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CHANGE IN THE BASIC THERMODYNAMIC CHARACTERISTICS OF POLYMERIC SORBENTS IN INTERACTION WITH INERT GASES IN A WIDE RANGE OF PRESSURES AND TEMPERATURES

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A model for calculating of the change in the basic thermodynamic characteristics of a sorbent (internal energy and entropy) with the phenomenological-thermodynamics method has been developed. Calculations for the systems polycarbonate–carbon dioxide and polymethylmethacrylate–carbon dioxide have been carried out.

The unique combination of strength characteristics and high transparency of glassy polymers extends the fields of their application and determines the need for further investigations of such polymers for glassy polymer–noninert gas systems. Polycarbonate is distinguished by its combination of high heat resistance, unique shock resistance, and high transparency at the same time. It possesses a high chemical stability to most noninert substances, which makes it possible to use it in aggressive media with no change in the chemical composition and properties. In connection with the fact that such glassy polymers are also used under higher-than-average pressures, the systems are investigated for a wide temperature and pressure range [1].

Despite the great number of existing models of description of the process of sorption, there has been no sufficiently accurate model of sorption and mechanical sorption deformation of a rigid body up to now. Moreover, the problems of determining the thermodynamic characteristics of a swelling noninert sorbent have hardly been considered. The extended field of application of glassy polymers has made it possible to study the thermodynamic behavior of glassy polymer–compressed gas systems at higher-than-average pressures. Experimental data for the glassy polymers in contact with gases at higher-than-average pressures are few in number or they have been obtained for bounded narrow ranges [2, 3].

For thermodynamic description of the change in the sorbent state we must obtain the equation of state for a rigid body. In general form, it is written as follows:

$$P = P(V, T)\,, \tag{1}$$

where P is a certain resultant pressure causing the sorbent to swell. In elastic uniform tension (or compression), the expanded form of Eq. (1) appears as

$$P = K\frac{V(T, P) - V(T, 0)}{V(T, 0)}\,, \tag{2}$$

where, for $P = 0$, we have

$$V(T, 0) = V(0, 0)\,(1 + \beta T)\,. \tag{3}$$

Using expressions (2) and (3), we obtain the equation of state

$$P = K\left[\frac{V}{V_0(1 + \beta T)} - 1\right], \tag{4}$$

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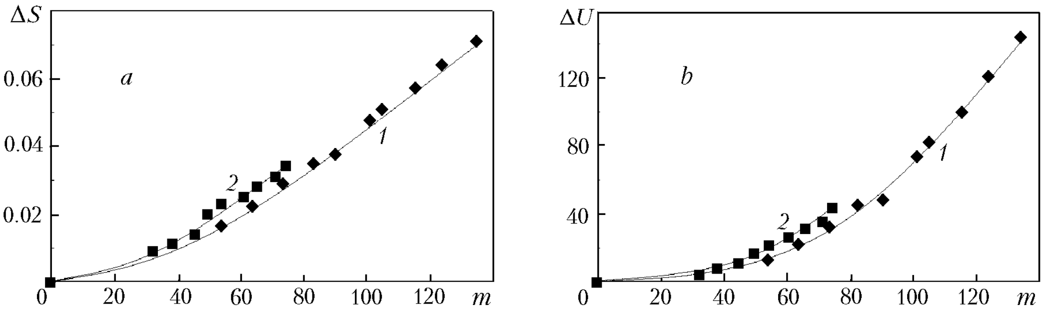

Fig. 1. Specific entropy (a) and specific internal energy (b) of polycarbonate vs. sorption of CO_2 at temperatures: 1) T = 308 and 2) 318 K (points, calculated values from experimental data, curves, results of modeling). ΔS, J/(K·g); m, mg/g; ΔU, J/g.

where $V_0 = V(0, 0)$, $V = V(T, P)$, and $K = \dfrac{E}{3(1-\mu)}$ is the bulk modulus of the rigid body. Before determining the basic characteristics of the sorbent, we must carry out a certain thermodynamic analysis. The work of swelling of the rigid body may be found as follows:

$$\delta A = - PdV\,.$$

Then the basic thermodynamic equation will be written as

$$dU\,(S, V) = TdS + PdV\,,$$

or, with the use of the Jacobian, in the form

$$\frac{\partial\,(T, S)}{\partial\,(P, V)} = - 1\,. \tag{5}$$

With account for expression (5) we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial\,(S, T)}{\partial\,(V, P)}\,\frac{\partial\,(V, P)}{\partial\,(V, T)} = -\left(\frac{\partial P}{\partial T}\right)_V\,.$$

Let us pass to the formula of change in the entropy of the swelling sorbent:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \left(\frac{\partial S}{\partial T}\right)_V dT - \left(\frac{\partial P}{\partial T}\right)_V dV\,.$$

In accordance with expression (4), we have

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\beta K V}{V_0\,(1 + \beta T\,)^2}\,.$$

Then we obtain

$$dS = \frac{C_V dT}{T} + \frac{\beta K V}{V_0\,(1 + \beta T\,)^2}\,dV\,. \tag{6}$$

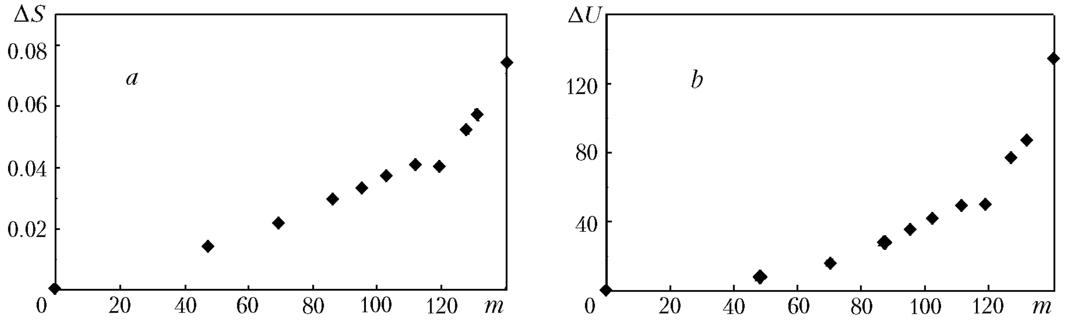

Fig. 2. Specific entropy (a) and specific internal energy (b) of PMMA vs. sorption of CO_2 at temperature T = 308 K. ΔS, J/(K·g); m, mg/g; ΔU, J/g.

The process of sorption is usually considered for isothermal conditions (T = const); therefore, expression (6) will take the following form:

$$dS = \frac{\beta K V}{V_0 (1 + \beta T)^2} dV . \tag{7}$$

In integral form, expression (7) may be written as

$$S - S' = \frac{\beta K (V^2 - (V')^2)}{2V_0 (1 + \beta T)^2} . \tag{8}$$

In accordance with expressions (4) and (6), we may represent the equation of changes in the internal sorbent energy in differential form:

$$dU = TdS + PdV = C_V dT + \left(\frac{\beta K T V}{V_0 (1 + \beta T)^2} + P \right) dV = C_V dT + \left(\frac{(V - V_0)(2\beta K T + K) - \beta^2 K T^2 V_0}{V_0 (1 + \beta T)^2} \right) dV$$

or in integral form, assuming that the process is isothermal:

$$U - U' = \frac{K (1 + 2\beta T)}{(1 + \beta T)^2} \frac{[(V - V_0)^2 - (V - V_0)^2]}{2V_0} - \frac{K \beta^2 T^2}{(1 + \beta T)^2} (V - V') . \tag{9}$$

Using the initial data on the systems polycarbonate–carbon dioxide and polymethylmethacrylate (PMMA)–carbon dioxide [4] and the expressions obtained for determination of the changes in the entropy (8) and the internal energy (9), we may calculate the dependences of these most important thermodynamic functions on the amount of the substance sorbed. Figures 1 and 2 present results of such calculations. In addition, we have modeled the change in the energy characteristics for the polycarbonate–carbon dioxide system; the modeling has shown that the experimental data are in fairly close agreement with the values calculated theoretically (see Fig. 1).

The dependences obtained made it possible to evaluate the change in the energy characteristics of polymeric sorbents in the sorption of low-molecular-weight gases.

NOTATION

A, work of swelling of a rigid body, J; C_V, specific heat at constant volume, J/(K·kg); E, Young's modulus, Pa; K, bulk modulus of a rigid body, Pa; m, sorption, kg/kg; P, pressure deforming a sorbent, Pa; S, specific entropy of a swelling sorbent, J/(K·kg); S', specific entropy of a swelling sorbent for a certain initial state, J/(K·kg); T, temperature, K; U, specific internal energy of a sorbent, J/kg; U'', specific internal energy of a sorbent for a certain initial state, J/kg; V, specific volume of a sorbent, m^3/kg; V_0, specific volume of a sorbent for the case $T = 0$ and $P = 0$, m^3/kg; V', specific volume of a sorbent for a certain initial state, m^3/kg; β, temperature coefficient of expansion, K^{-1}; μ, Poisson coefficient.

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