -1226 kJ/kg (with the metals), and -1400 kJ/kg (without metals) respectively.

The *standard entropy* S_{298}^o for the coals, as well as the *molar heat capacity* C_p cannot be exactly calculated for complex solid substances such as the coals. Values for specific heats can be estimated from Neumann and Kopp-like formulas, such as the formula proposed by Szadeczky [16] for coals, with increments for solids [9, 17, 18]. For molar heat capacities the following formula was used:

$$C_p = 7.56 + 9.6\, n_{\mathrm{H}} + 16.8\, n_{\mathrm{O}} + 13.0\, n_{\mathrm{N}} + 22.6\, n_{\mathrm{S}} + 26.0\, n_{\mathrm{M}}\ [\mathrm{J.mol^{-1}K^{-1}}] \qquad (3)$$

where n_i is the index of the element i in the formula (1); M - stands for the metals. The values 17.83 J.mol^{-1}K^{-1} (with metals) and 17.72 J.mol^{-1}K^{-1} (without metals) were found.

The standard entropy can be estimated for organic solids from the formula of I.I.Strelkov [19]: $S^o_{298} = 1.1\ C_p$. A somewhat higher value for the proportionality factor, viz. 1.2 [9, 19] resulted in 21.39 J.mol^{-1}K^{-1} (1398 J.kg^{-1}K^{-1}) for the formula (1) and 21.26 J.mol^{-1}K^{-1} (1405 J.kg^{-1}K^{-1}), without the metals. They are a reasonable good approximation of entropies, so much the more the reactions considered show large volume variations, and consequently important entropy variations.

For all substances, except the coals, enthalpies and entropies were calculated exactly with the formulae given above for the temperature dependence of C_p. For coal, the C_p value was assumed to be constant.

Molar Gibbs free energies at p = 1 atm: $\Delta G_T^o = \Delta H_T^o - \mathrm{T}\Delta S_T^o$ of some gasification reactions at standard temperature, as well as at the temperatures of 100, 200 ... 1000°C for the Illinois No.6 coal were calculated, with the consideration of metals in it an without them, as well as for graphite, for comparison.

Formulas of organic matter of coal per one carbon atom were used to calculate equilibrium gas composition for Wyoming coal gasification by Stephans [2] and Stephans and Miller [3], but the evaluation of indices for H and O was made in a conventional manner, and other elements were neglected.

* The Boudouard reaction (gasification with carbon dioxide):

$$\mathrm{C(s) + CO_2(g) = 2CO(g)\ (g)} \qquad (4)$$

is endothermic under standard conditions, with volume increase ($\Delta\nu = 1$).

For coal, there are two ways for this reaction, the one with H_2 formation:

$$\begin{aligned} &CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0,0021}Fe_{0.0017}Ca_{0.0005} + 0.929\ CO_2 = \\ &= 1.929\ CO + 0.412H_2 + 0.013\ SO_2 + 0.0085\ N_2 + 0.00105\ Al_2O_3 + \\ &+ 0.00085\ Fe_2O_3 + 0.0005\ CaO \end{aligned} \tag{4a}$$

with volume increase ($\Delta\nu = 1.4335$), and the other with H_2O formation:

$$\begin{aligned} &CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0,0021}Fe_{0.0017}Ca_{0.0005} + 1.341\ CO_2 = \\ &= 2.341\ CO + 0.412\ H_2O + 0.013\ SO_2 + 0.0085\ N_2 + 0.00105\ Al_2O_3 + \\ &+ 0.00085\ Fe_2O_3 + 0.0005\ CaO. \end{aligned} \tag{4b}$$

with the same volume increase ($\Delta\nu = 1.4335$). Both are endothermic at room temperature.

For these reactions, the Gibbs free energies are given in Table 4. For both, the values are always lower for coal as for graphite at the same temperature and reach the negative domain already between 400 and 500^oC (as compared with over 700^oC for graphite), thus coal exhibits a higher reactivity versus CO_2 than graphite. For the reaction with water formation (4b), the temperature dependence is greater than for hydrogen formation (4a); the ΔG values for the first reaction (4b) are higher than for the second (4a) at low temperature, but at higher temperatures the tendency for water formation (4b) prevails over that for H_2 formation.

Table 4

The Gibbs free energy ΔG^o_T (MJ/kg) of gasification with CO_2

T^{o}C	Reaction (4)	Reaction (4a)		Reaction (4b)	
	Graphite	Coal	Coal*	Coal	Coal*
25	10.01	6.46	6.79	7.23	7.57
100	8.90	5.37	5.69	6.05	6.38
200	7.42	3.90	4.20	4.48	4.78
300	5.93	2.41	2.69	2.89	3.17
400	4.45	0.90	1.17	1.28	1.55
500	2.97	-0.60	-0.35	-0.32	-0.07
600	1.50	-2.12	-1.89	-1.93	-1.70
700	0.04	-3.65	-3.44	-3.55	-3.33
800	-1.42	-5.18	-4.99	-5.17	-4.97
900	-2.86	-6.72	-6.54	-6.79	-6.61
1000	-4.31	-8.27	-8.11	-8.42	-8.26

*neglecting the metal oxides

- The steam gasification of graphite has two possibilities, the one producing H_2 and CO:

$$C(s) + H_2O(g) = CO(g) + H_2(g), \tag{5}$$

the other, H_2 and CO_2:

$$C(s) + 2H_2O(g) = CO_2(g) + 2H_2(g) \tag{6}$$

Both are endothermic at standard temperature and occur with volume increase ($\Delta\nu = 1$). For the coal under consideration the reactions are written as follows:

$$\begin{aligned} &CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0,0021}Fe_{0.0017}Ca_{0.0005} + 0.929\ H_2O = \\ &= CO + 1.341\ H_2 + 0.013\ SO_2 + 0,0085\ N_2 + 0.00105\ Al_2O_3 + \\ &+ 0.00085\ Fe_2O_3 + 0.0005\ CaO \end{aligned} \tag{5a}$$

and

$$\begin{aligned} &CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0,0021}Fe_{0.0017}Ca_{0.0005} + 1.929\ H_2O = \\ &= CO_2 + 2.341\ H_2 + 0.013\ SO_2 + 0,0085\ N_2 + 0.00105\ Al_2O_3 + \\ &+ 0.00085\ Fe_2O_3 + 0.0005\ CaO \end{aligned} \tag{6a}$$

Both have the same volume increase ($\Delta\nu = 1.4335$ mols of gas per carbon atom).

The trends are much the same as for coal gasification with CO_2 (Table 5). The higher reactivity of coal as compared with graphite may also be clearly seen. The thermodynamic reactivity of coal versus steam is greater, at low temperature, as versus CO_2; from round 800°C on, the trend is inverted. The steam gasification with formation of CO_2 (reaction (6a)) presents lower ΔG values than reaction (5a) for temperatures below 800°C, i.e. the formation of CO_2 prevails over the formation of CO. The opposite occurs at higher temperatures.

Table 5.

The Gibbs free energy ΔG_T^o (MJ.kg^{-1}) for coal gasification with H_2O (5,6), carbon oxide conversion (7) and hydrogenation (8)

T(°C)	Reaction (5)			Reaction (6)			Reaction (7)	Reaction (8)		
	C[1]	Coal	Coal*	C[1]	Coal	Coal*		C[1]	Coal	Coal*
25	7.62	4.72	5.04	5.24	2.85	3.15	-2.39	-4.23	-4.70	-4.55
100	6.78	3.82	4.14	4.65	2.16	2.46	-2.13	-3.71	-4.50	-4.35
200	5.63	2.59	2.89	3.83	1.18	1.46	-1.79	-2.95	-4.22	-4.07
300	4.46	1.33	1.61	2.99	0.18	0.44	-1.47	-2.14	-3.91	-3.75
400	3.28	0.06	0.32	2.12	-0.86	-0.61	-1.17	-1.29	-3.58	-3.42
500	2.10	-1.24	-0.99	1.23	-1.92	-1.69	-0.87	-0.42	-3.25	-3.09
600	0.92	-2.55	-2.32	0.33	-3.02	-2.79	-0.59	0.47	-2.92	-2.75
700	-0.27	-3.88	-3.67	-0.59	-4.13	-3.92	-0.32	1.38	-2.58	-2.41
800	-1.46	-5.22	-5.02	-1.52	-5.26	-5.06	-0.05	2.29	-2.25	-2.08
900	-2.66	-6.57	-6.39	-2.45	-6.41	-6.23	0.21	3.21	-1.93	-1.75
1000	-3.85	-7.94	-7.77	-3.39	-7.58	-7.41	0.46	4.13	-1.61	-1.43

[1] Graphite * neglecting the metal oxides

- The homogeneous reaction of carbon oxide conversion:

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \tag{7}$$

makes the difference between reactions (6) and (5). It is slightly exothermic and without volume variation. The values given in Table 5 for this reaction refer also to 1 kg of carbon.

- The coal hydrogenation reaction (possibly with hydrogen resulted from other reactions):

$$\begin{gathered}CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0,0021}Fe_{0.0017}Ca_{0.0005} + 1.728\ H_2 = \\ = CH_4 + 0.1025\ H_2O + 0.013\ SH_2 + 0,017\ NH_3 + 0.0021\ Al + \\ + 0.0017\ Fe + 0.0005\ CaO\end{gathered} \qquad (8)$$

is exothermic, with volume decrease ($\Delta\nu = -1$ for graphite, and $\Delta\nu = -0.5965$ for coal). It presents rather important negative ΔG-values at standard temperature (Table 5). ΔG increases with temperature and becomes positive for graphite at round 550°C; for coals the values are much lower and still negative at 1000°C.

- Some reactions of incomplete combustion, with formation of carbon monoxide (and possibly water or hydrogen) were also considered for graphite (9) and for coal (9a, 10):

$$C(graphite) + 0.5\ O_2(g) = CO(g), \qquad (9)$$

$$\begin{gathered}CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0.0021}Fe_{0.0017}Ca_{0.0005} + 0.6705\ O_2 = \\ = CO + 0.412\ H_2O + 0.013\ SO_2 + 0.0085\ N_2 + 0.00105\ Al_2O_3 + \\ + 0.00085\ Fe_2O_3 + 0.0005\ CaO\end{gathered} \qquad (9a)$$

$$\begin{gathered}CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0.0021}Fe_{0.0017}Ca_{0.0005} + 0.4645\ H_2O = \\ = CO + 0.412\ H_2O + 0.013\ SO_2 + 0.0085\ N_2 + 0.00105\ Al_2O_3 + \\ + 0.00085\ Fe_2O_3 + 0.0005\ CaO\end{gathered} \qquad (10)$$

All reactions occur with volume increase [$\Delta\nu = 0.5$ (9), $\Delta\nu = 0.763$ (9a), $\Delta\nu = 0.969$ (10)] and are exothermal. Their Gibbs free energies are compared in Table 6.

The partial oxidation of coal (9a) has more negative ΔG-values as that of graphite, while for the oxidation of coal with water (10) ΔG-values lie above those for partial oxidation of graphite and their temperature dependence is more pronounced, so that at 1000°C, the value for coal becomes equal to that of graphite.

It is of interest to calculate the Gibbs free energy for the formation of the maceral phase from elements:

$$\begin{gathered}C + 0.412\ H_2 + 0.0515\ O_2 + 0.013\ S + 0,0085\ N_2 + 0.0021\ Al + 0.0017\ Fe + \\ + 0.0005\ Ca = CH_{0.824}O_{0.103}S_{0.013}N_{0.017}Al_{0.0021}Fe_{0.0017}Ca_{0.0005}\end{gathered} \qquad (11)$$

as compared with the Gibbs free energy of graphite: $G_T^o(C) = H_T^o(C) - TS_T^o(C)$. This latter quantity is negative (Table 6), due to the prevailing influence of the entropy factor (the enthalpy being positive); there is a slight diminution of these values with increasing temperature. For coal, on the other hand, the reaction occurs with entropy diminution (gases are consumed), therefore ΔG increases with temperature. Since the standard enthalpy of formation is only slightly negative, the Gibbs free energy of formation becomes soon positive, at about 100°C.

Table 6.

The Gibbs free energy ΔG_T^o (MJ.kg^{-1}) for incomplete combustion (9,10) and for the formation of coal from elements (11)

T^{o}C	Reaction (9)			Reaction (10)		Reaction (11)	
	Graphite	Coal	Coal*	Coal	Coal*	Coal	Coal*
25	-11.43	-15.32	-15.14	-9.17	-8.91	-0.23	-0.41
100	-11.99	-15.93	-15.75	-9.86	-9.61	0.03	-0.16
200	-12.74	-16.73	-16.57	-10.80	-10.57	0.38	0.20
300	-13.49	-17.55	-17.40	-11.75	-11.53	0.74	0.57
400	-14.24	-18.38	-18.24	-12.72	-12.52	1.12	0.96
500	-14.99	-19.21	-19.09	-13.69	-13.51	1.51	1.35
600	-15.72	-20.06	-19.95	-14.68	-14.51	1.93	1.78
700	-16.94	-20.91	-20.81	-15.67	-15.52	2.36	2.21
800	-17.19	-21.76	-21.68	-16.68	-16.54	2.80	2.66
900	-17.91	-22.62	-22.55	-17.69	-17.57	3.25	3.11
1000	-18.63	-23.49	-23.43	-18.71	-18.60	3.71	3.58

* neglecting the metal oxides

This latter quantity is negative (Table 6), due to the prevailing influence of the entropy factor (the enthalpy being positive); there is a slight diminution of these values with increasing temperature. For coal, on the other hand, the reaction occurs with entropy diminution (gases are consumed), therefore Δ*G* increases with temperature. Since the standard enthalpy of formation is only slightly negative, the Gibbs free energy of formation becomes soon positive, at about 100^{o}C.

Equilibrium constants of gasification reactions

The equilibrium constant in partial pressures K_p is calculated from ΔG_T^o-values:

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

and the constant in mole fractions K_x is obtained by:

$$K_x = K_p \cdot p^{-\Delta\nu}$$

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

For reactions with strongly negative Δ*G*-values (for instance the combustion reaction) the value of the equilibrium constant is enormous and its calculation is of no interest; the reactions are virtually complete. So is also the hydrogenation reaction of coal (inasmuch the temperatures are not too high), except the graphite hydrogenation, where over 550^{o}C the equilibrium constant becomes less than 1. It is worth calculating the equilibrium constants for Δ*G* values near to zero, when the conversion (obtained from these constants) is neither close to 1 (as for Δ*G* << 0), nor close to 0 (as for Δ*G* >> 0).

Table 7.
The equilibrium constants K_p for some reactions of graphite and coal

T(^{o}C)	Reaction 4	Reaction 4a		Reaction 4b	
	Graphite	Coal	Coal*	Coal	Coal*
25	$9.17.10^{-22}$	$4.89.10^{-18}$	$1.02.10^{-18}$	$4.19.10^{-20}$	$8.71.10^{-21}$
100	$1.12.10^{-15}$	$3.17.10^{-12}$	$9.04.10^{-13}$	$1.08.10^{-13}$	$3.09.10^{-14}$
200	$1.49.10^{-10}$	$2.61.10^{-7}$	$9.72.10^{-8}$	$2.74.10^{-8}$	$1.02.10^{-8}$
300	$3.25.10^{-7}$	$4.37.10^{-4}$	$1.94.10^{-4}$	$9.47.10^{-5}$	$4.20.10^{-5}$
400	$7.25.10^{-5}$	$8.44.10^{-2}$	$4.22.10^{-2}$	$3.01.10^{-2}$	$1.51.10^{-2}$
500	$3.88.10^{-3}$	4.20	2.30	2.14	1.17
600	$8.34.10^{-2}$	87.9	51.6	58.8	34.5
700	0.941	993	616	817	507
800	6.73	$7.27.10^{3}$	$4.71.10^{3}$	$7.07.10^{3}$	$4.58.10^{3}$
900	33.9	$3.81.10^{4}$	$2.56.10^{4}$	$4.22.10^{4}$	$2.84.10^{4}$
1000	132	$1.55.10^{5}$	$1.08.10^{5}$	$1.93.10^{5}$	$1.34.10^{5}$

T(^{o}C)	Reaction 5			Reaction 7
	Graphite	Coal	Coal*	
25	$9.26.10^{-17}$	$2.24.10^{-13}$	$4.35.10^{-14}$	$1.04.10^{5}$
100	$4.09.10^{-12}$	$6.39.10^{-9}$	$1.74.10^{-9}$	$3.74.10^{3}$
200	$3.50.10^{-8}$	$4.20.10^{-5}$	$1.51.10^{-5}$	237.6
300	$1.32.10^{-5}$	$1.37.10^{-2}$	$5.96.10^{-3}$	40.94
400	$8.72.10^{-4}$	0.86	0.424	12.24
500	$1.97.10^{-2}$	19.1	10.4	5.11
600	0.220	218	127	2.66
700	1.50	$1.54.10^{3}$	951	1.60
800	7.17	$7.73.10^{3}$	$5.01.10^{3}$	1.07
900	26.3	$3.01.10^{4}$	$2.03.10^{4}$	0.77
1000	78.4	$9.59.10^{4}$	$6.68.10^{4}$	0.59

*neglecting the metal oxides

For the homogeneous equilibrium (7), the equilibrium constants are given in Table 7. They decrease rapidly with increasing temperature. The K_p values for the gasification with CO_2 and hydrogen formation (4a)

$$K_p = \frac{p_{CO}^{1.929} \cdot p_{H_2}^{0.412} \cdot p_{SO_2}^{0.013} \cdot p_{N_2}^{0.0085}}{p_{CO_2}^{0.929}}$$

or with neglect of the metals

$$K_p = \frac{p_{CO}^{1.923} \cdot p_{H_2}^{0.412} \cdot p_{SO_2}^{0.013} \cdot p_{N_2}^{0.0085}}{p_{CO_2}^{0.923}}$$

and for the reaction (4b) are given also in Table 7. 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 (5) are presented in Table 7 too. For the other reaction with steam (6) the equilibrium constants are simply the product of the K_p-values for reaction (5) with those for reaction (7).

Zero-affinity plots for gasification reactions

A means to characterize the reactivity as a function of both *temperature* and *pressure*, is the *iso-conversion-* and *zero-affinity plots,* proposed by Voiculescu and Niac [8-12]. These curves are plotted in lg p vs. T coordinates, and represent the place of the points of zero Gibbs free energy of reaction $\Delta G_T^p = 0$, i.e., where the equilibrium constant $K_x = 1$ for iso-conversion plots. These plots divide the space into 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.

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

$$\ln p = \frac{-\Delta G_T^o}{\Delta \nu RT}$$

In the case of reactions with $\Delta\nu = 0$, only the temperature affects the equilibrium, and there is a constant temperature for zero-affinity: $T_z = \Delta H_T^o / \Delta S_T^o$. So is reaction (7), with T_z (as mentioned above) about 800°C; the domain $\Delta G < 0$ is the area on the left of the vertical $T = T_z$ for any pressure.

The gasification reactions of coals with carbon dioxide (4a, 4b), steam (5a, 6a) and oxygen (9a, 10) proceed all with an increase of the number of gas moles ($\Delta\nu > 0$). For the steam gasification reactions (4a), (4b), (5), (5a), (6) and (6a), the pressures for $K_x = 1$ were calculated and the zero-affinity curves were plotted in Figures 1 and 2 within the pressure domain 1 to 10^3 bar. The area $\Delta G < 0$ is situated at the right and bellow the plots. This domain is shifted to the left (lower temperatures) for coal as against graphite. At lower temperatures, the plots for reactions (4a) and (4b) lie very near to one another, while the plots for the steam gasification reactions (5a), (6a) are shifted leftwards (higher reactivity). At 800°C, all the curves cross together: the thermodynamic coal reactivity becomes the same for all these reactions. The water gas reaction (Fig. 2) gives the vertical straight, since $\Delta\nu = 0$ and the reaction does not depend on pressure.

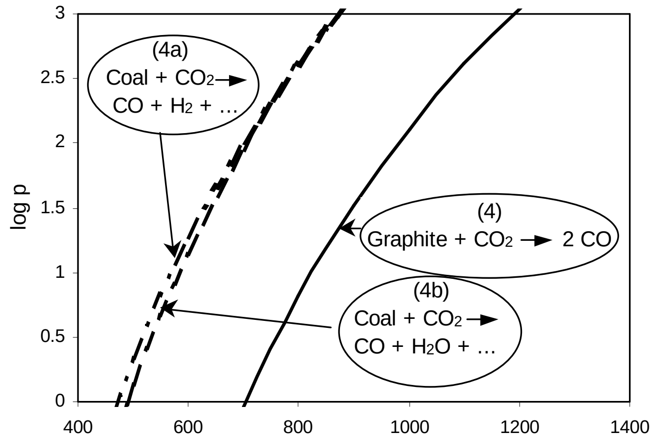

Fig. 1. Zero-affinity plots for the Boudouard reactions of graphite (4) and coal (4a, 4b)

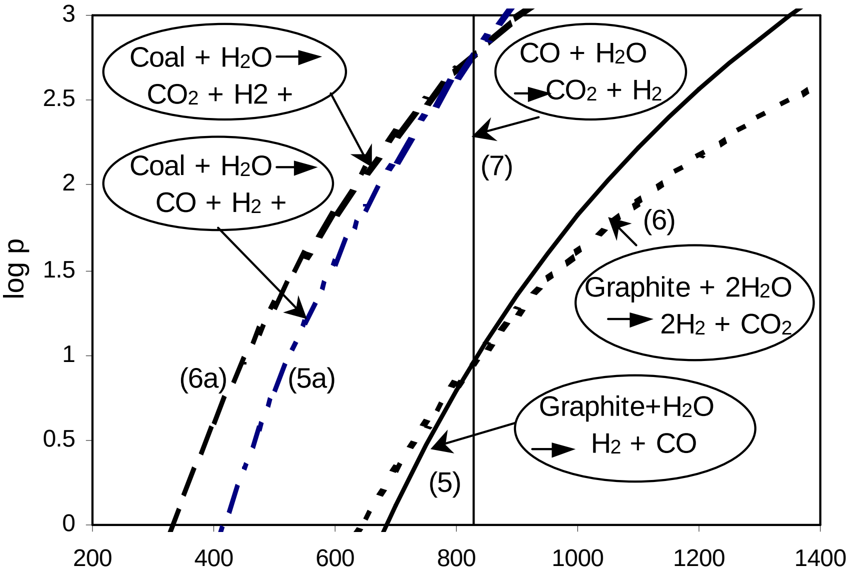

Fig. 2. Zero-affinity plots for reaction of graphite (5), (6), coal (5a), (6a) and carbon monoxide (7) with water vapor

CONCLUSIONS

During the first stage of coals gasification in ordinary technical conditions, 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, this means an important loss of reactivity. 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 [20-22]. 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 less help, since their equilibrium temperatures are much higher.

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