STUDY OF THE THERMODYNAMIC PARAMETERS INFLUENCE ON THE PHASE STATE OF METHANE IN COAL

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Abstract. The subject of research presented in the article is the processes that occur in the coal during change of its thermodynamic parameters. The aim of this research is to study the influence of pressure, temperature and binding energy of methane molecules on its distribution in coal. The analysis and generalization of the results conducted by the authors as well as referenced experimental and theoretical studies conducted by means of broad lines nuclear magnetic resonance method at high gas pressure as well as by means of spin echo method, physical and mathematical modeling are stated in the paper. The study of the influence of thermodynamic conditions change on the phase components of methane in coal has been further developed. The influence of pressure, temperature and binding energy of methane molecules on its distribution in coal has been studied. The redistribution of methane content between phases during pressure change has been studied. The nonlinear dependence of free and adsorbed methane on pressure that takes into account the relaxation time is established. The contribution of adsorbed and free methane varies with pressure change but proportion holds, which at low pressure is expressed by the Henry equation. At high pressure the Langmuir equation should be applied. It was established that the value of the methane phase components contribution to the total methane capacity significantly depends on the temperature. At low temperature, the amount of methane in coal could reach high values and it its value is determined mainly by adsorbed and dissolved methane content. As the temperature rises, the amount of methane contained in the coal decreases sharply - methane predominates as a free gas. It was found that at temperature value $T = 300$ K the solid solution contains a small amount of methane. Given that the solid state diffusion coefficient is very small, the contribution of methane to solid solution could be neglected in case of mine disasters. As the temperature increases from 300 K up to 350 K, the partial pressure of methane in the solid solution increases nearly in order of magnitude, so the gasdynamic situation in mines becomes more dangerous. According to the research results, the values of the desorption energy change for methane molecules and molar energy of methane desorption from the adsorbed state depending on the free methane pressure at $T = 300$ K are obtained, which allows estimation of the adsorbed methane amount.

Keywords: coal mine, gasdynamic phenomena, phase state, thermodynamic parameters.

Introduction. It is obvious that a significant risk factor during mining operations in coal mines is the risk of sudden coal and gas release. Among the main factors leading to the sudden coal and gas release in the working coal seams is methane which is contained in the coal seams, herewith, the amount of emitted gas significantly exceeds the natural gas amount within the coal produced. The coal seam is a complicated physical and chemical system, which balance depends on external parameters – temperature and pressure. During mining operations, the stresses affecting the outer hole volume of the coal seam are redistributed, the pore space changes, the gas is filtered towards the face of the working, the intrapore methane pressure is reduced. Both gas desorption processes and phase transitions could occur.

Preliminary studies have assessed the contribution of the main phase components of methane to the gas content of the coal seams and established the volume of free methane, adsorbed methane in solid solution and gas hydrate components of methane in the coal seam for certain thermodynamic conditions [1] – [3]. The purpose of the study is modeling the influence of the thermodynamic conditions change on the abovementioned phase components of methane in the coal seam.

Methods. The analysis and generalization of the results conducted by the authors as well as referenced experimental and theoretical studies conducted by means of broad lines nuclear magnetic resonance method (NMR) at high gas pressure as well as by means of spin echo method, physical and mathematical modeling are stated in the paper.

Results and discussion. The analysis of the studies for this field of science was performed [4] – [10]. The influence of pressure, temperature and binding energy of methane molecules on its distribution in coal has been studied. The redistribution of methane content between phases during pressure change is studied and the nonlinear dependence of free and adsorbed methane on pressure is established (Fig. 1).
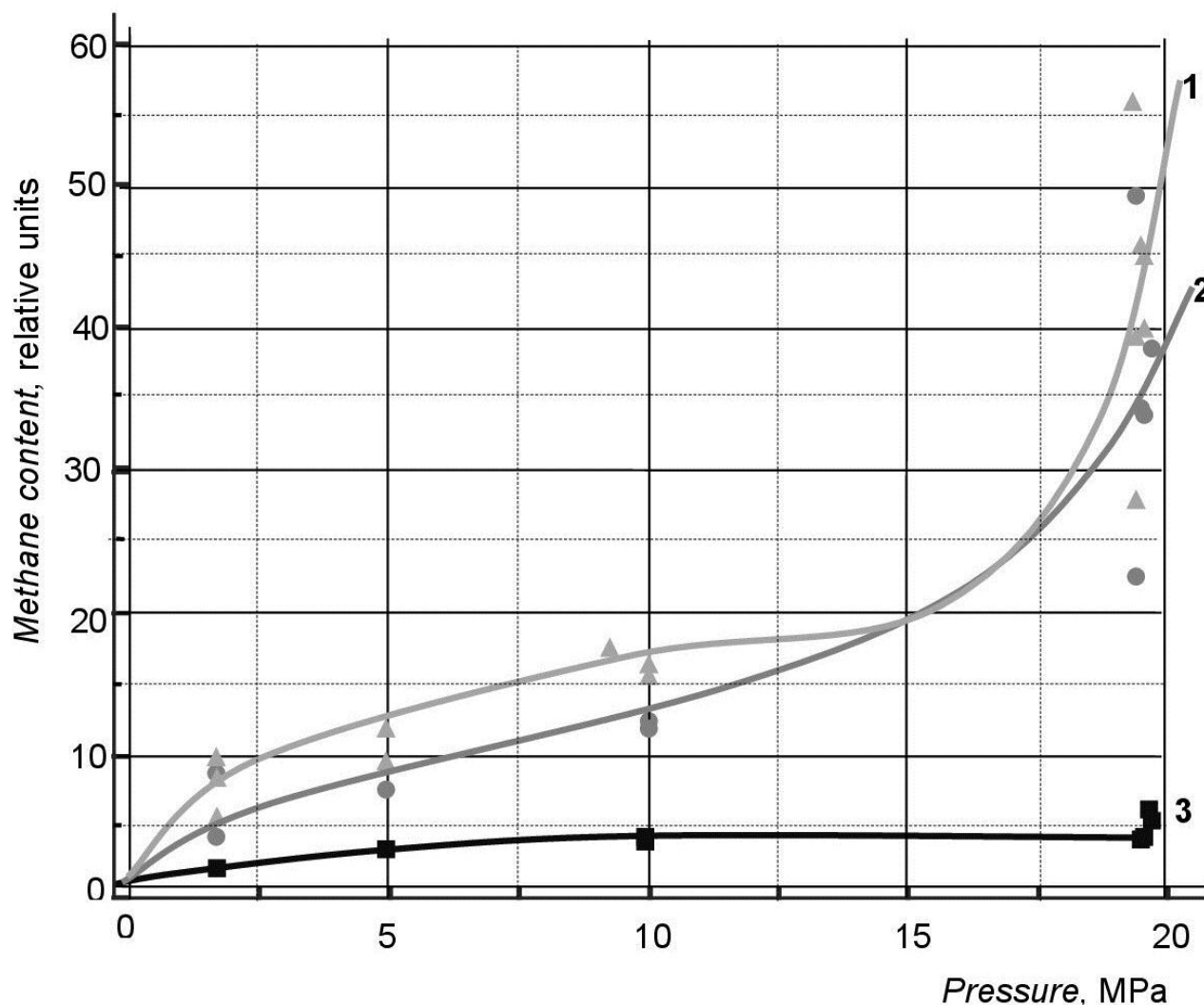
1 – total amount; 2, 3 – content of free and adsorbed methane respectively

Figure 1 – Dependence of methane content in coal on pressure [5]

The contribution of adsorbed and free methane varies with pressure change but proportion holds on, which at low pressure is expressed by the Henry equation. At high pressure the Langmuir equation should be applied. It was established that the value of the methane phase components contribution to the total methane capacity significantly depends on the temperature [10]. The total amount of gas released due

to temperature increasing is the amount of methane released in solid solution and in the adsorbed state. At low temperature, the amount of methane in coal could reach out high values. Its amount is determined mainly by adsorbed and dissolved methane. As the temperature rises, the amount of methane contained in the coal decreases sharply, thus, methane predominates in the state of a free gas. The value of the characteristic (low - high) temperature depends on the properties of the coal-gas system, in particular, it depends on the binding energy of methane with coal, and could vary widely.

It is obvious that under constant external conditions, the gas content of the seam could maintain its value as long as desired [11]. When the stresses decrease, for example, within the area affected by mining operations and wells, methane is released from the solid solution into the fractured-porous formation system, forming the free gas pressure and, thereafter, the filtration flow directed to the exposed surface. Since the initial mechanical load (geostatic pressure) is 2.5 times greater than the gas pressure (hydrostatic pressure), probable increase of free methane pressure released from the solution is largely determined by the decrease of mechanical stresses. As a result, the pressure of methane above the coal surface increases, the corresponding part of the methane, which has turned into the free state gas, is adsorbed as well, reducing the increase of gas pressure. The higher the coal sorption potential, the greater its influence on the "damping" of the dynamics for free methane pressure in cracks. It should be noted that decomposition of the solid solution is accompanied by an increase of the temperature; sorption is described by an increase of the temperature, while desorption is described by decrease of the temperature. Given the loosening bond of adsorbed methane with the surface of coal compared to the "dissolved" one, the initial desorption rate is significantly higher than the decomposition rate of solid solution (for example, in case of destruction of preliminary unloaded but not degasified coal).

It should be noted that at present several opinions on determination of methane state in coal exist. They are often very different because coal is a very complicated object of study. There are no reliable experimental results, for example, for studies of coal samples, which properties differ from the coal properties of the seam. Many researchers assert that methane in coal mostly could be found in solid state. Using the fact that for coal equilibrium chemical potentials of methane for all the states of methane are the same, it is possible to determine the pressure and concentration of methane molecules in solid solution, depending on the pressure of free methane. The lack of accurate values for the energy of methane desorption from solid solution to adsorbed and free state respectively. The molar heat of physical adsorption is in the range 8–30 kJ/mol, while the heat of solid-state adsorption is obviously even higher. Based on the above conditions, numerical calculations of thermodynamic parameters were performed (Tables 1 - 4). Table 1 shows the values of the relative pressure P_s/P_f for methane in solid solution depending on the pressure of free methane at a temperature $T = 300$ K.

Table 1 shows that solid solution contains small amount of methane. Given that the solid-state diffusion coefficient is small enough, the contribution of methane to solid solution could be neglected during mine disasters.

Table 2 shows the values of the methane molecules concentration per unit volume in solid solution depending on the pressure of free methane and the energy of solid desorption at a temperature $T = 300$ K.

Table 1 – Relative pressure of methane molecules in solid solution
depending on the molar energy of methane desorption ψ and pressure P_f at $T = 300$ K

P_f, MPa	ψ, kJ/mol				
	30	35	40	45	50
1	$5.94 \cdot 10^{-6}$	$7.99 \cdot 10^{-7}$	$1.08 \cdot 10^{-7}$	$1.45 \cdot 10^{-8}$	$1.95 \cdot 10^{-9}$
5	$2.97 \cdot 10^{-5}$	$4.0 \cdot 10^{-6}$	$5.38 \cdot 10^{-7}$	$7.25 \cdot 10^{-8}$	$9.74 \cdot 10^{-9}$
10	$5.94 \cdot 10^{-5}$	$7.99 \cdot 10^{-6}$	$1.08 \cdot 10^{-6}$	$1.45 \cdot 10^{-7}$	$1.95 \cdot 10^{-8}$
20	$1.19 \cdot 10^{-4}$	$1.6 \cdot 10^{-5}$	$2.15 \cdot 10^{-6}$	$2.9 \cdot 10^{-7}$	$3.9 \cdot 10^{-8}$
50	$2.97 \cdot 10^{-4}$	$4.0 \cdot 10^{-5}$	$5.38 \cdot 10^{-6}$	$7.24 \cdot 10^{-7}$	$9.74 \cdot 10^{-8}$
70	$4.16 \cdot 10^{-3}$	$5.6 \cdot 10^{-5}$	$7.53 \cdot 10^{-6}$	$1.08 \cdot 10^{-6}$	$1.36 \cdot 10^{-7}$
100	$5.94 \cdot 10^{-4}$	$7.99 \cdot 10^{-5}$	$1.08 \cdot 10^{-5}$	$1.45 \cdot 10^{-6}$	$1.95 \cdot 10^{-7}$
150	$8.91 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$1.61 \cdot 10^{-5}$	$2.17 \cdot 10^{-6}$	$2.92 \cdot 10^{-7}$
200	$1.19 \cdot 10^{-3}$	$1.6 \cdot 10^{-4}$	$2.15 \cdot 10^{-5}$	$2.9 \cdot 10^{-6}$	$3.9 \cdot 10^{-7}$
250	$1.48 \cdot 10^{-3}$	$2.0 \cdot 10^{-4}$	$2.69 \cdot 10^{-5}$	$3.62 \cdot 10^{-6}$	$4.87 \cdot 10^{-7}$
300	$1.78 \cdot 10^{-3}$	$2.4 \cdot 10^{-4}$	$3.23 \cdot 10^{-5}$	$4.34 \cdot 10^{-6}$	$5.84 \cdot 10^{-7}$
350	$2.08 \cdot 10^{-3}$	$2.8 \cdot 10^{-4}$	$3.77 \cdot 10^{-5}$	$5.07 \cdot 10^{-6}$	$6.82 \cdot 10^{-7}$
400	$2.38 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$	$4.3 \cdot 10^{-5}$	$5.79 \cdot 10^{-6}$	$7.79 \cdot 10^{-7}$

Table 2 – Concentration change of methane molecules in solid solution
depending on the molar energy of methane desorption ψ and pressure P_f at $T = 300$ K

P_f, MPa	ψ, kJ/mol				
	30	35	40	45	50
1	$1.45 \cdot 10^{20}$	$1.96 \cdot 10^{19}$	$2.64 \cdot 10^{18}$	$3.55 \cdot 10^{17}$	$4.77 \cdot 10^{16}$
5	$7.28 \cdot 10^{20}$	$9.79 \cdot 10^{19}$	$1.32 \cdot 10^{19}$	$1.77 \cdot 10^{18}$	$2.39 \cdot 10^{17}$
10	$1.45 \cdot 10^{21}$	$1.96 \cdot 10^{20}$	$2.64 \cdot 10^{19}$	$3.55 \cdot 10^{18}$	$4.77 \cdot 10^{17}$
20	$2.9 \cdot 10^{21}$	$3.92 \cdot 10^{20}$	$5.27 \cdot 10^{19}$	$7.09 \cdot 10^{18}$	$9.55 \cdot 10^{17}$
50	$7.28 \cdot 10^{21}$	$9.79 \cdot 10^{20}$	$1.32 \cdot 10^{19}$	$1.77 \cdot 10^{18}$	$2.39 \cdot 10^{18}$
70	$1.02 \cdot 10^{22}$	$1.37 \cdot 10^{21}$	$1.84 \cdot 10^{20}$	$2.48 \cdot 10^{19}$	$3.34 \cdot 10^{18}$
100	$1.45 \cdot 10^{22}$	$1.96 \cdot 10^{21}$	$2.64 \cdot 10^{20}$	$3.55 \cdot 10^{19}$	$4.77 \cdot 10^{18}$
150	$2.18 \cdot 10^{22}$	$2.94 \cdot 10^{21}$	$3.95 \cdot 10^{20}$	$5.32 \cdot 10^{19}$	$7.16 \cdot 10^{18}$
200	$2.9 \cdot 10^{22}$	$3.92 \cdot 10^{21}$	$5.27 \cdot 10^{20}$	$7.09 \cdot 10^{19}$	$9.55 \cdot 10^{18}$
250	$3.64 \cdot 10^{22}$	$4.9 \cdot 10^{21}$	$6.59 \cdot 10^{20}$	$8.87 \cdot 10^{19}$	$1.19 \cdot 10^{19}$
300	$4.37 \cdot 10^{22}$	$5.88 \cdot 10^{21}$	$7.91 \cdot 10^{20}$	$1.06 \cdot 10^{20}$	$1.43 \cdot 10^{19}$
350	$5.09 \cdot 10^{22}$	$6.86 \cdot 10^{21}$	$9.22 \cdot 10^{20}$	$1.24 \cdot 10^{20}$	$1.67 \cdot 10^{19}$
400	$5.82 \cdot 10^{22}$	$7.83 \cdot 10^{21}$	$1.05 \cdot 10^{21}$	$1.42 \cdot 10^{20}$	$1.91 \cdot 10^{19}$

During bearing zone formation an intensive process of crack formation takes place. New surface formation is a low energy consumption process, because significant amount of energy is spent on the rock heating process. The rock strength is heterogeneous one. The centers of quasi-static failure emerge in places of stress concentration which leads to local heating of rock and coal. It would be useful to evaluate

how the pressure and concentration of methane in solid solution change with increasing temperature values. Table 3 shows the values of the methane relative pressure in solid solution depending on the free methane pressure P_f and the energy of methane desorption from solid solution into the free state ψ at a temperature $T = 350$ K.

Table 3 – Relative pressure of methane molecules in solid solution
depending on the molar energy of methane desorption ψ and pressure P_f at $T = 350$ K

P_f, MPa	ψ, kJ/mol				
	30	35	40	45	50
1	$3.31 \cdot 10^{-5}$	$5.94 \cdot 10^{-6}$	$1.06 \cdot 10^{-6}$	$1.91 \cdot 10^{-7}$	$3.42 \cdot 10^{-8}$
5	$1.66 \cdot 10^{-4}$	$2.97 \cdot 10^{-5}$	$5.32 \cdot 10^{-6}$	$9.54 \cdot 10^{-7}$	$1.71 \cdot 10^{-8}$
10	$3.31 \cdot 10^{-4}$	$5.94 \cdot 10^{-5}$	$1.06 \cdot 10^{-5}$	$1.91 \cdot 10^{-6}$	$3.42 \cdot 10^{-7}$
20	$6.62 \cdot 10^{-4}$	$1.19 \cdot 10^{-4}$	$2.12 \cdot 10^{-5}$	$3.82 \cdot 10^{-6}$	$6.84 \cdot 10^{-7}$
50	$1.66 \cdot 10^{-3}$	$2.97 \cdot 10^{-4}$	$5.32 \cdot 10^{-5}$	$9.54 \cdot 10^{-6}$	$1.71 \cdot 10^{-6}$
70	$2.32 \cdot 10^{-3}$	$4.16 \cdot 10^{-4}$	$7.45 \cdot 10^{-5}$	$1.34 \cdot 10^{-5}$	$2.39 \cdot 10^{-6}$
100	$3.31 \cdot 10^{-3}$	$5.94 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$	$1.91 \cdot 10^{-5}$	$3.42 \cdot 10^{-6}$
150	$4.97 \cdot 10^{-3}$	$8.91 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$2.86 \cdot 10^{-5}$	$5.13 \cdot 10^{-6}$
200	$6.62 \cdot 10^{-3}$	$1.19 \cdot 10^{-3}$	$2.12 \cdot 10^{-4}$	$3.82 \cdot 10^{-5}$	$6.84 \cdot 10^{-6}$
250	$8.29 \cdot 10^{-3}$	$1.48 \cdot 10^{-3}$	$2.66 \cdot 10^{-4}$	$4.77 \cdot 10^{-5}$	$8.55 \cdot 10^{-6}$
300	$9.93 \cdot 10^{-3}$	$1.78 \cdot 10^{-3}$	$3.18 \cdot 10^{-4}$	$5.72 \cdot 10^{-5}$	$1.03 \cdot 10^{-5}$
350	$1.16 \cdot 10^{-2}$	$2.08 \cdot 10^{-3}$	$3.73 \cdot 10^{-4}$	$6.68 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$
400	$1.33 \cdot 10^{-2}$	$2.38 \cdot 10^{-3}$	$4.26 \cdot 10^{-4}$	$7.63 \cdot 10^{-5}$	$1.37 \cdot 10^{-5}$

Table 3 shows that with increasing temperature from 300 K to 350 K, the partial pressure of methane in solid solution increases by about an order of magnitude.

Table 4 shows the values of the concentration of methane in solid solution depending on the pressure of free methane P_f and the energy of desorption of methane from solid solution into the free state ψ at a temperature $T = 350$ K.

Table 4 – Concentration change of methane molecules in solid solution
depending on the molar energy of methane desorption ψ and pressure P_f at $T = 350$ K

P_f, MPa	ψ, kJ/mol				
	30	35	40	45	50
1	$8.12 \cdot 10^{20}$	$1.45 \cdot 10^{20}$	$2.61 \cdot 10^{19}$	$4.67 \cdot 10^{18}$	$8.38 \cdot 10^{17}$
5	$4.06 \cdot 10^{21}$	$7.28 \cdot 10^{20}$	$1.3 \cdot 10^{20}$	$2.34 \cdot 10^{19}$	$4.19 \cdot 10^{18}$
10	$8.12 \cdot 10^{21}$	$1.45 \cdot 10^{21}$	$2.61 \cdot 10^{20}$	$4.67 \cdot 10^{19}$	$8.38 \cdot 10^{18}$
20	$1.62 \cdot 10^{22}$	$2.9 \cdot 10^{21}$	$5.22 \cdot 10^{20}$	$9.35 \cdot 10^{19}$	$1.68 \cdot 10^{19}$
50	$4.06 \cdot 10^{22}$	$7.28 \cdot 10^{21}$	$1.3 \cdot 10^{21}$	$2.34 \cdot 10^{20}$	$4.19 \cdot 10^{19}$
70	$5.68 \cdot 10^{22}$	$1.02 \cdot 10^{22}$	$1.83 \cdot 10^{21}$	$3.27 \cdot 10^{20}$	$5.87 \cdot 10^{19}$
100	$8.12 \cdot 10^{22}$	$1.45 \cdot 10^{22}$	$2.61 \cdot 10^{21}$	$4.67 \cdot 10^{20}$	$8.38 \cdot 10^{19}$
150	$1.22 \cdot 10^{23}$	$2.18 \cdot 10^{22}$	$3.91 \cdot 10^{21}$	$7.01 \cdot 10^{20}$	$1.26 \cdot 10^{20}$
200	$1.62 \cdot 10^{23}$	$2.9 \cdot 10^{22}$	$5.22 \cdot 10^{21}$	$9.35 \cdot 10^{20}$	$1.68 \cdot 10^{20}$
250	$2.03 \cdot 10^{23}$	$3.64 \cdot 10^{22}$	$6.52 \cdot 10^{21}$	$1.17 \cdot 10^{21}$	$2.09 \cdot 10^{20}$
300	$2.44 \cdot 10^{23}$	$4.37 \cdot 10^{22}$	$7.83 \cdot 10^{21}$	$1.4 \cdot 10^{21}$	$2.51 \cdot 10^{20}$
350	$2.84 \cdot 10^{23}$	$5.09 \cdot 10^{22}$	$9.13 \cdot 10^{21}$	$1.64 \cdot 10^{21}$	$2.93 \cdot 10^{20}$
400	$3.25 \cdot 10^{23}$	$5.8 \cdot 10^{22}$	$1.04 \cdot 10^{22}$	$1.87 \cdot 10^{21}$	$3.35 \cdot 10^{20}$

Note that the concentration of methane molecules at $P_a = 101325$ Pa and $T = 300$ K equals $n_a = 2.45 \cdot 10^{25}$ $1/m^3$.

I order to study the adsorbed methane, it is necessary to determine the desorption energy of methane molecules. Nowadays it is impossible to accurately determine the desorption energy value. In case of multilayer adsorption, it is difficult to determine the bulk density of the adsorbed layer. In addition it should be noted, the more layers, the lower value of the desorption energy is.

Taking into account the fundamentals of statistical physics and thermodynamics [12], let's estimate the desorption energy value. The Gibbs energy, i.e. thermodynamic potential for methane in the adsorbed state could be calculated as follows

$$\Phi_{ad} = C_V T - TC_p \, lnT + PV_{ad} + \psi_{ad}, \tag{1}$$

where C_v, C_p – molar heat capacity of methane in the adsorbed state at constant volume and pressure respectively, J/mol·K; V_{ad} – molar volume of methane, m^3; ψ_{ad} – molar energy of methane desorption from the adsorbed state, kJ/mol.

The chemical potentials of methane in the adsorbed and free state are the following:

$$\mu_{ad} = \frac{C_V}{N_A}T - \frac{C_p T \, lnT}{N_A} + \frac{PV_{ad}}{N_A} + \varepsilon_{ad}, \tag{2}$$

$$\mu_f = \frac{i+2}{2}kT(1 - lnT) + kT \, lnP, \tag{3}$$

where i – number of degrees of freedom; k – Boltzmann constant, J/K; N_A – Avogadro's number, mol^{-1}; ε_{ad} – adsorption energy of methane molecules, kJ/mol.

At thermodynamic equilibrium, the chemical potentials are equal to each other. Being equated an expression for ε_{ad} could be obtained:

$$\varepsilon_{ad} = \frac{i+2}{2}kT(1 - lnT) + kT \, lnP - \frac{C_V}{N_A} + \frac{C_p T \, lnT}{N_A} - \frac{PV_{ad}}{N_A}, \tag{4}$$

Using relationships (1) – (4), the values ε_{ad} and ψ_{ad} could be calculated depending on the pressure of free methane at a temperature of 300 K and 350 K (Tables 5, 6), which allow to estimate the amount of adsorbed methane.

The values of adsorption energy given in the tables above suggest that the increase of ψ_{ad} with increasing pressure is explained by the fact that the entropy of free methane is much more dependent on pressure. In order to obtain more accurate values of ψ_{ad}, the dependence of the molar volume of adsorbed methane on pressure and temperature must be taken into account. This dependence does not significantly change the value of adsorption energy.

Table 5 – The adsorption energy of molecules ε_{ad} as well as molar adsorption energy of methane molecules ψ_{ad} at $T = 300$ K depending on the free methane pressure

P, MPa	0.1	0.5	1	5	10	15	20	25	30	35	40
$\varepsilon_{ad} \cdot 10^{20}$, J	2.84	3.5	3.78	4.39	4.61	4.71	4.76	4.79	4.8	4.8	4.78
ψ_{ad}, kJ/mol	17.07	21.5	22.74	26.43	27.76	28.37	28.67	28.84	28.89	28.88	28.81

Table 6 – The adsorption energy of molecules ε_{ad} as well as molar adsorption energy of methane molecules ψ_{ad} at $T = 350$ K depending on the free methane pressure

P, MPa	0.1	0.5	1	5	10	15	20	25	30	35	40
$\varepsilon_{ad} \cdot 10^{20}$, J	2.23	3	3.33	4.05	4.32	4.45	4.52	4.56	4.58	4.592	4.59
ψ_{ad}, kJ/mol	13.4	18.05	20.02	24.32	26.0	26.78	27.21	27.46	27.59	27.64	27.63

Conclusions. Thus, as a result of research, the study for the influence of thermo-dynamic conditions change on the phase components of methane in coal was further developed. The influence of pressure, temperature and binding energy of methane molecules on its distribution in coal has been studied. The redistribution of methane content between phases at pressure change was investigated as well as nonlinear dependence of free and adsorbed methane on pressure that takes into account the relaxation time is established. The contribution of adsorbed and free methane varies with pressure change but proportion holds on, which at low pressure is expressed by the Henry equation. At high pressure the Langmuir equation should be applied. It was determined that the value of the methane phase components contribution to the total methane capacity significantly depends on the temperature At low temperature values, the amount of methane in coal could reach out large values and is determined mainly by adsorbed and dissolved methane. As the temperature rises, the amount of methane contained in the coal decreases sharply, thus, methane predominates in the state of a free gas.

It was found that at $T = 300$ K the solid solution contains only a small amount of methane. Given that the solid-state diffusion coefficient is small enough, the contribution of methane to solid solution could be neglected during mine disasters. As the temperature increases from 300 K to 350 K, the partial pressure of methane in the solid solution increases by about an order of magnitude, so the gas-dynamic situation becomes more dangerous.

According to the research results the values of the desorption energy change for methane molecules ε_{ad} and the molar energy of methane desorption from the adsorbed state ψ_{ad} depending on the free methane pressure at T = 300 K were obtained, which allows to estimate the amount of adsorbed methane.

The increase of ψ_{ad} with increasing pressure is explained by the fact that the entropy of free methane is much more dependent on pressure.

To obtain more accurate ψ_{ad} values, the dependence of the molar volume of adsorbed methane on pressure and temperature must be taken into consideration. This dependence does not significantly change the value of adsorption energy.

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ДОСЛІДЖЕННЯ ВПЛИВУ ТЕРМОДИНАМІЧНИХ ПАРАМЕТРІВ НА ФАЗОВИЙ СТАН МЕТАНУ У ВУГІЛЛІ
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Анотація. Предмет досліджень, викладених в статті, це процеси, що відбуваються у вугільній речовині при зміні термодинамічних параметрів. Метою даної статті є дослідження впливу тиску, температури та енергії зв'язку молекул метану на його розподіл у вугільній речовин. В роботі використано аналіз та узагальнення результатів власних і сторонніх експериментальних та теоретичних досліджень, виконаних методом ядерного магнітного резонансу широких ліній в умовах високих газових тисків, а також методом спін-ехо, фізичного та математичного моделювання. Отримало подальший розвиток вивчення впливу зміни термодинамічних умов на фазові складові метану у вугільній речовині. Вивчено вплив тиску, температури та енергії зв'язку молекул метану на його розподіл у вугільній речовині. Досліджено перерозподіл вмісту метану між фазами при зміні тиску. Встановлена нелінійна залежність вільного та сорбованого метану від тиску за часом їх релаксації. При різному тиску внесок сорбованого та вільного метану буде різним, однак між ними зберігається пропорційність, яка при малому тиску виражається через рівняння Генрі. При високому тиску виникає необхідність користуватися рівнянням Ленгмюра. Встановлено, що величина внеску фазових складових метану в загальну метаноємність суттєво залежить від температури. При низьких температурах кількість метану у вугіллі може досягати великих величин і визначаєть-

ся, в основному, адсорбованим та розчиненим метаном. При зростанні температури кількість метану, що міститься у вугіллі, різко скорочується – переважає метан у вільному стані. Встановлено, що при Т = 300 К в твердому розчині міститься лише незначна кількість метану. Якщо врахувати, що коефіцієнт твердотільної дифузії дуже малий, то внеском метану у твердому розчині можна нехтувати при катастрофічних явищах. При збільшенні температури з 300 К до 350 К парціальний тиск метану у твердому розчині збільшується приблизно на порядок, тому газодинамічна ситуація стає більш небезпечна. За результатами досліджень отримані значення зміни енергії десорбції молекул метану і мольної енергії десорбції метану з адсорбованого стану в залежності від тиску вільного метану при Т=300 К, що дозволяє оцінити кількість адсорбованого метану.

Ключові слова: вугільна шахта, газодинамічні явища, фазовий стан, термодинамічні параметри.

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