ISSN 0361-5219, Solid Fuel Chemistry, 2017, Vol. 51, No. 2, pp. 111–114. © Allerton Press, Inc., 2017.
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Mathematical Simulation of the Hydrogenation of Borodino Coal

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Received June 8, 2016

Abstract—The kinetic and thermodynamic parameters of the hydrogenation of Borodino brown coal were calculated. With the use of equilibrium-kinetic analysis, the second-order reaction rate constants of forward and reverse reactions, the equilibrium constant, the activation energy, and the thermal effects of brown coal hydrogenation reactions were determined in a temperature range of 648–698 K at a hydrogen pressure of 10 MPa. In the course of the study, it was found that the experimental data are indicative of the adequacy of the equilibrium-kinetic analysis model for second-order reactions.

DOI: 10.3103/S0361521917020021

A combination of kinetic and equilibrium approaches to the studies of complex systems, in particular, chemical systems, is the subject matter of nonequilibrium thermodynamics as an academic discipline [1]. In the current context of the development of computer technology and software, computational methods, including the thermodynamic calculations of complex systems based on iterative procedures, are finding ever-increasing use in coal chemistry studies [2].

The thermodynamic properties of substances impose hard constraints on the kinetic parameters utilized for describing systems that change with time [3–5]. The dynamic nature of an equilibrium state is the reason for this circumstance. The apparent macroscopic invariability of the composition and properties of a system is a consequence of the fact that the buildup rate of each species $d[Mj]$ is equal to the rate of its disappearance $d(Mj)/dt = 0$ in the equilibrium state. For each independent stoichiometric equation of chemical reaction, the concentrations are related to each other by stoichiometric coefficients.

According to the second law of thermodynamics, any closed isolated system approaches an equilibrium state in which its properties become time-independent. If the numerical values of enthalpy and entropy and the equations of state of chemical system components are known, it is possible to accurately predict the chemical composition of the final equilibrium state. However, thermodynamics does not give any indications of the equilibration time and the behavior and composition of the system in the course of approaching equilibrium. Chemical kinetics, which studies the systems whose properties depend on time, can give answers to these questions.

The problem of the joint determination of the kinetic and equilibrium characteristics of reversible chemical processes can be solved because of a combination of probabilistic and deterministic descriptions within the framework of a united mathematical model [6, 7] based on the law of mass action. Malyshev et al. [8] developed an equilibrium-kinetic analysis method, which makes it possible to directly relate equilibrium and kinetic characteristics and to obtain additional information from a common body of experimental data, i.e., to intensify chemical studies.

Its form depends on the consideration of the reversibility, reaction steps, phase composition, and stoichiometry of a particular chemical process.

Previously, Baikenov et al. [9] presented a model of the equilibrium-kinetic analysis of the hydrogenation of an anthracene–benzothiophene model mixture in the presence of a catalyst containing iron and established that the calculated model of the equilibrium-kinetic analysis is adequate for second-order reactions. In this work, we consider in detail the equilibrium-kinetic analysis of a second-order reaction; this can be of general interest in terms of methodology because of taking into account optimum procedures for mathematical modeling and experimental data processing based on experience in the application of this method. In accordance with the above ideas, the aim of this work was to determine the thermodynamic

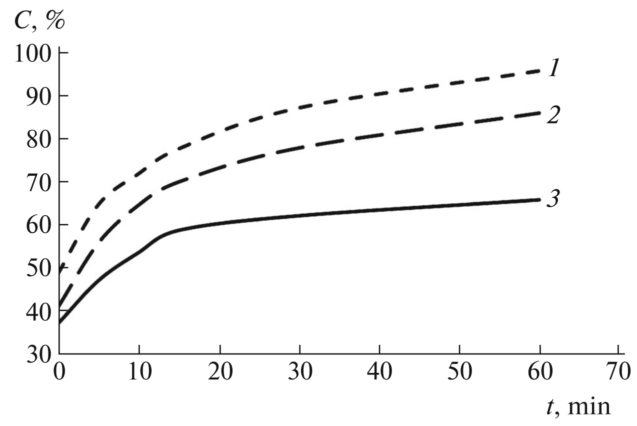

Fig. 1. Degree of conversion of the brown coal in a temperature range of 648–698 K: (*1*) 648, (*2*) 673, and (*3*) 698 K.

and kinetic parameters of the test process of brown coal hydrogenation by applying the method of equilibrium-kinetic analysis to second-order reactions.

The test process was the hydrogenation of Borodino brown coal in a temperature range from 648 to 698 K at an initial hydrogen pressure of 10 MPa [10]. The proximate and ultimate analyses of the test material were reported elsewhere [10]. The order of reaction was determined based on the law of mass action. With the use of the least squares method as applied to kinetic data represented in a linear form, from the slope of a straight line, we found that the hydrogenation of brown coal occurs by second-order reactions.

The equilibrium-kinetic analysis calculations were performed based on the concentration of the released product (oil + water):

$$\mathrm{OMC} + \mathrm{H_2} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{oil} + \text{water}.$$

Figure 1 illustrates the degree of conversion of the organic matter of coal (OMC).

Krichko et al. [10] found that the degree of conversion of the organic matter of coal increases with temperature and experiment time. They attempted at performing a computer simulation of chemical and phase equilibriums in a multicomponent system, which is reliable a priori information on the thermodynamic properties of each particular component.

The integral equilibrium-kinetic model of the hydrogenation of brown coal takes the form

$$\frac{3aD}{A-B}\left[-\frac{1}{6A^{2/3}}\ln\frac{(A^{1/3}-x)^2}{A^{2/3}+A^{1/3}x+x^2}+\frac{1}{A^{2/3}\sqrt{3}}\right.$$

$$\times\arctan\frac{2x+A^{1/3}}{A^{1/3}\sqrt{3}}+\frac{1}{6A^{2/3}}\ln\frac{(A^{1/3}-1)^2}{A^{2/3}+A^{1/3}x+1}$$

$$-\frac{1}{A^{2/3}\sqrt{3}}\arctan\frac{2x+A^{1/3}}{A^{1/3}\sqrt{3}}$$

$$+\frac{1}{6B^{2/3}}\ln\frac{(B^{1/3}-x)^2}{B^{2/3}+B^{1/3}x+x^2}$$

$$-\frac{1}{B^{2/3}\sqrt{3}}\arctan\frac{2x+B^{2/3}}{B^{2/3}\sqrt{3}}-\frac{1}{3B^{2/3}}\ln\frac{(B^{1/3}-1)^2}{B^{2/3}+B^{1/3}+1}$$

$$\left.-\frac{1}{B^{2/3}\sqrt{3}}\arctan\frac{2+B^{2/3}}{B^{2/3}\sqrt{3}}\right]=q\tau.$$

The method of equilibrium-kinetic analysis does not require bringing the process to an equilibrium concentration, which is found from a mathematical model of reaction with the aid of a random-search procedure; in this case, the accuracy of this procedure is sufficient with the use of initial data with a standard error of ±5 rel %.

Generally, the analysis of all paired combinations of experimental data and the need for averaging the resulting values of C_p is dictated by the inevitable inaccuracy of the initial data. Qualitatively, each particular experimental point can take an underestimated or overestimated value relative to the true value of current concentration. Thus, the two points to be compared

Table 1. Results of the calculations of equilibrium concentrations at temperatures of 648, 673, and 698 K (*i*/*j* are the numbers of coupled experimental points)

C_p at *i*/*j* at temperatures of 648–698 K															C_p, average
1/2	1/3	1/4	1/5	1/6	2/3	2/4	2/5	2/6	3/4	3/5	3/6	4/5	4/6	5/6	
648 K															
0.3638	0.4130	0.4610	0.4406	0.4739	0.4230	0.4601	0.4606	0.4598	0.4497	0.4597	0.4902	0.4599	0.4831	0.4803	0.4519
673 K															
0.4226	0.4729	0.5049	0.5060	0.5416	0.4684	0.4971	0.5217	0.5541	0.4987	0.5202	0.5541	0.5150	0.5352	0.5426	0.5102
698 K															
0.4350	0.5167	0.5242	0.5411	0.5591	0.5051	0.5195	0.5399	0.5593	0.5197	0.5599	0.5301	0.5392	0.5611	0.5690	0.5317

Table 2. Kinetic and thermodynamic parameters of the reaction of brown coal hydrogenation in a temperature range of 648–698 K

T, K	Forward		Reverse		K_p, MPa^{-1}	ΔH, kJ/mol	ΔS, J mol^{-1} K^{-1}
	k_1, min^{-1}	E_a, kJ/mol	k_2, min^{-1}	E_a, kJ/mol			
648	6.627×10^{-5}	89.9	1.363×10^{-4}	139.6	0.966	49.7	2.5
673	9.956×10^{-5}		3.332×10^{-4}		0.748		
698	2.191×10^{-4}		8.720×10^{-4}		0.560		

potentially contain six versions of the strictness of the initial data, from which, by combinations of two from six, we obtain

$$C_6^2 = \frac{6!}{2!(6-2)!} = 15$$

versions of their different combinations, which include regularly overestimated, regularly underestimated, randomly strict, unilateral overestimated or underestimated, and maximally different or maximally close paired values.

The general scientific concepts of the equilibrium-kinetic analysis based on a reasonable combination of the deterministic and probabilistic approaches make it possible to solve this problem based on a body of experimental data by a probabilistic method with any assigned degree of accuracy. This is achieved by the selection of C_p that corresponds to a maximum coefficient of correlation of the straight line $Z - Z_0 = q_0\tau$ with the experimental results. This concentration is phenomenologically most probable for this model. In the calculations for each isotherm, the first search value of the equilibrium concentration C_p is specified in the equation $Z - Z_0 = q_0\tau$ (for example, that deliberately smaller than the true or model equilibrium concentration); then, Z is calculated and q_0 are further calculated according to the least squares method for determining the computed values of Z_T on their basis. The found Z_T are compared with Z_E in terms of the correlation coefficient R and its significance t_R.

The processing of experimental data for solving the equation with respect to equilibrium concentration was carried out using a random-search procedure for paired experimental points in the Equilibrium-Kinetic Analysis program system (Delphi 7 Studio) with the output of the results in Microsoft Excel.

The average value of equilibrium concentration was considered as a calculated-experimental one for the entire set of processed points. Table 1 summarizes the search values of equilibrium concentrations at temperatures of 648, 673, and 698 K.

For confirming the adequacy of the developed model, it is necessary to compare its linear forms in experimental and calculated versions. From the found values of Z depending on τ, the relationships were plotted for the three test temperatures. Figure 2 shows the results of calculations.

First, according to Fig. 2, we are convinced that, indeed, the developed model is reduced a straight line that passes through the origin of the coordinates. The correlation coefficients for the developed integral equilibrium-kinetic model of the hydrogenation of brown coal were the following: $R(648\text{ K}) = 0.822$; $t_R = 2.8 > 2$; $R(673\text{ K}) = 0.934$; $t_R = 2.7 > 2$; $R(698\text{ K}) = 0.914$; $t_R = 2.69 > 2$. Consequently, it is possible to consider that the proposed equilibrium-kinetic analy-

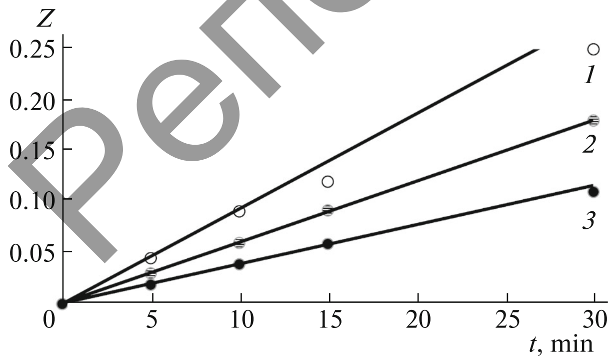

Fig. 2. Dependence of Z on time at temperatures of (*1*) 648, (2) 673, and (3) 698 K; points refer to experimental data, and lines are plotted according to the equation $Z = qt$.

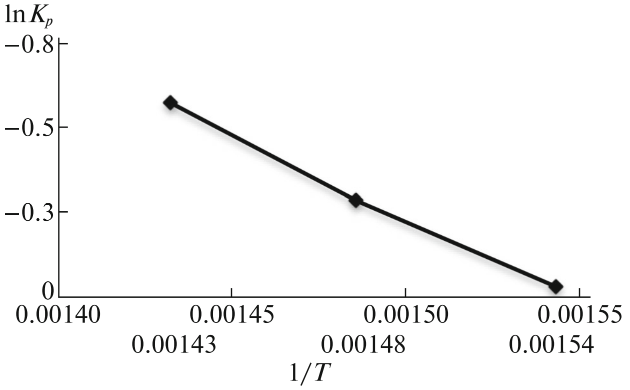

Fig. 3. Dependence of equilibrium constant on the reciprocal of temperature.

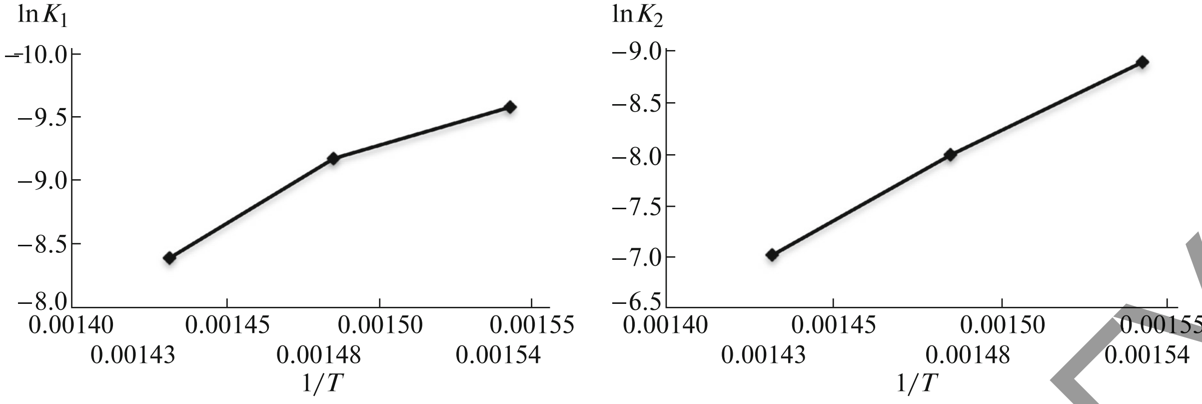

Fig. 4. Dependence of rate constants on the reciprocal of temperature.

sis model for a second-order reaction is sufficiently correct for the process of coal hydrogenation. Then, with the use of the found value of C_p, the average value of q is found form an inverted relation for all pairs of the set according to the equation.

The results of the calculations of q at temperatures of 648, 673, and 698 K are the following: $q_1 = 0.00613$; $q_2 = 0.00598$; and $q_3 = 0.00392$. The calculations were repeated for all isotherms; this made it possible to calculate the average enthalpy and entropy of the process based on the data on C_p and using Gibbs–Helmholtz equations. Correspondingly, the activation energies of forward and reverse reactions can be calculated from the values of k_1 and k_2 in a temperature range of 648–698 K based on the Arrhenius equation; thus, the use of the equilibrium-kinetic analysis method according to its intended purpose was complete (Figs. 3, 4).

The combination of the probabilistic and deterministic descriptions of reversible chemical processes within the framework of a united mathematical model for the process of Borodino brown coal hydrogenation makes it possible to directly relate equilibrium and kinetic characteristics and to obtain additional information from the experimental results (Table 1, Figs. 2–4) and, thus, to intensify chemical studies. With the use of Gibbs–Helmholtz and Arrhenius equations, we carried out the calculations of the activation energy, enthalpy, entropy, and equilibrium constant of the hydrogenation of brown coal in a temperature range from 648 to 698 K (Table 2). The results of the calculations of the activation energies of forward and reverse reactions of the hydrogenation of Borodino coal allowed us to assume that OMC hydrogenation occurs in the kinetic region.

Thus, we determined the rate coefficients of forward and reverse reactions, the equilibrium constant and equilibrium concentrations, the activation energies, and the heat effect of the hydrogenation of Borodino brown coal in a temperature range of 648–698 K at an initial hydrogen pressure of 10 MPa. The dependence of the correlation coefficient Z of the equilibrium-kinetic analysis on the duration of the hydrogenation process is plotted as a straight line that passes through the origin. The data obtained based on the dependence of the correlation coefficient Z on the process duration of the hydrogenation of brown coal in a temperature range of 648–698 K are indicative of the adequacy of the used model of equilibrium-kinetic analysis for second-order reactions.

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Translated by V. Makhlyarchuk