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## ORIGINAL ARTICLE

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# The study of compensation effect in reverse Boudouard reaction on graphite in presence of activating additives

Pavel Anatolyevich Nikolaychuk\*, Aleksandr Vasilyevich Kolesnikov

Department of Analytical and Physical Chemistry, Chelyabinsk State University, 454001,  
Brat'yev Kashirinykh Street, 129, Chelyabinsk, (RUSSIAN FEDERATION)

E-mail: npa@csu.ru; avkzinc-gu@yandex.ru

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**Abstract :** In this study the results of calculation of rate constants for graphite gasification reaction (reverse Boudouard reaction) taking into account heat and mass transfer processes at temperatures of 900-1200°C are presented. The calculation of rate constants of  $C + CO_2$  reaction on graphite in presence of calcium, magnesium, strontium, iron (II) and iron (III) oxides, strontium carbonate and metallic iron was performed. The graphs of linear dependencies of pre-exponential factor on acti-

vation energy for calcium, strontium and iron compounds were plotted. The isokinetic temperatures for various groups of catalysts were calculated.

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**Keywords :** Graphite gasification; Reverse Boudouard reaction; Compensation effect; Isokinetic temperature.

## INTRODUCTION

The interaction of carbon dioxide with carbon plays a major role in many pyrometallurgical high temperature processes, where coke, coal and other carbon materials are used as solid reductants. Many studies are devoted to investigation of  $C + CO_2$  reaction in order to increase yield of carbon monoxide, which is one of the most important raw materials for chemical production<sup>[1]</sup>. It was noted in papers<sup>[2-4]</sup>, that basic solutions of the problem of carbon gasification reaction speeding can be obtained from fundamentals of reaction kinetics, stream dynamics, diffusion, heat and mass transfer. Therefore, the various aspects of this reaction were stud-

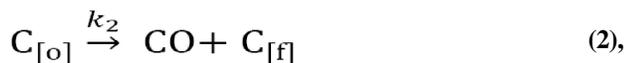
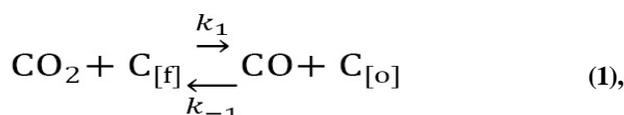
ied very widely. Particularly, the studies concerning the influence of temperature on kinetics of the reverse Boudouard reaction reveal the presence of compensation effect.

Compensation effect is the dependency between pre-exponential factor ( $A$ ) and activation energy ( $E_A$ ) in Arrhenius equation ( $k = A \cdot e^{-\frac{E_A}{RT}}$ ), which reveals often, when studying heterogeneous catalytic processes<sup>[5-7]</sup>. In this case values of  $A$  and  $E_A$  increase or decrease simultaneously, compensating each other, and the influence of temperature on rate constant becomes less substantial. If the relationship between  $E_A$  and  $A$  for multiple reactions strictly obeys linear nature ( $\log A = \alpha + \beta \cdot E_A$ ), rate constants for all reactions become

equal at one certain temperature, which is called "isokinetic temperature"  $T_\theta$ <sup>[7-9]</sup>.

The presence of compensation effect was noticed at catalytic gasification of carbons, activated by various additives such as sodium lignosulphate<sup>[10]</sup>, ferric nitrate<sup>[10]</sup>, sodium and potassium carbonates<sup>[11,12]</sup>, organometallic compounds with V, Cr, Mn, Fe and Co<sup>[13]</sup>, sodium vanadate<sup>[14]</sup> and others<sup>[15]</sup>. The influence of temperature on rate constants of C + CO<sub>2</sub> reaction and compensation effect in presence of calcium and magnesium oxides, strontium oxide and carbonate, iron and iron oxides is the subject of the present work.

The reverse Boudouard reaction C + CO<sub>2</sub> was studied very widely<sup>[2,4,16-19]</sup>, including studies with different coal types and at various carbon dioxide partial pressures. The mechanism of this reaction is postulated to be the following<sup>[3,4,16,17,19]</sup>:



where C<sub>[f]</sub> is a free active center on carbon surface, able to reaction, and C<sub>[o]</sub> is an active center, occupied by oxygen atom,  $k_1$ ,  $k_{-1}$  and  $k_2$  are rate constants of corresponding elementary stages.

Reaction (1) proceeds relatively fast and is characterized by following equilibrium constant:

$$K_p = \frac{k_1}{k_{-1}} = \frac{[\text{CO}] \cdot [\text{C}_{[o]}]}{[\text{CO}_2] \cdot [\text{C}_{[f]}]} \quad (3).$$

Here equilibrium concentrations of gases, [CO] and [CO<sub>2</sub>], are expressed in mol cm<sup>-3</sup> and [C<sub>[o]</sub>] and [C<sub>[f]</sub>] are the numbers of moles of occupied and free active centers per one gram of carbon.

Reaction (2), corresponding to carbon transfer from solid phase to gaseous one, which proceeds on occupied active centers, is much slower.

In this case, rate of gasification of carbon sample, surrounded by gas of unified composition, can be expressed in following way<sup>[3,4]</sup>:

$$\frac{dn}{dt} \equiv N_c = k_2 \cdot [\text{C}_{[o]}] \cdot P \quad (4),$$

where  $N_c = \frac{dn}{dt}$  is the rate of carbon transfer from solid phase to the gaseous one, mol s<sup>-1</sup>,  $P$  – mass of carbon, g.

It is stated<sup>[3]</sup>, that full amount of active centers per gram of carbon [C<sub>[t]</sub>] is the sum of amounts of free and occupied active centers:

$$[\text{C}_{[t]}] = [\text{C}_{[f]}] + [\text{C}_{[o]}] \quad (5).$$

Assuming that rates of formation and vanishing of occupied active centers are equal and using steady-state approximation, the following kinetic equation can be derived:

$$\frac{d[\text{C}_{[o]}]}{dt} = k_1 \cdot [\text{CO}_2] \cdot [\text{C}_{[f]}] - k_{-1} \cdot [\text{CO}] \cdot [\text{C}_{[o]}] - k_2 \cdot [\text{C}_{[o]}] = 0 \quad (6).$$

Expressing [C<sub>[f]</sub>] from equation (5) and substituting it into equation (6) yields:

$$k_1 \cdot [\text{CO}_2] \cdot [\text{C}_{[t]}] = k_1 \cdot [\text{CO}_2] \cdot [\text{C}_{[o]}] + k_{-1} \cdot [\text{CO}] \cdot [\text{C}_{[o]}] + k_2 \cdot [\text{C}_{[o]}] \quad (7).$$

Solving for [C<sub>[o]</sub>] from equation (7) gives:

$$[\text{C}_{[o]}] = \frac{k_1 \cdot [\text{CO}_2] \cdot [\text{C}_{[t]}]}{k_1 \cdot [\text{CO}_2] + k_{-1} \cdot [\text{CO}] + k_2} \quad (8).$$

Dividing both numerator and denominator by  $k_1 \cdot [\text{CO}_2]$  gives:

$$[\text{C}_{[o]}] = \frac{[\text{C}_{[t]}]}{1 + \frac{k_{-1} \cdot [\text{CO}]}{k_1 \cdot [\text{CO}_2]} + \frac{k_2}{k_1 \cdot [\text{CO}_2]}} \quad (9).$$

Defining the value of  $I_2 = \frac{k_1}{k_2}$  and substituting it and the value of  $K_p$  from equation (3) into equation (9) yields:

$$[\text{C}_{[o]}] = \frac{[\text{C}_{[t]}]}{1 + \frac{[\text{CO}]}{[\text{CO}_2] \cdot K_p} + \frac{1}{[\text{CO}_2] \cdot I_2}} \quad (10).$$

Substituting equation (10) into equation (4) gives the expression for overall carbon gasification rate:

$$\frac{dn}{dt} = \frac{k_2 \cdot [\text{C}_{[t]}] \cdot P}{1 + \frac{[\text{CO}]}{[\text{CO}_2] \cdot K_p} + \frac{1}{[\text{CO}_2] \cdot I_2}} \quad (11),$$

The values of  $K_p$  and  $I_2$  do not involve any parameter that is a function of physical properties of carbon, they also are expected to be independent of pressure. The dependencies of these parameters on temperature are taken from paper<sup>[20]</sup>.

The aim of this study is: 1) to investigate C + CO<sub>2</sub> reaction on graphite in a flow reactor in presence of calcium, magnesium, strontium and iron compounds using kinetic equation (11) and considering heat and mass transfer processes; 2) to calculate rate constants and evaluate possible compensation effect between activation energy and Arrhenius prefactor in presence of studying additives.

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## EXPERIMENTAL

### Performing of experiments

The commercially available graphite powder which comes in the graphite pots was used in all experiments. The graphite was of spectral analysis quality and had the particle size  $d = 0.1$  mm and impurities content of no more than  $2 \cdot 10^{-5}$  weight percent. Activating additives were of analytical quality with particle size  $d = 0.1$  mm and purity of 99%. Carbon dioxide from balloons, containing no more than 0.1% CO and 0.01% H<sub>2</sub> was used.

The initial samples with the various concentrations of the catalysts were prepared by the mechanical mixing of corresponding amounts of the graphite and the additive in plastic cups during 10 minutes. A weight taken from the sample mixture using analytical balance ADV-200 with measurement error of  $\pm 0.0001$  g was placed into alundum bath that was preliminarily calcined at 1200°C during 1 hour. The bath had been injected into porcelain tube and placed into thermobalance ATV-14 with carborundum heaters. Carbon dioxide flow was passed through the tube with determined rate. The studies were performed at temperature range of 900–1200°C. Carbon dioxide consumption was 50 cm<sup>3</sup> min<sup>-1</sup> and gas flowing rate in reaction tube was 1.06 and 1.32 cm s<sup>-1</sup> at temperatures of 900 and 1200°C respectively. The alundum baths used in experiments were weighted before and after the experiment and no mass loss was detected.

Thermogravimetric analysis was applied to study reaction kinetics. According to paper<sup>[21]</sup>, TGA can be freely used without needing to pay attention to chemisorption dynamics if carbon active surface area does not exceed 312 m<sup>2</sup> g<sup>-1</sup>. However, active surface area of graphite without special processing is much lower<sup>[22]</sup>, which allows using of TGA method freely. Thermogravimetric curves obtained from different weights taken from one sample mixture show good reproducibility and compatibility with each other.

Since the heating area in thermobalance is small, there was no possibility to place a gas analyzer close to reaction zone in order to avoid decreasing temperature of the gas stream. Therefore, the concentrations of CO and CO<sub>2</sub> in downstream were not directly measured. They were calculated according to gas flowing rate in reaction tube and graphite mass loss rate.

### Analysis of experimental data

The experimental results were presented in form of dependencies of mass loss of graphite ( $F$ ) on time ( $t$ ):

$$F(t) = \frac{P_o - P_k}{P_o} \cdot 100\% = \frac{\Delta P}{P_o} \cdot 100\% \quad (12),$$

where  $P_k$  is current graphite mass,  $P_o$  is initial graphite mass and  $\Delta P = P_o - P_k$  is graphite mass loss.

Kinetic curves were conditionally divided into three sections: section I – from start of experiment to time of 3 minutes, section II – from third minute to the moment of 65–70 % graphite mass loss and section III – from 65–70 to 100 % graphite mass loss. The example of the kinetic curves is shown at Figure 1. The rate constants were calculated according to section II. In most cases the experimental points in this section were described by straight lines. The slopes of these lines ( $\Delta F / \Delta \tau$ ) were determined using least squares technique. After this the average rates of graphite mass loss at the second section were determined:

$$\Delta P / \Delta \tau = \frac{\Delta F / \Delta \tau \cdot P_o}{100\%} \quad (13).$$

After dividing the values of  $\Delta P / \Delta \tau$  by carbon molar mass (12.0107 g mol<sup>-1</sup>) the rates of loss of graphite amount of moles (graphite consumption rates) were calculated.

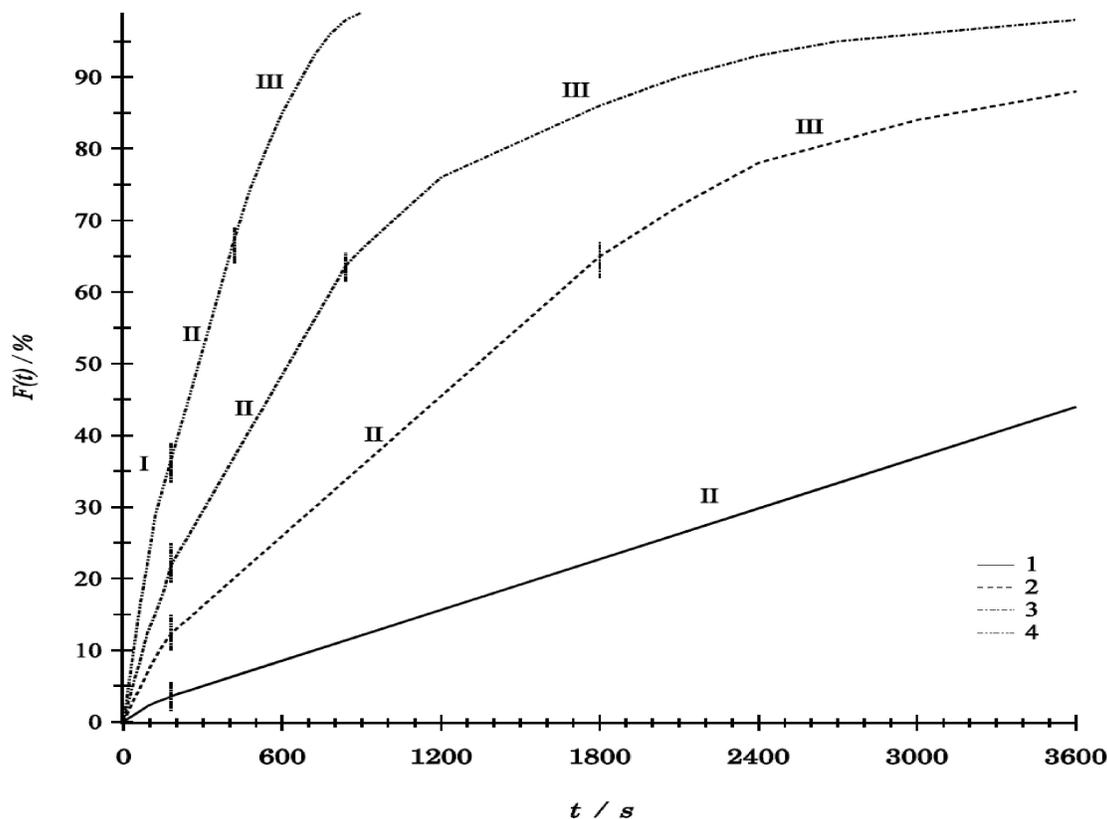
According to<sup>[23]</sup>, the average reaction rate inflow system ( $\frac{dn}{dt}$ ) can be calculated independently by equation:

$$\frac{dn}{d\tau} \equiv N_c = \frac{(X_{a,o} - X_{a,i}) \cdot F_a}{V} \quad (14),$$

where  $N_c$  is the average rate of interaction of carbon dioxide with graphite,  $X_{a,i}$  and  $X_{a,o}$  – the amounts of CO<sub>2</sub> at reactor inlet and outlet respectively, cm<sup>3</sup>,  $F_a$  – the rate of incoming substance, mol s<sup>-1</sup>,  $V$  – reaction space volume, cm<sup>3</sup>.

The values of  $N_c$  calculated in accordance with equation (14) were found to be compatible with the values of graphite consumption rate within their ranges of uncertainty. Therefore, the graphite consumption rates ( $\Delta n / \Delta \tau$ ) were used for further rate constants calculations.

Substituting these values into equation (11), taking into account that carbon mass ( $P$ ) in equation (11) is identical to initial graphite mass ( $P_o$ ) and solving the



**Figure 1 :** Thermogravimetric curves for the gasification of graphite doped with 0.1 mol %  $\text{SrCO}_3$  at: 1 – 950°C; 2 – 1000°C; 3 – 1050°C; 4 – 1100°C. The kinetic parameters were calculated from section II of the curves.

resulting equation for  $k_2 \cdot [\text{C}_{[t]}]$  gives the expression for the apparent rate constants of reaction  $\text{C} + \text{CO}_2$ :

$$k_2 \cdot [\text{C}_{[t]}] = \frac{\Delta n}{\Delta \tau} \cdot \left(1 + \frac{[\text{CO}]}{[\text{CO}_2] \cdot K_p} + \frac{1}{[\text{CO}_2] \cdot b_2}\right) \cdot \frac{1}{P_o} \quad (15)$$

Variables  $[\text{CO}]$  and  $[\text{CO}_2]$  in equation (15) are average actual gases concentrations on graphite surface. In flow reactors, even at high flowing speed, in case when reaction on surface proceeds with significantly high rate, a difference exist between reacting gas concentrations in gas phase and on the surface. Taking into account  $\text{CO}_2$  mass transfer from stream to graphite surface<sup>[24]</sup> was performed according to equation:

$$\varepsilon = \frac{3}{2} \cdot \frac{\Phi_{cl}}{C_R} \cdot \frac{1}{D^{2/3}} \cdot X_{cl}^2 \cdot \gamma_V^{1/6} \cdot U_F \quad (16)$$

where  $C_{R(o)} = C_R \cdot (1 - \varepsilon)$ ,  $C_{R(o)}$  is gas concentration (either  $\text{CO}$  or  $\text{CO}_2$ ) on solid reagent surface,  $C_R$  – average gas concentration in stream,  $\Phi_{cl}$  – the average flow, referred to the outer contour of the solid reagent,  $D$  – diffusion coefficient;  $X_{cl}$  – powder filling length,  $\gamma_V$  – gas kinematical viscosity,  $U_F$  – the average gas flowing rate in tube.

It is well known, that reverse Boudouard reaction

is endothermic. At high reaction rates and big amount of initial weights it is necessary to consider temperature difference between solid material and gas stream. At the temperatures of 900 – 1200°C heat transfer proceeds mainly by emission mechanism. The approximate expression for temperature difference calculation is the following<sup>[24]</sup>:

$$\Delta T \cong \frac{1}{\sigma_{SB}} \cdot \left(\frac{dQ}{d\tau}\right)_{\max} \cdot \frac{1}{\Phi'_{cl}} \cdot \frac{1}{4T^3} \quad (17)$$

where  $\sigma_{SB}$  is Stefan-Boltzmann constant,  $\left(\frac{dQ}{d\tau}\right)_{\max}$  is maximal amount of heat, produced during reaction per time unit,  $\Phi'_{cl}$  is square of outer contour of solid body,  $T$  – temperature, K. The dimensions and definition ranges of variables, needed for calculations according to formulae (16, 17), are listed in TABLE 1.

## RESULTS AND DISCUSSION

### Determination of initial graphite weight

The influence of graphite initial weight on gasifica-

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tion reaction rate and apparent rate constant ( $k_2 \cdot [C_{(g)}]$ ) was studied, according to equation (15) taking into account heat and mass transfer according to equations (16,17). The experiments were performed at temperature of 1000°C with different weights of graphite, doped by 0.5 mol % CaO with CO<sub>2</sub> flowing rate of 150 cm<sup>3</sup> min<sup>-1</sup>. The results are presented in TABLE 2.

The differences between values of ( $k_2 \cdot [C_{(g)}]$ ) at various graphite weights are small, therefore used calculation formulae are reliable. The average apparent rate constant value is  $(9.61 \pm 1.58) \cdot 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$ . Temperature difference between gas stream and graphite layer was insignificant for weights of 0.01 and 0.05 g. At the same time difference between partial pressures of CO<sub>2</sub> and CO in gas stream and graphite layer was substantial. For example, at the rate of interaction of carbon dioxide with graphite equal to  $3.16 \cdot 10^{-6} \text{ mol s}^{-1}$  it was obtained according to formula (16) that  $\varepsilon = 0.39$ . This means that average value of CO<sub>2</sub> partial pressure in gas phase is 1.64 times higher than that in graphite layer.

**TABLE 1 : The dimensions and definition ranges of physical and chemical variables, used in calculations according to formulae (16, 17)**

Variable	Dimension	Definition range
$\varepsilon$	Dimension less	0 ÷ 1
$C_R, C_{R(o)}$	mol m <sup>-3</sup>	1 ÷ 1000
$\Phi_{cl}$	mol s <sup>-1</sup> m <sup>-2</sup>	10 <sup>-4</sup> ÷ 10 <sup>-1</sup>
$D$	m <sup>2</sup> s <sup>-1</sup>	(1.2 ÷ 2.0) · 10 <sup>-4</sup>
$X_{cl}$	m	0.033
$\gamma_v$	m <sup>2</sup> s <sup>-1</sup>	(0.95 ÷ 1.25) · 10 <sup>-4</sup>
$U_F$	m s <sup>-1</sup>	(0.5 ÷ 1.0) · 10 <sup>-2</sup>
$\Delta T$	K	0 ÷ 5
$\sigma_{SB}$	J m <sup>-2</sup> s <sup>-1</sup> K <sup>-4</sup>	5.67 · 10 <sup>-8</sup>
$(\frac{dQ}{d\tau})_{\max}$	J s <sup>-1</sup>	0.8 ÷ 16
$\phi'_{cl}$	m <sup>2</sup>	(5 ÷ 20) · 10 <sup>-4</sup>

**TABLE 2 : The dependence of graphite consumption rate ( $N_c$ ), apparent rate constant ( $k_2 \cdot [C_{(g)}]$ ), calculated graphite layer temperature ( $T / ^\circ\text{C}$ ) and average carbon dioxide partial pressure on graphite initial weight**

Graphite weight, g	$N_c / 10^{-6} \text{ mol s}^{-1}$	CO <sub>2</sub> partial pressure, bar		$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$T / ^\circ\text{C}$
		in gas stream	in graphite layer		
0.01	0.676	0.99	0.964	10.56	1000
0.05	3.18	0.96	0.92	10.21	999
0.2	5.97	0.89	0.63	8.33	997
0.5	9.375	0.83	0.43	9.375	995

All further experiments were performed using initial weights equal to 0.02 g and CO<sub>2</sub> flowing rate of 50 cm<sup>3</sup> min<sup>-1</sup>. Temperature difference between gas phase and graphite layer was not been taken into account due to its insignificance at small weights (as mentioned afore). The difference between gas concentrations in steam and on graphite surface was taken into account. The values of  $\varepsilon$  were calculated according to equation (16) and then actual gas concentrations were calculated.

## Studying kinetics of C + CO<sub>2</sub> reaction with graphite doped by various additives

Kinetic data for gasification of pure graphite and graphite with additives of 0.5, 1.0 and 2.0 mol % of calcium oxide, 2.0 mol % of magnesium oxide, 0.2 mol % CaO + 0.8 mol % MgO, 0.1, 0.25 and 0.5 mol % of strontium carbonate 0.5 mol % of strontium oxide 0.5 and 1.0 mol % of metallic iron, 1.0 mol % of iron (II) and iron (III) oxides are presented in TABLE 3 at temperature range of 900-1200°C with temperature alteration step of 50°C. Express in gap parent rate constant in form of Arrhenius equation, values of activation energy  $E_A$  and prefactor  $A$  are calculated.

The dependencies between  $E_A$  and  $\log A$  are plotted for three different catalyst groups – one for calcium and magnesium oxides, one for strontium carbonate and oxide and one for iron and iron oxides. These relationships are approximated using less squares technique. The graphic representations of these relationships are presented at Figures 2, 4 and 6. The values of  $E_A$  and  $\log A$  for pure graphite are marked in these figures only for comparison; they were not used for less squares technique optimization.

In order to verify isokinetic relationship hypothesis Arrhenius relations for each group of catalysts are plotted. Isokinetic temperatures are calculated according to method, proposed in<sup>[25,26]</sup>. The statistical criteria which allow accept or reject isokinetic hypothesis, proposed by the authors of<sup>[27]</sup> are used.

**TABLE 3 :** The data on gasification rate ( $N_c$ ), apparent rate constant ( $k_2 \cdot [C_{(g)}]$ ), activation energy ( $E_A$ ) and pre-exponential factor ( $A$ ) for gasification of graphite with various additives

$T / ^\circ\text{C}$	Graphite without additives (C)		C+0.5 mol % CaO	
	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$
900	–	–	1.8	1.34
950	–	–	2.94	2.56
1000	0.5	0.38	6.97	6.09
1050	1.18	0.91	14.5	15.0
1100	1.14	1.19	21.1	23.6
1150	1.89	1.58	–	–
1200	3.11	2.75	–	–
$E_A / \text{kJmol}^{-1}$	141.2 ± 16.9		201.1 ± 10.7	
log A	0.438 ± 0.246		4.045 ± 0.441	
$T / ^\circ\text{C}$	C+1 mol % CaO		C+2 mol % CaO	
	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$
900	0.87	0.61	0.66	0.47
950	1.95	1.47	1.20	0.88
1000	4.61	3.53	5.30	4.49
1050	8.85	7.39	11.9	10.6
1100	17.2	17.7	21.9	24.9
$E_A / \text{kJmol}^{-1}$	223.5 ± 5.1		279.2 ± 22.0	
log A	4.724 ± 0.209		7.031 ± 0.907	
$T / ^\circ\text{C}$	C+2 mol % MgO		C + 0.2 mol % CaO + 0.8 mol % MgO	
	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$
950	0.83	0.61	1.67	0.86
1000	1.09	0.82	2.16	1.64
1050	3.19	1.57	10.8	10.2
1100	4.28	3.43	17.2	17.8
$E_A / \text{kJmol}^{-1}$	161.6 ± 25.8		304.7 ± 48.7	
log A	1.623 ± 1.040		7.887 ± 1.967	
$T / ^\circ\text{C}$	C+ 0.1 mol % SrCO <sub>3</sub>		C+ 0.25 mol % SrCO <sub>3</sub>	
	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$
950	0.66	0.48	0.98	0.72
1000	1.57	1.24	2.4	1.89
1050	6.46	6.27	10.7	10.0
1100	27.7	37.1	30.0	43.8
$E_A / \text{kJmol}^{-1}$	407.3 ± 47.7		389.1 ± 36.7	
log A	11.96 ± 1.92		11.38 ± 1.48	

$T / ^\circ\text{C}$	C+ 0.5 mol % SrCO <sub>3</sub>		C+ 0.5 mol % SrO	
	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$
900	0.54	0.37	2.08	1.57
950	1.65	1.24	5.47	4.61
1000	5.12	4.88	5.30	10.4
1050	18.1	20.9	11.9	32.9
1100	32.2	48.8	21.9	57.6
$E_A / \text{kJmol}^{-1}$	337.3 ± 12.8		245.9 ± 10.7	
log A	9.557 ± 0.526		6.156 ± 0.441	
$T / ^\circ\text{C}$	C + 0.5 mol % Fe		C + 1.0 mol % Fe	
	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$
1000	0.72	0.48	1.88	1.27
1050	1.7	1.33	2.85	2.36
1100	3.19	2.63	5.04	4.28
1150	5.59	4.92	9.69	9.05
1200	12.1	13.6	23.5	28.5
$E_A / \text{kJmol}^{-1}$	249,2 ± 14.0		234,3 ± 25.3	
log A	4.915 ± 0.533		4.642 ± 0.968	
$T / ^\circ\text{C}$	C+ 1.0 mol % FeO		C+ 1.0 mol % Fe <sub>2</sub> O <sub>3</sub>	
	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$	$N_c / 10^{-7} \text{ mol s}^{-1}$	$(k_2 \cdot [C_{(g)}]) / 10^{-5} \text{ mol s}^{-1} \text{ g}^{-1}$
1000	1.79	1.46	1.83	1.55
1050	3.17	2.62	4.17	3.63
1100	5.34	4.76	7.44	10.4
1150	17.8	19.0	24.8	32.9
1200	29.8	41.4	33.2	50.1
$E_A / \text{kJmol}^{-1}$	268.7 ± 30.8		286.0 ± 18.3	
log A	6.081 ± 1.178		6.906 ± 0.699	

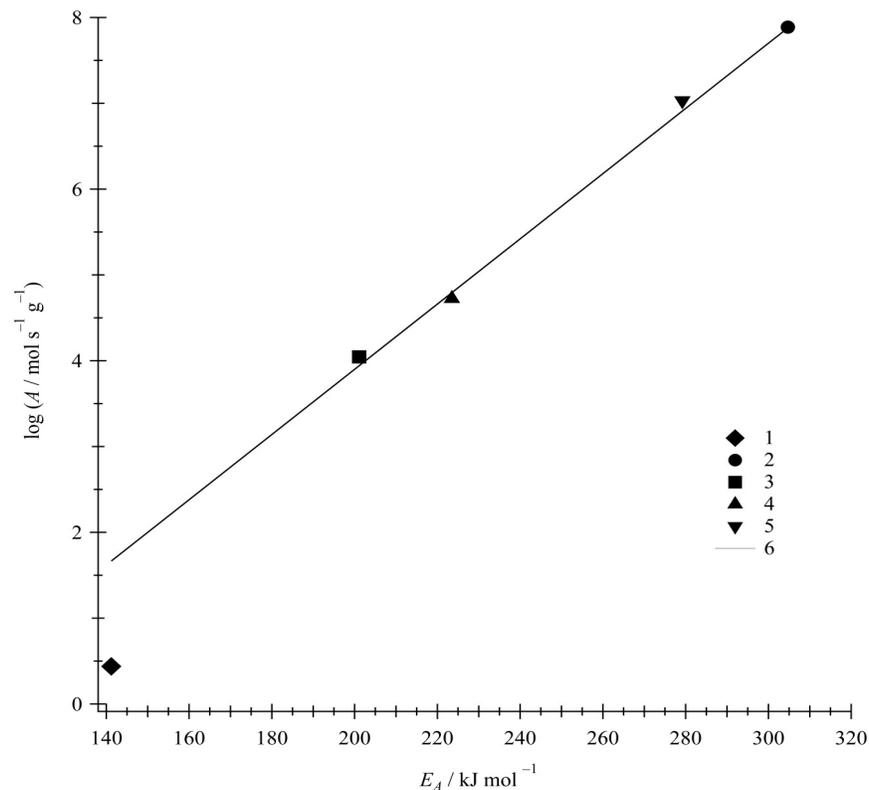
### (a) Calcium and magnesium oxides

It should be noted that catalytic activity of CaO is much better than that of MgO. For example, rate of graphite gasification reaction at 1100°C increases in following sequence: pure graphite (C) > C + 2% MgO > C + 0.2% CaO + 0.8% MgO > C + 0.5% CaO > C + 2% CaO. Reaction rate of sample of C + 1.0% CaO slightly drops out of this sequence. Therefore, addition even of 0.2 mol % of calcium oxide speeds up the reaction 5 more times than addition of 2.0 mol % magnesium oxide. However, addition of MgO raises activation energy and prefactor values dramatically.

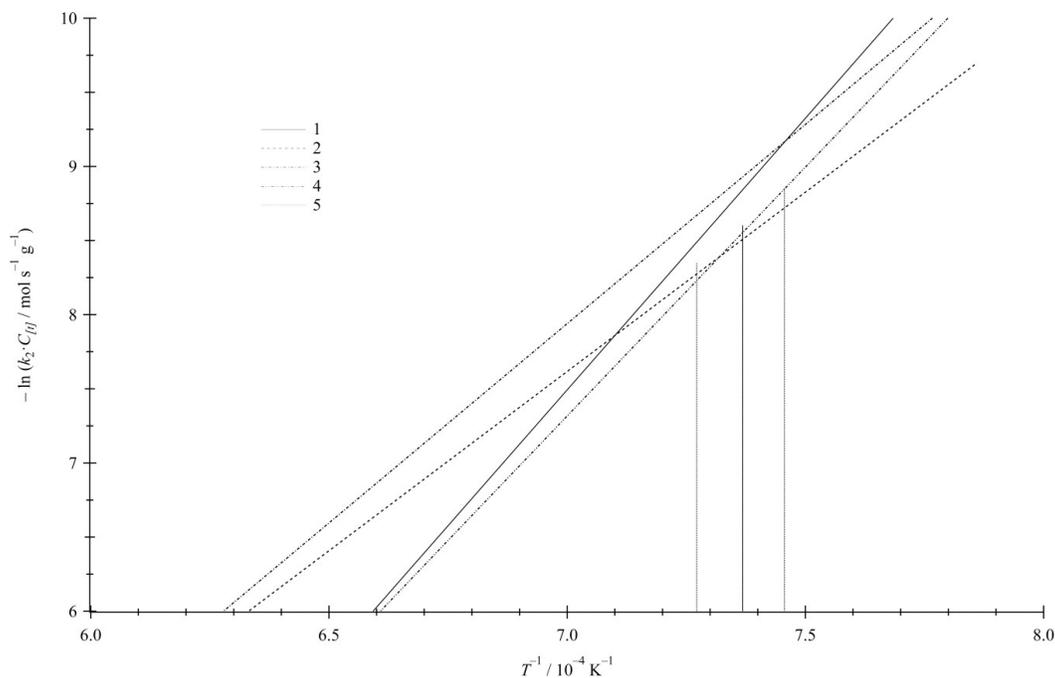
As can be seen from TABLE 3, both values of  $E_A$  and  $A$  grow with increment of added calcium oxide amount. This is clearly shown at Figure 2. Therefore, compensation effect occurs.

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Figure 3 shows the Arrhenius plots and MgO. Isokinetic temperature  $T_\theta$  is equal to 1084 ( $\ln(k_2 \cdot [C_{(g)}]) = f(\frac{1}{T})$ ) for reactions with additives of CaO  $\pm 18^\circ\text{C}$ .



**Figure 2 :** The dependency of prefactor logarithm ( $\log A$ ) on activation energy ( $E_A$ ) for graphite gasification reaction with presence of: 1 – pure graphite (C); 2 – C + 0.2 mol % CaO + 0.8 mol % MgO; 3 – C + 0.5 mol % CaO; 4 – C + 1 mol % CaO; 5 – C + 2 mol % CaO; 6 – approximated line,  $\log A = (38 \pm 1) \cdot 10^{-3} \cdot E_A - (3.7 \pm 0.3)$ ,  $R^2 = 0.9977$ .



**Figure 3 :** Arrhenius plots for graphite gasification reaction with additives of: 1 – 0.2 mol % CaO + 0.8 mol % MgO; 2 – 0.5 mol % CaO; 3 – 1.0 mol % CaO; 4 – 2.0 mol % CaO; 5 – isokinetic temperature  $T_\theta = (1357 \pm 18)$  K.

**(b) Strontium carbonate and oxide**

The data on rate constants of C + CO<sub>2</sub> reaction in presence of strontium compounds are listed in TABLE 3. As can be seen from table, at temperature range of 900-1000°C the highest gasification rate is achieved with addition of strontium oxide. The apparent rate constant grows with strontium carbonate content increase from 0.1 до 0.5 mol % at all studied temperatures. At low temperatures catalytic activity of strontium carbonate is less effective, than that of strontium oxide, because reaction rates with addition of strontium carbonate are lower, than with oxide. However, when temperature increases up to 1100°C, reaction rates become relatively equal. This is because strontium carbonate begins to decompose at temperatures above 1020°C forming strontium oxide.

The dependency between  $\log A$  and  $E_A$  for reaction with presence of strontium compounds is depicted at Figure 4. With activation energy decrease, prefactor drops also; therefore compensation effect is present

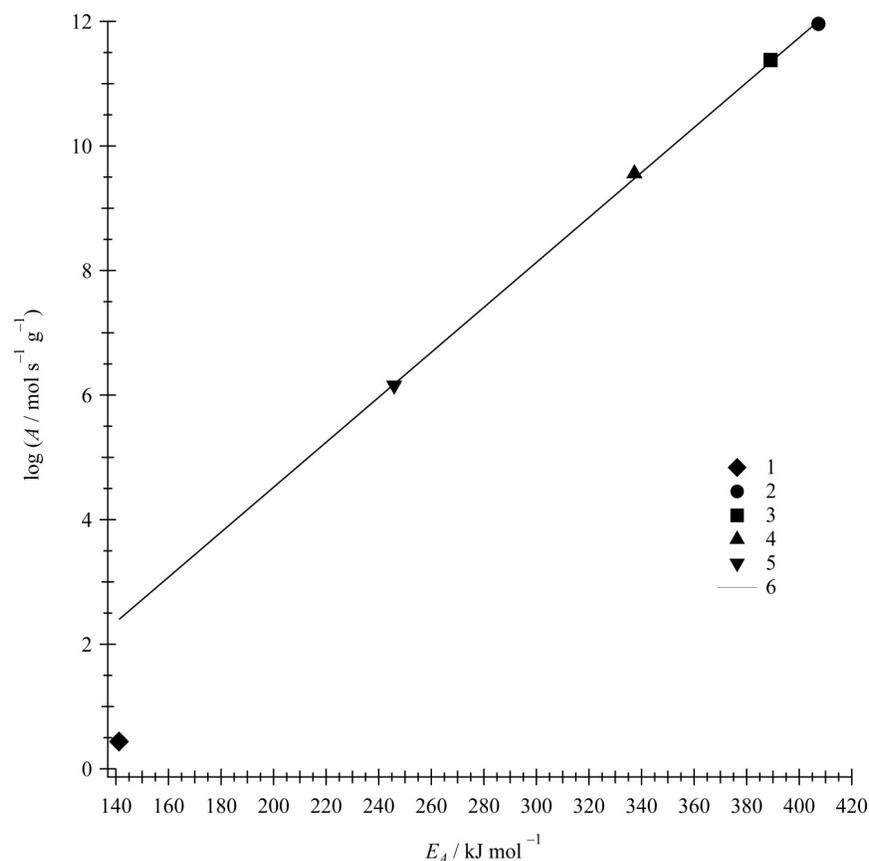
in this case.

The Arrhenius plots for corresponding reactions are shown at Figure 5. Isokinetic temperature can be calculated very precisely and is equal to  $1171 \pm 3^\circ\text{C}$ .

**(c) Iron and iron oxides**

In cases of adding metal iron to graphite gasification reaction speeding is observed only up to 900°C, in addition, reaction rate grows significantly with increasing of additive amount. Iron oxides increase rate of C+CO<sub>2</sub> reaction even more. In relation to iron compounds linear dependency between  $\log A$  and  $E_A$  is also present and has high approximation rate (see Figure 6). However, isokinetic temperature is determined with large uncertainty (see Figure 7). Moreover, statistical verification of isokinetic hypothesis<sup>[26]</sup> fails in this case, and it is not possible to argue about reliable compensation. According to<sup>[28]</sup> it is quite possible that observed correlation between  $\log A$  and  $E_A$  is a consequence of random data scarce.

According to<sup>[28]</sup> the formation of CO comes easier



**Figure 4 :** The dependency of prefactor logarithm ( $\log A$ ) on activation energy ( $E_A$ ) for graphite gasification reaction with presence of: 1 – pure graphite (C); 2 – C + 0.1 mol % SrCO<sub>3</sub>; 3 – C + 0.25 mol % SrCO<sub>3</sub>; 4 – C + 0.5 mol % SrCO<sub>3</sub>; 5 – C + 0.5 mol % SrO; 6 – approximated line,  $\log A = (361 \pm 5) \cdot 10^{-4} \cdot E_A - (2.7 \pm 0.2)$ ,  $R^2 = 0.9995$ .

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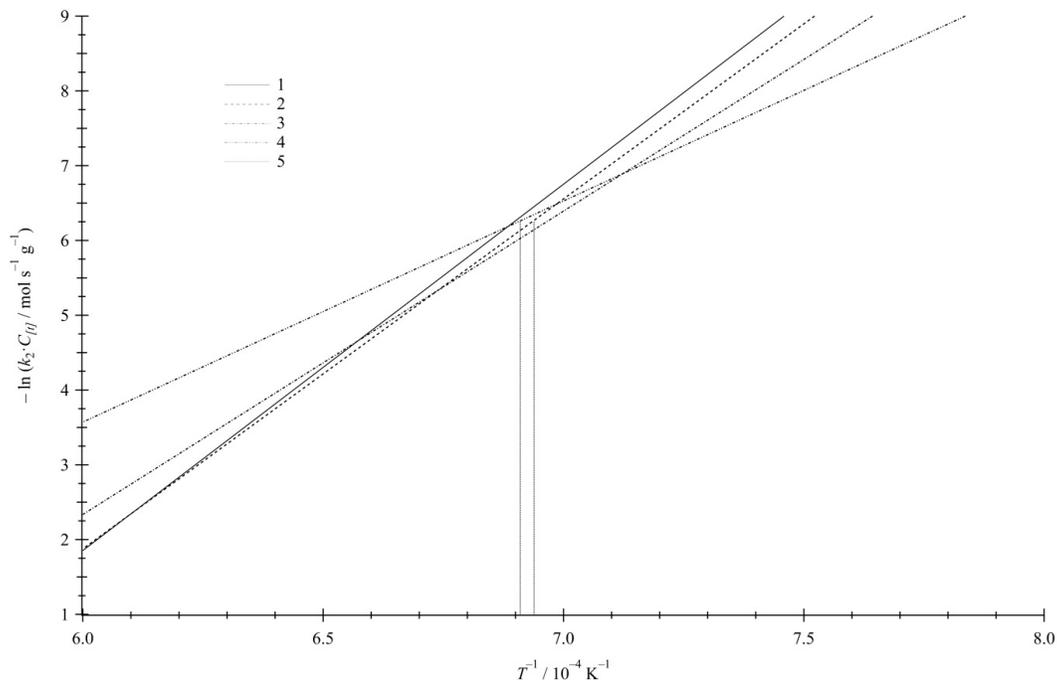


Figure 5 : Arrhenius plots for graphite gasification reaction with additives of: 1 – 0.5 mol % SrO; 2 – 0.5 mol % SrCO<sub>3</sub>; 3 – 0.25 mol % SrCO<sub>3</sub>; 4 – 0.1 mol % SrCO<sub>3</sub>; 5 – isokinetic temperature  $T_0 = (1444 \pm 3)$  K.

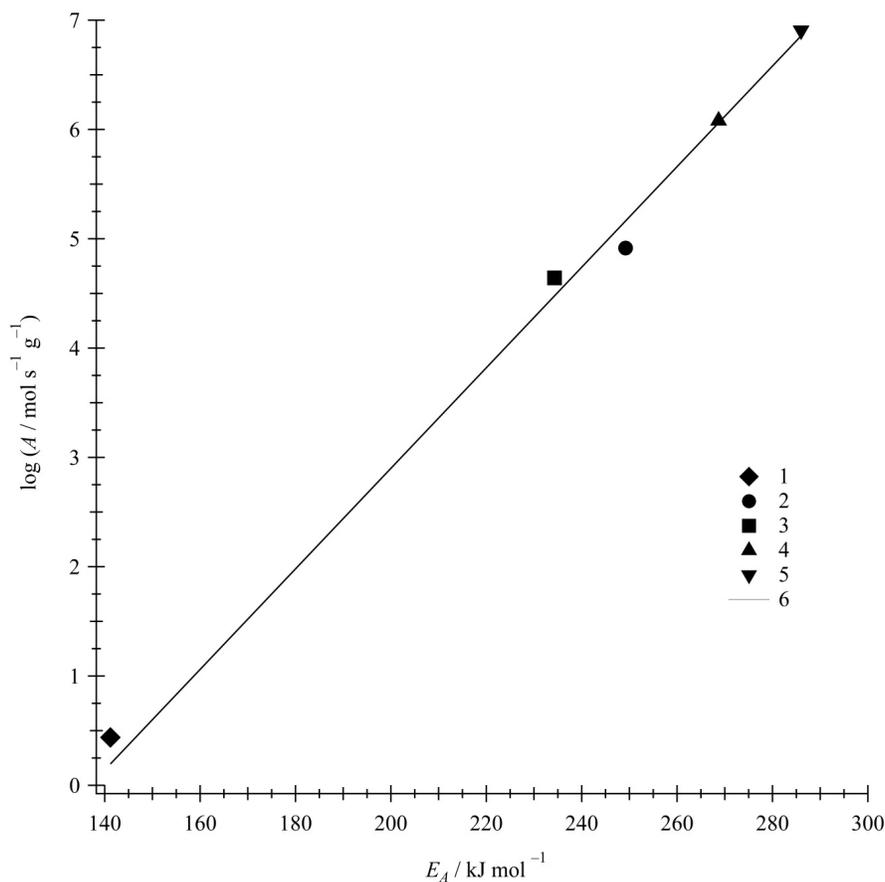
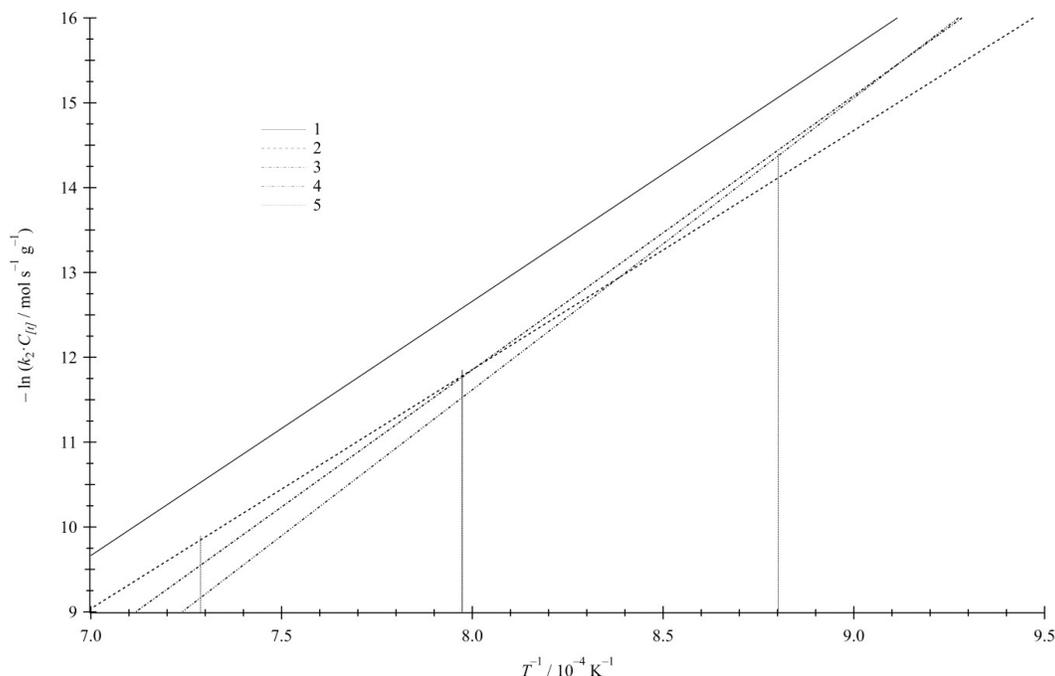


Figure 6 : The dependency of prefactor logarithm ( $\log A$ ) on activation energy ( $E_A$ ) for graphite gasification reaction with presence of: 1 – pure graphite (C); 2 – C + 0.5 mol % Fe; 3 – C + 1 mol % Fe; 4 – C + 1 mol % FeO; 5 – C + 1 mol % Fe<sub>2</sub>O<sub>3</sub>; 6 – approximated line,  $\log A = (46 \pm 5) \cdot 10^{-3} \cdot E_A - (6.3 \pm 1.4)$ ,  $R^2 = 0.9724$ .



**Figure 7 :** Arrhenius plots for graphite gasification reaction with additives of: 1 – 0.5 mol % Fe; 2 – 1.0 mol % Fe; 3 – 1.0 mol % FeO; 4 – 1.0 mol % Fe<sub>2</sub>O<sub>3</sub>; 5 – isokinetic temperature  $T_0 = (1254 \pm 118)$  K.

if C – C bonds, that should be broken, are weakened. This can take place, if graphite crystal lattice transfers an electron to intermediary metallic ion or if covalent bond forms between carbon matrix and metal atom.

According to data in present study the following consequence of gasification reaction rate increase can be provided: C (without additives) > Fe > MgO > FeO > CaO > SrO. It is almost coincident with consequence of oxides ranged with respect to electron work function decreasing. Therefore, catalytic properties of noted compounds can be linked with their ability to donate electrons, which take part in active centers formation, weakening C – C bonds and increasing graphite gasification rate.

## CONCLUSIONS

1. Kinetics of reverse Boudouard reaction on graphite was studied with presence of additives of calcium, magnesium, strontium, iron (II) and iron (III) oxides, strontium carbonate and metallic iron. Apparent rate constants are calculated.
2. The dependencies between activation energy and pre-exponential factor for various catalysts were studied. Compensation effect was revealed. Isokinetic temperatures were calculated.

3. The relationship between electron work functions of the oxides and their catalytic activity was noticed.

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