





















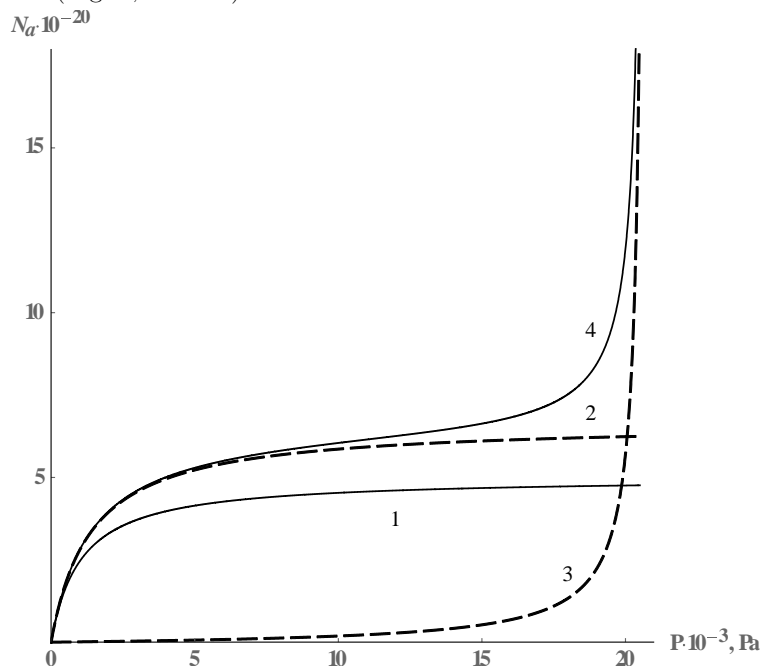


$$N_a = \frac{k_{a1} N_c N_g}{V + k_{a1} N_g - k_{a2} N_g} \quad (19)$$

If in this equation substitute  $V$  from (11), it is converted to an interesting sight:

$$N_a = \frac{k_{a1} N_c P}{k_{a1} P - k_{a2} P + k_B T} \quad (20)$$

Equation (20) represents the isotherm of polymolecular adsorption. We see immediately that in the absence of adsorption in the second and subsequent layers, i.e.  $k_{a2}$  equal to zero, it takes the form of the Langmuir isotherms (Fig. 7, curve 1).



**Figure 7.** The adsorption isotherm was calculated according to the equation (20) for different values of constituent constants:  $T = 150, k_B = 1,38 * 10^{-23}$ ;  $1 - N_c = 5 \cdot 10^{20}, k_{a1} = 2 \cdot 10^{-24}, k_{a2} = 0$ ;

$2 - N_c = 5 \cdot 10^{20}, k_{a1} = 2 \cdot 10^{-24}, k_{a2} = 7 \cdot 10^{-25}$ ;  $3 - N_c = 1 \cdot 10^{20}, k_{a1} = 2 \cdot 10^{-26}, k_{a2} = 1,2 \cdot 10^{-25}$

If  $k_{a2}$  is not zero, it is, of course, can be either less than  $k_{a1}$  or more. When  $k_{a2} < k_{a1}$  the calculation by the equation (20) gives the results, a graphical representation of which coincides in form with the Langmuir isotherm (Fig. 7, curve 2). More filling is justified, as the curve 2 in Fig. 7 is isotherm of polymolecular adsorption, while the curve 1 of this figure represents the monomolecular adsorption isotherm. Apparently this is a new approach to the problem, because in the literature it is impossible to find statements that the isotherms of monomolecular and poly molecular adsorption can be identical in form. It is clear that in addition to purely cognitive interest of this assertion requires a more careful approach to the use of the adsorption methods for the determination of solid surfaces.

When  $k_{a2} > k_{a1}$  increase in pressure will result in a reduction of the denominator of expression (20), and thus to increase the fill. Thus, from physical considerations, it is clear that the pressure in such a system may not exceed a certain value determined by the requirement of equality to zero of the denominator of expression (20), and represents the saturation pressure  $P_0$ . For its definition we have

$$P_0 = \frac{k_B T}{k_{a2} - k_{a1}} \quad (21)$$

If  $k_{a1}$  in the latter equation is so small that its value can be neglected, it coincides in form with the dependence (8), obtained for the system not containing in the compressible volume of the centres of condensation.

The results of the calculation in (20) for the case when  $k_{a2} > k_{a1}$  is curve 3 of figure 7, as well as the curve 2, is the isotherm of polymolecular adsorption of a gas on a solid surface. This considerable difference in the shapes of isotherms occurs as a consequence of different relationships between the constants  $k_{a1}$  and  $k_{a2}$  for these cases. If we accept that  $k_{a2}$  is constant, everything begins to depend on the characteristics of the surface  $k_{a1}$ . If the surface is formed by the centres with  $k_{a1}$  more than  $k_{a2}$ , the isotherm of poly molecular adsorption will be in the form of curve 2 of figure 7. If it is formed by centres with  $k_{a1}$  less than  $k_{a2}$ , the corresponding isotherm will be in the form of a curve 3 of this figure. An interesting situation is when the surface is presented by the centres and the first and second type. It is clear that total filling will be equal to the sum of fill centres of each type. For the cases of curves 2 and 3 figure 7 the summation leads to curve 4 of the same figure. We immediately see that this curve is well reflected by numerous experimental data. Traditionally, the initial portion it is interpreted as the filling of the monolayer and a subsequent increase coverage at higher pressures due to the formation of a second and next adsorbed layer on the surface, i.e. the development of polymolecular adsorption. Based on the foregoing it is clear that such an understanding may not always correspond to objective reality. The shape of the curve 4, for example, in every section depends on polymolecular adsorption. Two mechanisms to increase the fill are explained in the analysis of figure 7 and they are connected with the presence on the surface of two types of centres with different values of the parameter  $k_{a1}$ . The proposed understanding enables changes in a wide range of curve 4 in figure 7, and, as a consequence, allows to obtain a satisfactory agreement of calculation results with experimental data.

## 7 Conclusion

In conclusion of this work, we can say that the proposed approach to the analysis of the gas compression process in the presence of condensation centres in the compressible volume allowed us to obtain a physically consistent picture of it, explaining, apparently, all experimentally known features of its flow.

1. It is shown for the first time that the investigated process is described by functions having hidden special points, which becomes apparent only under certain conditions of its maintenance.

2. The presence of these points made it possible to solve the old problem of describing transitions from the hyperbolic gas compression region to its condensation section with constant pressure under a varying volume.

3. It is shown that an increase in the number of condensation centres makes the special points hidden, the corresponding functional dependencies become monotonous.

4. Taking into account these results, the equation of state of real gases is proposed, which naturally describes the hyperbolic section of their compression, the region of their condensation with constant pressure at a varying volume, and the compression section of the formed liquid.

5. This analysis made it possible to determine the filling of the condensation centres by adsorbed gas, i.e. obtain isotherms of polymolecular adsorption for the studied system. The latter differs from those known by a simpler form and opens up the possibility of a physically more realistic simulation of the process described by them. The resulting equation of state and isotherm of polymolecular adsorption for the studied system were obtained, leading to a new understanding of the flowing in it processes.

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