

# THE ISOKINETIC EFFECT AS RELATED TO THE ACTIVATION ENERGY FOR THE GASES DIFFUSION IN COAL AT AMBIENT TEMPERATURES

## Part II. Fick's diffusion and isokinetic effect

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Using the earlier theoretical achievements, it was possible to elaborate a full description of adequate transport properties, including the determination of activation energy for the sorption of such gases as CO<sub>2</sub> and CH<sub>4</sub> on coal, as well as the formulation of model solutions. The interrelation of the kinetic-diffusion parameters was also demonstrated. We then analyse the experimental kinetic curve over the entire time range with a constant of a kinetic character and with the application of two typical solutions of Fick's law, for fast and slow processes. These three constants may be compared with one another, since they are expressed using the same unit, and, in effect, may be used to determine the isokinetic effect. Finally, we suggest a new approach to the estimation of the activation energy, despite the fact that the measurements were performed at two close temperatures, 293 and 303 K.

In the presented investigations, the isokinetic effect for sorption process has been found to be statistically less significant when compared with that of chemical reactions/processes.

**Keywords:** activation energy, coal, isokinetic effect, sorption process

### Introduction

The investigations in the pressures range up to about 0.1 MPa of the sorption kinetics and diffusion of gases in coal represent one of the basic methods which allow to examine these phenomena taking into account the natural properties of coal sorbents [1].

It is often assumed that the activation energy is directly proportional to the heat of adsorption [2]. In order to determine the activation energy for diffusion, it is necessary to carry out the investigations at least at two different temperatures, accepting the law of the mathematical structure of Arrhenius classical law [2–5]:

$$P = P(\infty) \exp(-E/RT) \quad (1)$$

The quantity  $P$  in general can be expressed as a diffusion coefficient ( $D$ ) [2, 6–8], diffusivity ( $D/r^2$ ) [2, 9] or as any other constant with the character of a kinetic constant ( $k$ ) [10]. Constants  $P(\infty)$  are limiting values for the temperature  $T \rightarrow \infty$ . The formulation of any other possibilities of defining the rate constants, however, should be made with caution. The main problem here is the use of justified terminology, because of the dependence of the thermodynamic diffusion coefficient on temperature [8, 11]:

$$D_T = BRT \quad (2)$$

It is obvious that an alternative choice of the definition of the kinetic rate constant will affect the values of the calculated parameters of Arrhenius equation. To avoid any misunderstanding, it is enough to use the Eq. (1) for the analysis of the experimental data [3, 4].

Next, from literature we know well the unexpected correlation between the parameters of Arrhenius law for many types of chemical reactions/processes, which is referred to compensation (CE) [12–15] or isokinetic effect (IE) [16–18]. The latter effect can be represented as the linear dependence:

$$\ln P(\infty) = -\frac{E}{RT_{\text{iso}}} + \ln C_{\text{iso}} \quad (3)$$

### The aim of the study

The results of previous investigations may be presented in a review.

One approach to understanding the diffusion process in the coal sorbent was presented in paper [19], in which departures from the simplified analytical solution of the partial differential equation (Eq. (5) or even better, Eq. (3), Part I in [1], short time range) for experimental data, presented in the func-

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tional scales  $y$  vs.  $\sqrt{\tau}$ , were observed. This provides a basis for carrying out further theoretical analysis in our successive studies.

In the study [10] the sorption of small molecule gases (CO<sub>2</sub> and CH<sub>4</sub>) on anthracite (isothermal-isobaric conditions, ambient temperatures) has been described in the whole range of the measured times in the form of a kinetic equation F2. Detailed analyses of the justification of using equation F2 for modelling the diffusion of gases in coal and for determining the model parameters from the experimental curves for kinetics in relation to variation of the size grain of coal samples were performed. It was clearly stated that model F2 enables not only to estimate the constant of a kinetic nature but also allows to predict some measure of the distance from the state of sorption equilibrium, such as limit parameter  $y_\infty$ . Moreover, the authors proved the existence of a close relation between the kinetic constant  $k$  and the diffusion coefficient  $D$  resulting from Fick's classic law. The proposed model F2 is definitely justified, as opposed to the pseudo-second-order model cited in the literature [20–25], since the fractional uptake rate in our model is directly proportional to the expression  $((y_\infty - y)/y_\infty)^2$  [10]. In consequence, the kinetic constant  $k$  is an expression adequate to the kinetic model of the second order in relation to asymptotic values  $y_\infty$ .

Next, the empirical verification of the model F2 for the sorption of CO<sub>2</sub> and CH<sub>4</sub> on coal was presented for the first time in paper [26]. The theoretical kinetic curves based on our model equation were compared with the experimental data.

Moreover, in paper [1], computational experiments providing adequate estimates of the transport processes were demonstrated in order to explain the experimentally observed changes in the diffusion coefficient in time. Finally, the two aforementioned different kinetic models (the classic approach introduced by Fick and the empirical model F2) may be used to check the effects of temperature on kinetic curves.

The present study also discusses the possibilities of modelling the sorption kinetics process on coal, at the same time focusing on the occurrence of the isokinetic effect.

## Theoretical aspect

### Equations

It is proposed that the experimental kinetic curve of the sorption process for  $y=a/a_m$ , and for three linear forms, is as follows:

- in the whole measured time range [10]:

$$\frac{\tau}{y} = \frac{\tau}{y_\infty} + \frac{1}{k} \tag{4}$$

- in the initial portion of the plot [1], i. e. for the fractional uptake  $0 < y < y_i$ , where  $y_i$  for many authors is in the range  $0.5 < y_i < 1$ :

$$y^2 = \frac{36D}{\pi r^2} \tau = C_1 \tau \tag{5}$$

- in the final portion of the plot [1], e.g. for  $y > y_i$ :

$$-\ln \frac{\pi^2}{6} (1-y) = \frac{\pi^2 D}{r^2} \tau = C_2 \tau + C_3 \tag{6}$$

where  $C_1$ ,  $C_2$  and  $C_3$  are the constants, and  $C_3$  has often the character of an incidental free term ( $C_3 \neq 0$ ).

Equation (6) is the first term of a series, and is often used with Fick's II law [27]:

$$y = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 D \tau / r^2}}{n^2} \tag{7}$$

In accordance with the studies [1–4, 7, 8, 27–32] for different sorbent-sorbate systems we can observe the correctness of Eqs (5) and (7), either independent of each other or simultaneous. In the literature related to this problem, kinetic equations for slow processes – Eq. (2) in [1] – are proposed for the conditions referring most often to a spherical sorbent with radius ( $r$ ).

For the analysis of Eq. (3), the mathematical formulae (4) to (6) have been used, which allow to determine the constants:  $k$ ,  $C_1$  and  $C_2$ , respectively for two temperatures. Thus, a set of diffusion-kinetic constants has been obtained, in accordance with Eq. (1) for  $P=k$ ,  $C_1$  and  $C_2$  and, accordingly, for  $P(\infty)=k(\infty)$ ,  $C_1(\infty)$  and  $C_2(\infty)$  of identical dimension ( $s^{-1}$ ). The relation of the expression containing a series (Eq. (7)) to its first term from Eq. (6) requires a commentary concerning the calculation technique.

After inserting the constant  $C_2$  from Eq. (6) into Eq. (7), we obtain:

$$y = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 C_2 \tau}}{n^2} \tag{8}$$

Formally, both constants  $C_2$  to be determined should be equal to each other. However, they are not from the point of view of the calculation techniques, which had been demonstrated earlier [1]. Starting with series (8), the kinetic constant is calculated using nonlinear procedures, whereas for higher values of fractional uptake (e.g. literature [32] gives  $y_i > 0.86$ ), we may select one from the two possibilities according to Eq. (6):

- estimation for one-parametric line, i.e.  $C_3=0$ ,
- estimation for two-parametric line,  $C_3 \neq 0$ .

A detailed analysis of the discussed problem for the examined cases (four grain fractions, two temperatures and two gases) show that, as the number of terms ( $n$ ) in Eqs (6) or (8) increases, the free term  $C_3$  tends to zero, and, simultaneously, the constant  $C_2$  is estimated in a more reliable way. It is apparent that the isokinetic effect is determined for the rate constants according to Eqs (4) to (6). In this case, it is important to discuss the extent of Fick's law applicability taking into account Eq. (5) and Eqs (6) to (8).

### Fick's law according to Eq. (5)

It is proposed that the extent of the validity of formula (5) be defined by the conventional measure of length:

$$d = \left[ y_i^4 + \left( \frac{\tau_i}{\tau_{0.5}} \right)^2 \right]^{1/2} \quad (9)$$

where  $d$  – dimensionless measure of length, and  $y_i$  – fractional uptake for  $i^{\text{th}}$  time,  $\tau_{0.5}$  – half-time of the sorption process for  $y=0.5$ , s,  $\tau_i$  – time for which the linear dependence (5) is valid, s.

For the adopted scale, the suitability of Eq. (5) in relation to Eq. (9) can be presented in the most convenient manner as:

$$u = (d/d_{\max}) \cdot 100\% \quad (10)$$

where  $d_{\max} = \sqrt{1+4^2} = 4.123$  is a constant value and it does not depend on the diffusion coefficient  $D$ .

The method of application of the discussed procedure is shown in Table 1. The applicability of Eq. (5) varies within very wide limits, from 0.4 to 94.4%, and it depends to a very high degree on temperature.

On the other hand, for a small specific surface area ( $R_4 - S_{\text{BET}} = 0.11 \text{ m}^2 \text{ g}^{-1}$  [10]) at the same temperature conditions used in this study, the fractions ( $u$ ) have been estimated at 0.6% ( $\text{CH}_4$ ) and 3.62% ( $\text{CO}_2$ ).

The results suggest that the relations (9) and (10) are quite general and very useful in calculations.

### The isokinetic effect (IE)

In Eq. (3), at the temperature  $T=T_{\text{iso}}$ , the rate constant has constant  $C_{\text{iso}}$  value for all cases considered in the data set. Agreement with Eq. (3) has been reported in literature for many heterogeneous kinetic processes.

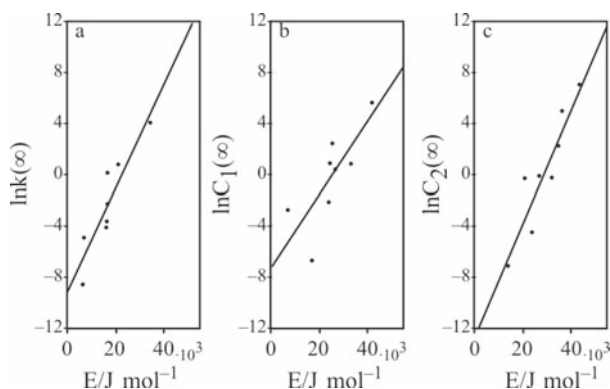
The shape of the dependence (3) for chemical reactions/processes both in isothermal and in dynamic conditions, as observed for many examples, has its origin in the assumed hierarchy of factors, according to their importance. These factors are defined in the literature data [12–18, 33–38].

In the majority of the published data, the isokinetic effect appears with the statistical significance  $R^2 > 98\%$ , and is thus very distinct (for chemical reactions/processes).

Figures 1a-c show the graphic interpretation of Eq. (3) for the constant –  $k(\infty)$  (Fig. 1a),  $C_1(\infty)$  (Fig. 1b) and  $C_2(\infty)$  (Fig. 1c), respectively. In accordance with the cited sequence, the significance level

**Table 1** Estimated values of the conventional measure of length (Eq. (10)), data as an example

Sorbate	Temperature/K	Grain fraction of coal samples	Range of fractional uptake by Eq. (9)	$d$ (Eq. (9))	$u$ (Eq. (10))/%
CH <sub>4</sub>	293	R1	0.5657	2.06	50.0
		R2	0.3317	0.32	7.7
		R3	0.1871	0.05	1.2
		R4	0.1225	0.02	0.4
	303	R1	0.6442	3.34	80.9
		R2	0.4123	0.66	16.5
		R3	0.2025	0.08	1.9
		R4	0.1378	0.02	0.6
CO <sub>2</sub>	293	R1	0.6928	3.67	89.03
		R2	0.4123	0.50	12.23
		R3	0.3317	0.30	7.24
		R4	0.2828	0.12	2.98
	303	R1	0.7141	3.89	94.38
		R2	0.4583	0.71	17.11
		R3	0.3742	0.38	9.20
		R4	0.2828	0.15	3.62



**Fig. 1** Graphical interpretation of Eq. (3) for individual kinetic parameters a – constant  $k(\infty)$ , b – constant  $C_1(\infty)$ , c – constant  $C_2(\infty)$ , respectively, and for the sorption systems

(and determination coefficient  $R^2$ ) for dependence (3) is equal to:

for  $k(\infty)$ :  $0.0015 (R^2=0.8337)$

for  $C_1(\infty)$ :  $0.0190 (R^2=0.6298)$

for  $C_2(\infty)$ :  $0.0010 (R^2=0.8507)$

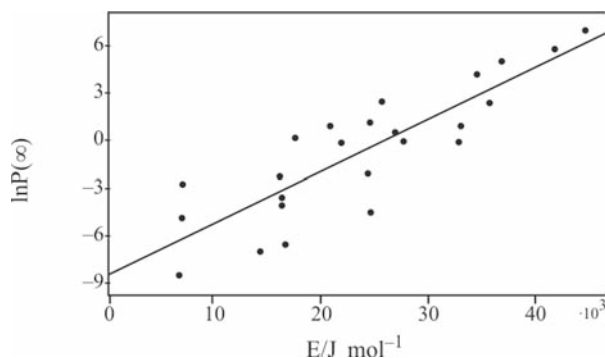
The significance levels are usually close to those statistically accepted at the level of 0.001 (99.9% probability) to 0.02 (98%). However, they are only satisfactory when equal to 63–85%.

After combining all the parameters, we obtain the analytical form of Eq. (3) – Fig. 2:

$$\ln P(\infty) = 0.3444 \cdot 10^{-3} E - 8.3686 \quad (11)$$

where  $P(\infty)$  is  $k(\infty)$  and  $C_1(\infty)$ ,  $C_2(\infty)$ , respectively, and  $R^2=0.7370$  for the significance level  $0.0^{(5)}$ .

From Eq. (11) the isokinetic temperature ( $T_{iso}=365.6$  K) and the isokinetic constant ( $C_{iso}=18.16 \cdot 10^{-3} \text{ s}^{-1}$ ) for sorption kinetics are obtained. By theoretically assuming the best estimation of the isokinetic effect, it can be stated that the experiments were carried out below the isokinetic temperature



**Fig. 2** Compensation line showing a linear correlation of all the parameters ( $k(\infty)$ ,  $C_1(\infty)$ ,  $C_2(\infty)$ ), for the sorption systems under study

( $T < T_{iso}$ ). At isokinetic temperature, a convergence of the values of all three considered constants of kinetic character  $k$ ,  $C_1$ ,  $C_2$ , which result from three different mathematical forms (Eqs (4)–(6)), takes place. This confirms the earlier speculations about Fick’s model of sorption process [10].

### Conclusions

- When analyzing the experimental kinetic curves for the sorption process of  $\text{CO}_2$  and  $\text{CH}_4$  at two temperatures ( $T=293$  and  $303$  K) (isothermal-isobaric conditions) by means of Fick’s law for fast processes (high diffusion coefficient) and slow processes (lower diffusion coefficient), and for the whole range of the measured times according to F2 kinetics, it has been established that the determined activation energies satisfy the isokinetic effect. The linear correlation between the logarithm of the pre-exponential constant and the activation energy for diffusion makes it necessary to consider these quantities together. The observed dependences for the system: coal – gases are, however, observed at a lesser statistical significance (according to the determination coefficient) than in the case of many chemical reactions/processes.
- The performed investigations have revealed the different character of the coal fraction R1 for both gases ( $\text{CO}_2$  and  $\text{CH}_4$ ). Moreover, at both temperatures, the applicability of Fick’s law (Eq. (5)) for  $\text{CO}_2$  according to the scale (Eq. (10)) is equal to 94.4%.
- Assuming statistical significance of the kinetic effect (Eq. (11)) - although it is equal only to 73.7% – the temperatures under examinations are lower than the isokinetic temperature. Thereby, at the isokinetic temperature the values of all three kinetic rate constants under consideration ( $k$  – typically kinetic and  $C_1$ ,  $C_2$  – similar to one another) are identical, even though they result from three different mathematical forms of Fick’s II law and the kinetic model F2.
- In our paper, we make the following implications:

$$k, C_1, C_2 \rightarrow E \rightarrow \text{isokinetic effect (IE)}$$

which we find satisfactory, despite the fact that they were based on experimental data obtained for a close range of temperatures.

- It must be emphasized, however, that the observed effect is of mixed nature, i.e. both physicochemical and kinetic, on account of the character of the respective diffusion-kinetic constants.

## Nomenclature

$a$	Amount adsorbed after time $\tau$ , mmol g <sup>-1</sup>
$a_m$	Maximal amount adsorbed at equilibrium state, mmol g <sup>-1</sup>
$B$	Hydrodynamics parameter of diffusing particle, mol s kg <sup>-1</sup>
$C_1, C_2, C_3$	Complex kinetic parameter in Eqs. (5), (6), ( $C_2$ is $C$ in Part I, [1]), s <sup>-1</sup>
$C_{iso}$	Constant at the isokinetic point, s <sup>-1</sup>
$d$	Dimensionless measure of length
$D$	Fickian diffusivity, cm <sup>2</sup> s <sup>-1</sup>
$D_T$	Thermodynamic diffusion coefficient, m <sup>2</sup> s <sup>-1</sup>
$E$	Activation energy, J mol <sup>-1</sup>
$F$	Statistical test
$F1, F2$	Mechanism symbol according to first and second kinetic order, respectively
$k$	Kinetic constant, s <sup>-1</sup>
$n$	Integer, $n \geq 1$ , number of terms of the series
$P$	$k$ or $C_1, C_2$ , s <sup>-1</sup>
$P(\infty)$	Limiting value of the constant $P$ for $T \rightarrow \infty$ , s <sup>-1</sup>
$r$	Grain radius, cm
$R^2$	Coefficient of linear determination, $0 \leq R^2 \leq 1$
$R$	$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$T$	Absolute temperature, K
$u$	Fractional values defined by Eq. (10)
$y = a/a_m$	Fractional uptake, $0 \leq y \leq 1$
$y_i$	Fractional uptake for $i^{\text{th}}$ time

## Subscripts

$iso$  Refers to isokinetic point

## Greek symbols

$\tau$	Time, s
$\tau_{0.5}$	Half-time of the sorption process for $y=0.5$ , s
$\tau_i$	Time for which the linear dependence (5) is valid, s

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