

# Analysis of argon isotope separation by low temperature adsorption

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## ABSTRACT

In this work, the estimated calculated values of the critical parameters of argon isotopes  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ,  $^{40}\text{Ar}$  and the corresponding values of the constants of the Van der Waals, Redlich-Kwong and Peng-Robinson equations of state are obtained. The data obtained make it possible to calculate the adsorption isotherms of argon isotopes on microporous adsorbents. The technique proposed for obtaining analytical expressions for the adsorption isotherms of argon isotopes at cryogenic temperatures makes it possible to estimate the degree of influence of the pressure of the isotope mixture and its composition on the mixture separations coefficients.

**Keywords:** low-temperature adsorption, adsorption isotherm, adsorption of the isotopes, inert gases, argon

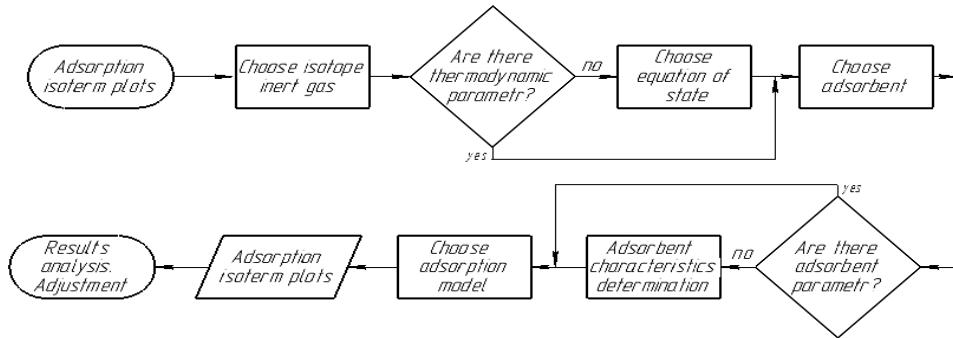
## INTRODUCTION

One of the indicators of the technical and metal consuming parameters of the gas mixture separation unit is the separations coefficients. The numerical value of the separations coefficients make it possible to estimate the number of contact stages in the mass transfer apparatus.

The separation of a mixture of isotopes of inert gases is of particular interest today. Inert gas isotopes are used to obtain various radioisotopes, in MRI machines, in particle accelerators, in fast neutron detectors, for physical and medical research [1, 2, 3]. Experimental separation of a mixture of isotopes is a complex and laborious process; therefore, it is especially important to obtain calculated values of the separations coefficients. At present, rectification, thermal diffusion and centrifugation are used to separate isotopes of inert gases, which have a number of disadvantages, including large mass and size characteristics, the presence of moving elements, the impossibility of separation of more than two components, and a complex automation system. Low-temperature adsorption as a separation method is devoid of these drawbacks, but has been little studied. The experimental values of the separations coefficients of isotopes of helium, argon, and neon for the adsorption method are partially presented in [4, 5], but this information is insufficient for theoretical estimates.

### Calculation of argon adsorption isotherm

Figure 1 shows the developed flow chart for the estimated calculation of the isotope separation of inert gases by the method of low-temperature adsorption.



**Figure 1.** Flow chart for the calculation of the isotope separation of inert gases by the method of low-temperature adsorption

According to the flow chart, a mixture of isotopes for fractionation is initially selected. In this article, the subsequent evaluation calculation and analysis will be carried out for a mixture of argon isotopes. Natural argon has 3 stable isotopes:  $^{36}\text{Ar}$  – 0,34 vol.%,  $^{38}\text{Ar}$  – 0,06 vol.%,  $^{40}\text{Ar}$  – 99,6 vol.%. Stable isotopes of argon  $^{36}\text{Ar}$  and  $^{40}\text{Ar}$  are used in various fields of science and technology. The most common is the production of artificial radioisotopes  $^{37}\text{Ar}$  and  $^{41}\text{Ar}$ . The  $^{37}\text{Ar}$  isotope is used as a radioactive marker in pharmacology, and the  $^{41}\text{Ar}$  isotope is used in the study of gas flows and the ventilation systems efficiency.

Next, it is necessary to determine the thermodynamic parameters of the isotopes. The required parameters for argon isotopes are not available in open sources. Therefore, at the next step of the calculation, it is necessary to choose an equation of state. The gas equations of state allow one to calculate all thermodynamic properties with two characteristic constants, which depend on the type of gas and its bottleneck. The paper considers the widely used cubic equations of state of Van der Waals (VDW), Peng-Robinson (PR), and Redlich-Kwong (RK), taking into account different degrees of influence of bottleneck on constants  $a$  and  $b$ , taking into account the volume of molecules and the forces of intermolecular interaction. The equations of state and their corresponding constants are presented in Table 1. The calculation of the constants is carried out through the critical volume, which makes it possible to bind to a specific gas, in this particular case argon.

No	Equation of state	Equation of state	Constant, $a$	Constant, $b$	Critical volume, $V_{cr}$
1	Van der Waals	$p = \frac{RT}{V-b} - \frac{a}{V^2}$	$\frac{9}{8} \cdot RT_{cr} V_{cr}$	$\frac{V_{cr}}{3}$	$\frac{M}{\rho_{cr}}$

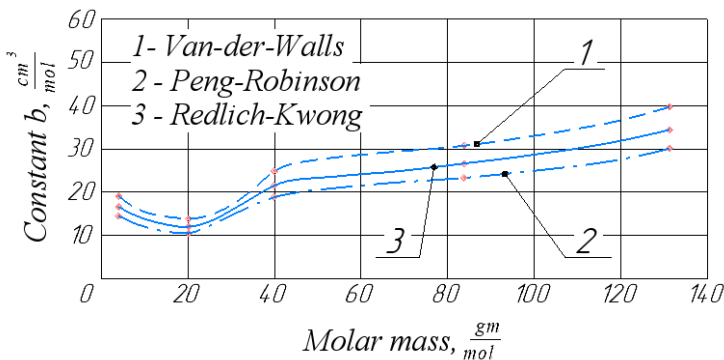
2	Peng-Robinson	$p = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2}$	$a_0 \cdot RT_{cr} V_{cr}^*$	$V_{cr} \cdot 0,253$	$\frac{M}{\rho_{cr}}$
3	Redlich-Kwong	$p = \frac{RT}{V-b} - \frac{a}{\sqrt{TV}(V+b)}$	$a_0 \cdot RbT_{cr}^{1,5**}$	$V_{cr} \cdot 0,289$	$\frac{M}{\rho_{cr}}$
Constants: * - $a_0 = 1,487$ ; ** - $a_0 = 4,934$ .					

**Table 1.** The equations of state and their corresponding constants

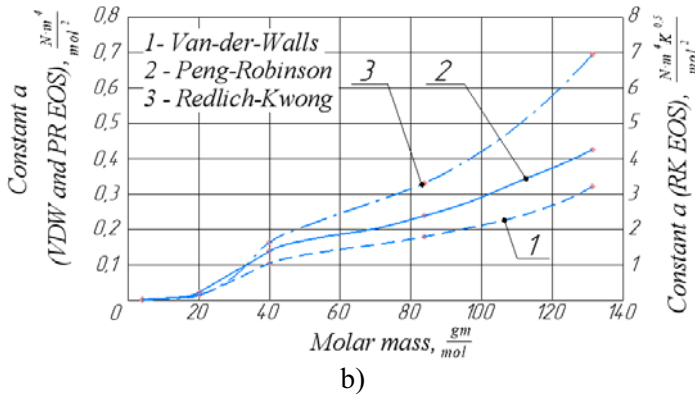
Figure 2 shows a method for determining the constants  $a$  and  $b$  for argon isotopes. For inert gases (helium, neon, argon, krypton and xenon), the equation constants are found for each equation of state. The obtained values were plotted on a diagram, the coordinates of which are the constant of the equation - molar mass. The Mathcad program was used to select a function passing through the obtained points and representing a power polynomial. Knowing the nature of the dependence, the constants of the equations for argon isotopes were determined using formulas (1) and (2).

$$b_{36Ar}, b_{38Ar}, b_{40Ar} \cong b_{Ar} + \left(\frac{db(M)}{dM}\right)_{Ar} \cdot dM \tag{1}$$

$$a_{36Ar}, a_{38Ar}, a_{40Ar} \cong a_{Ar} + \left(\frac{da(M)}{dM}\right)_{Ar} \cdot dM \tag{2}$$



a)



**Figure 2.** Plot of VDW (1), PR (2), RK (3) equations of state constants  
 a) constant *b*; b) constant *a*

The values of the equations *a* and *b* do not always ensure the adequacy of the calculated values of the gas thermodynamic parameters. One of the ways to correct the obtained values is to introduce a correction of the universal critical coefficient  $S_{un}$  to the value determined experimentally  $S_{real}$ . Table 2 shows the values of the critical coefficient for each of the equations of state and for a real gas - argon. When this amendment is made, the constants *a* and *b* in the equation remain unchanged, then it is permissible to take:

$$p_{cr}^{adj} \cong \frac{S_{un}}{S_{real}} \cdot (p_{cr})_{un} \text{ at } T_{cr}^{adj} \cong (T_{cr})_{un} \text{ and } V_{cr}^{adj} \cong (V_{cr})_{un} \quad (3)$$

where,  $(p_{cr})_{un}$  and  $p_{cr}^{adj}$  is a critical pressure before and after adjustment, MPa;  $S_{un}$  is an universal critical coefficient;  $S_{real}$  is a critical coefficient of real gas;  $T_{cr}^{adj}$  and  $(T_{cr})_{un}$  are critical temperature before and after adjustment, respectively, K;  $V_{cr}^{adj}$  and  $(V_{cr})_{un}$  is acritical volume before and after adjustment, respectively,  $\frac{cm^3}{mol}$

Equation of state	Van der Waals	Peng-Robinson	Redlich-Kwong	Argon
Coefficient value	2,667	3,257	3,003	3,424

**Table 2.** Critical coefficient values

The calculated constants of equations *a* and *b* for the isotopes of argon and natural argon are presented in Table 3 (using the  $^{40}\text{Ar}$  isotope as an example). Solving the equations of constants, *a* and *b* together for each of the equations of state, the critical parameters of each isotope are determined. The calculated values of the critical parameters of argon isotopes, taking into account the correction, are presented in Table 4 (using the example of the PR equation of state).

According to the data in Table 4, it can be seen that the difference between the critical temperatures of argon and  $^{40}\text{Ar}$  is insignificant, as well as the pressure

value after correction. The calculated values obtained can be considered adequate, because natural argon consists of 99.6% of the  $^{40}\text{Ar}$  isotope.

№	Equation of State	Gas	Constant $a$		Constant $b$	
			Value	physical dimension	Value	physical dimension
1	Van der Waals	Ar	0,1050	$\frac{N \cdot m^4}{mol^2}$	24,862	$\frac{cm^3}{mol}$
2		$^{40}\text{Ar}$	0,1052		24,895	
3	Peng-Robinson	Ar	0,1390	$\frac{N \cdot m^4}{mol^2}$	18,870	$\frac{cm^3}{mol}$
4		$^{40}\text{Ar}$	0,1393		18,890	
5	Redlich-Kwong	Ar	1,635	$\frac{N \cdot m^4 \cdot K^{0.5}}{mol^2}$	21,555	$\frac{cm^3}{mol}$
6		$^{40}\text{Ar}$	1,6388		21,579	

**Table 3.** Equation of state constants for argon isotopes

Equation of State	Gas	Molar mass	Critical parameter				Footnote
			$T_{cr}, K$	$p_{cr}, MPa$	$V_{cr}, \frac{cm^3}{mol}$	$\rho_{cr}, \frac{kg}{m^3}$	
Peng-Robinson	Ar	39,948	150,69	4,863	74,586	535,6	Real
	$^{36}\text{Ar}$	35,968	134,990	4,724	68,834	522,53	Calculated
	$^{38}\text{Ar}$	37,963	142,924	4,789	71,881	528,13	Calculated
	$^{40}\text{Ar}$	39,962	150,983	5,159	74,664	535,22	Calculated (before adjustment)
	$^{40}\text{Ar}$	39,962	150,983	4,871	74,664	535,22	Calculated (after adjustment)

**Table 4.** Calculated critical parameters of argon isotopes

The next step is an adsorbent selection. To solve the problem, it is necessary to have data on the adsorption isotherms of argon on an industrial adsorbent. The sources [8] experimental data on the adsorption of natural argon on active carbons SKT-4 and PAU-1 at the normal boiling point of liquid nitrogen is presented. Data on adsorbents are presented in table 5 (nitrogen is the standard substance). The results will be used for a qualitative check of the calculations performed in this work. Estimated calculations of adsorption isotherms for natural argon and its isotopes were performed using the Dubinin equation according to the theory of micropore volume filling (MVF) using the calculated values of the critical parameters.

The Dubinin equation for gases in the temperature range below the critical is the following:

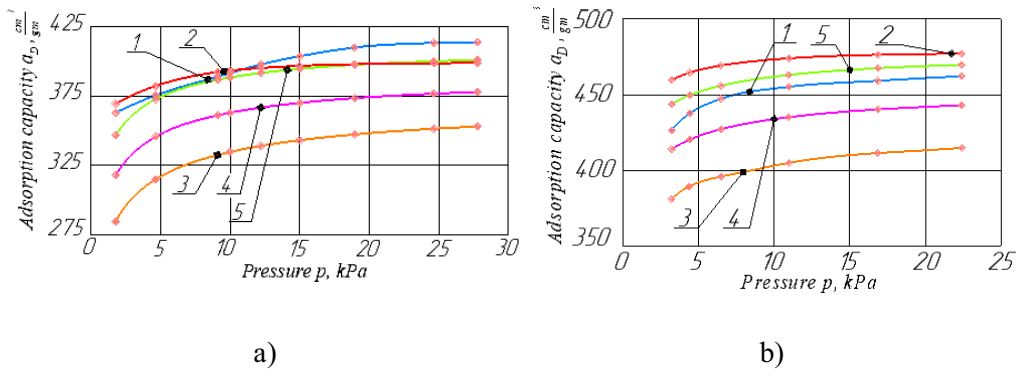
$$a_D = \frac{W_0}{v} \cdot \exp[-B_0 \cdot (\frac{T_{ad}}{\beta})^2 \cdot (\lg(\frac{p_s}{p}))^2] \quad (4)$$

where  $W_0$  is the limiting volume of the adsorption space of a characteristic porous structure,  $cm^3/g$ ;  $B_0$  is a structural constant characteristic of the predominant pore size,  $K^{-2}$ ;  $\beta = \sqrt{a}/\sqrt{a_{st}}$  is the coefficient of affinity of the adsorptive (relative to the standard substance);  $p_s$  is a saturation pressure, MPa;  $p$  is an adsorption pressure, MPa;  $T_{ad}$  is an adsorption temperature, K;  $v = M/\rho$  is the molar mass of the gas in the adsorbed state,  $cm^3/mol$ ;  $M$  is molar mass, g / mol;  $\rho$  is the density of the gas in the adsorbed state,  $kg/m^3$ .

№	Adsorbent	Tapped density, $kg/m^3$	MVF equation parameters (for nitrogen)	
			$W_0, \frac{cm^3}{g}$	$B_0 \cdot 10^6, \frac{1}{K^2}$
1	SKT	0,43	0,515	8,4
2	PAU-1	0,5	0,603	5,1

**Table 5.** Adsorbent parameters SKT-4 and PAU-1

The affinity coefficient  $\beta$  was determined as the ratio of the constant  $a$  of the equations of state of the VDW of argon and nitrogen isotopes. The constant  $a$  for nitrogen was found from the critical parameters of nitrogen taken from the reference data. Figure 3 shows the obtained adsorption isotherms of argon isotopes on active carbons SKT-4 and PAU-1.



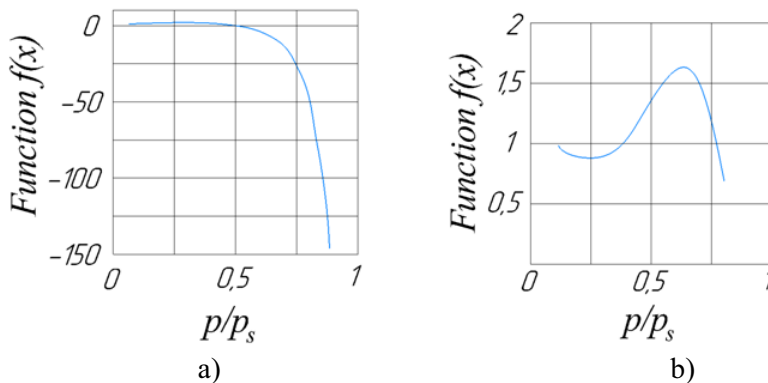
**Figure 3.** Adsorption isotherms according to the PR equation of state at  $T=77K$ :  
 Ar proof of conc. (1), Ar calc. (2),  $^{36}Ar$  (3),  $^{38}Ar$  (4),  $^{40}Ar$  (5)  
 a) SKT-4; b) PAU-1

The calculation of adsorption isotherms for isotopes according to the Dubinin equation did not give satisfactory results. The calculated and experimental isotherm for argon has a relative deviation of 1.4% at the SKT-4 angle, and the nature of the change in the curves is different. Also note that the maximum relative deviation of 6% between the calculated argon isotherm and the calculated  $^{40}Ar$  isotherm. According to similar indicators at PAU-1 angle, the relative deviation is 3.5 and 7.3%, respectively. Therefore, an attempt was made to approximate the adsorption isotherms of argon and its ego isotopes on the SKT-4 and PAU-1 adsorbents by an equation of the form

$$a = \frac{W_0}{v} \cdot \exp[-B_0 \cdot (\frac{T_{ad}}{\beta})^2 \cdot (\lg(\frac{p_s}{p}))^2 \cdot (f(\frac{p}{p_s})_T)^2] \quad (5)$$

where,  $f(\frac{p}{p_s})_T$  constant temperature pressure ratio function  $T$ .

The function  $f(\frac{p}{p_s})_{T=77K}$  is an adjustment of the calculated adsorption isotherm relative to the real one and was determined from the experimental isotherms of argon adsorption on active carbons SKT-4 and PAU-1 at a temperature of 77K. Based on the known experimental and calculated data, discrete values of the function were calculated and its analytical dependence was derived. Figure 4 shows the function diagram.



**Figure 4.** Function  $f(p/p_s)_{T=77K}$  for: a) SKT-4; b) PAU-1

The form of the function is a power equation, which has the form:

$$f(\frac{p}{p_s})_{T=77K} = A + B_{Ar} \cdot \frac{p}{p_s} + C_{Ar} \cdot (\frac{p}{p_s})^2 + D_{Ar} \cdot (\frac{p}{p_s})^3 + E_{Ar} \cdot (\frac{p}{p_s})^4 \quad (6)$$

where,  $A, B_{Ar}, C_{Ar}, D_{Ar}, E_{Ar}$  – equation constants.

Knowing the form of the equation and the values of the constants that were selected using the Mathcad program, let us estimate the adsorption isotherms of argon isotopes on the SKT-4 and PAU-1 angles. Equation constants are recalculated according to the critical parameters of argon and its isotopes. Using the  $^{40}\text{Ar}$  example, the constants of the equation:

$$B_{40Ar} = B_{Ar} \cdot \frac{p_{cr40Ar}}{p_{crAr}} \cdot \frac{T_{cr40Ar}}{T_{crAr}} \quad (7)$$

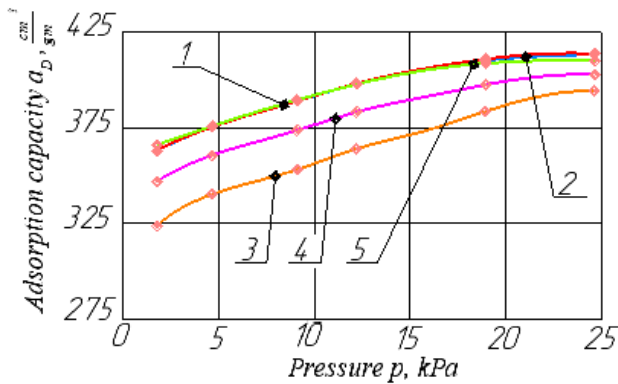
$$C_{40Ar} = C_{Ar} \cdot \left( \frac{p_{cr40Ar}}{p_{crAr}} \cdot \frac{T_{cr40Ar}}{T_{crAr}} \right)^2 \quad (8)$$

$$D_{40Ar} = D_{Ar} \cdot \left( \frac{p_{cr40Ar}}{p_{crAr}} \cdot \frac{T_{cr40Ar}}{T_{crAr}} \right)^3 \quad (9)$$

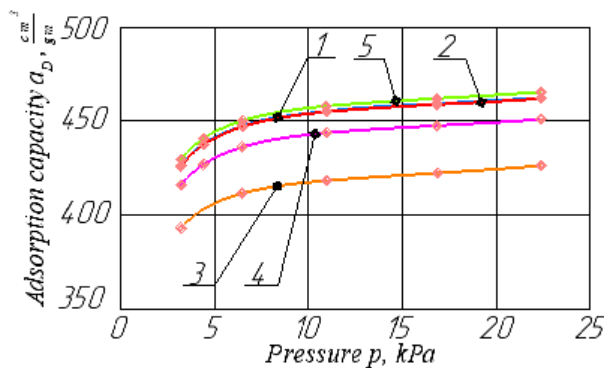
$$E_{40Ar} = E_{Ar} \cdot \left( \frac{p_{cr40Ar}}{p_{crAr}} \cdot \frac{T_{cr40Ar}}{T_{crAr}} \right)^4 \quad (10)$$

Similarly, using formulas (7) - (10), the constants for the isotopes  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  are calculated and equation (6) is used to calculate the adsorption isotherms at  $T = 77\text{K}$ . Figure 5 shows the obtained adsorption isotherms on the SKT-4 and PAU-1 for coal, using the PR equation of state.

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a)



b)

**Figure 5.** Adsorption isotherms  $^{36}\text{Ar}$  (3),  $^{38}\text{Ar}$  (4),  $^{40}\text{Ar}$  using the PR equation of state a) SKT-4; b) PAU-1

From the calculation results presented in Figure 5, it follows that when applying the correction function, the relative deviation of the calculated argon isotherm from the experimental one was 0.26% and 0.07% for SKT-4 and PAU-1 coals, respectively, which does not contradict the experimental data. presented in [6]. The relative deviation of the argon 40 isotherm from the argon isotherm was 0.9% and 0.7% for SKT-4 and PAU-1 coals, respectively. The results obtained are



presented using the PR equation, since when using this equation of state, the smallest design error is obtained.

### Determination of the separations coefficients of argon isotopes

According to the known adsorption isotherms, we determine the fractionation factor of argon isotopes on active carbons SKT-4 and PAU-1 according to the Bering-Sierpinski equation:

$$\ln(K_P) = \frac{Q_1 - Q_2}{R \cdot T_{ad}} \quad (10)$$

where,  $Q_1$  and  $Q_2$  are the heats of adsorption "better" and "worse" of the adsorbed components, respectively,  $\frac{J}{mol}$ .  $R = 8.31$  is an absolute gas constant,  $J / (mol \cdot K)$ .

The adsorption heats were found based on the recommendations presented in [7]. The calculated values of the adsorption heat of isotopes and their separations coefficients on active carbons SKT-4 and PAU-1 are presented in Table 6 and Table 7.

Adsorbent	Gas	Adsorption heat, $\frac{J}{mol}$	Adsorbent	Gas	Adsorption heat, $\frac{J}{mol}$
SKT-4	$^{36}\text{Ar}$	4105	PAU-1	$^{36}\text{Ar}$	4872
	$^{38}\text{Ar}$	4122		$^{38}\text{Ar}$	4888
	$^{40}\text{Ar}$	4136		$^{40}\text{Ar}$	4890

**Table 6.** Adsorption heat of argon isotopes

SKT-4				PAU-1			
	$^{36}\text{Ar}$	$^{38}\text{Ar}$	$^{40}\text{Ar}$		$^{36}\text{Ar}$	$^{38}\text{Ar}$	$^{40}\text{Ar}$
$^{36}\text{Ar}$	1	1,021	1,05	$^{36}\text{Ar}$	1	1,025	1.028
$^{38}\text{Ar}$	1,021	1	1,028	$^{38}\text{Ar}$	1,025	1	1,003
$^{40}\text{Ar}$	1,05	1,028	1	$^{40}\text{Ar}$	1,028	1,003	1

**Table 7.** Separations coefficients of argon isotopes

### CONCLUSION

1. For inert gases, a method for determining the constants  $a$  and  $b$  for the equations of state (VDW, PR, RK) is proposed. The critical parameters of argon isotopes are determined.

2. A method for adjusting Dubinin's equation for building of adsorption isotherms of argon isotopes on active carbons SKT-4 and PAU-1 at temperatures

below critical is proposed. When using the PR equation, the relative error is the smallest and was less than 0.3%.

3. From the obtained adsorption isotherms, the integral heats of adsorption were determined and the separations coefficients of argon isotopes on the adsorbents SKT-4 and PAU-1 were obtained.

### NOMENCLATURE

$\rho_{cr}$	critical density, $\text{kg}/\text{m}^3$	$V_{cr}$	critical point volume, $\text{cm}^3/\text{mol}$
$p_{cr}$	stagnation pressure, MPa	$T_c$	critical point temperature, K
$S_{real}$	real critical coefficient	$S_{ic}$	integrated critical coefficient
$B_0$	structural constant of the predominant pore size, $\text{K}^{-2}$	$W_0$	limit volume of adsorption space, $\text{cm}^3/\text{g}$
$p_s$	saturated pressure, MPa	$\beta$	coefficient of affinity of the adsorptive
$p$	adsorption pressure, kPa	$T_{ad}$	adsorption temperature, K
$v$	molar volume of adsorbed gas, $\text{cm}^3/\text{mol}$	$M$	molal mass, $\text{g}/\text{mol}$
$\rho$	gas density in the adsorbed state, $\text{kg}/\text{m}^3$	$R$	absolute gas constant, $\text{J}/(\text{mol} \cdot \text{K})$
$Q$	integral adsorption heat, $\text{J}/\text{mol}$	$K_{fr}$	fractionation factor

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