Entropy of adsorption of n-pentane on molecular sieve Calsit 5

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A relation for calculation of the entropy of translational motion of molecules with one degree of freedom as well as a relation for calculating the rotational entropy of CH_3 groups is derived. The number of degrees of freedom of the adsorbate molecules is determined by comparing the entropy found from experimental data with the entropy calculated for the molecules of adsorbate with different degrees of freedom. We have found out that the number of translational degrees of freedom of the adsorbate molecules decreases with the quantity adsorbed while the rotational and vibrational degrees of freedom remain in the main unchanged.

We tested the equilibrium data of the adsorption of *n*-pentane on molecular sieve Calsit 5 by means of the Volmer equation [1]. The Volmer equation was derived independently for one and two degrees of translational freedom of molecules. It may be used for the description of the systems in which the number of degrees of freedom decreases during adsorption by one or two degrees of translational freedom. In this study we examined the concentration and temperature dependence of the number of the degrees of freedom of the molecules adsorbed.

The mobility of the molecules of adsorbate is affected mainly by these factors: the intracrystalline arrangement of adsorbent, the degree of occupation of adsorbent Θ , temperature of experiment, and the character of the force field of adsorbent. The intracrystalline volume of molecular sieve Calsit 5 is represented by the cavities with the diameter of 11.28×10^{-8} cm which are joined to each other by a ring of oxygen atoms with the effective diameter of 5×10^{-8} cm. The entry openings as well as a part of the cations blocking these openings cause a decrease in the translational degrees of freedom of the adsorbate molecules. The intracrystalline volume available for the molecules of *n*-pentane decreases with increasing degree of occupation Θ . We assume that a localized arrangement of the adsorbed phase or a volume occupation of the intracrystalline cavities is probable for $\Theta \rightarrow 1$. The thermal energy of the adsorbate molecules and the character of the force field of adsorbent determine whether a molecule remains in a certain locality or moves in the region of adsorption forces. With decreasing temperature the molecules lose their ability to move and conversely the mobility is very probable if the temperature increases especially over the boiling point or if the region of critical temperature is reached. A homogeneous adsorbent or an adsorbent with a regular, defined internal structure, e.g. a molecular sieve gives a better opportunity for the adsorbate molecules to move than an adsorbent with conspicuous minima and maxima of adsorption potential. The adsorbate is represented by relatively small, symmetrical, nonlinear molecules, the critical diameter of which is 4.9×10^{-8} cm.

Since n-pentane is a nonpolar substance, we assume that the interaction between the adsorbate and the lattice of adsorbent is in principle due to the van der Waals forces.

Calculation of entropy from experimental data

For the calculation of thermodynamical quantities it is necessary to define the standard conditions. The entropy of gaseous phase is unambiguously a function of pressure and temperature while the entropy of adsorbate depends on both the quantity of adsorbate occurring on the surface of adsorbate and the temperature. In view of the possible confrontation of the results with the literature data [2, 7] we took the pressure of 760 torr for the standard pressure of the gaseous phase p^0 .

Table 1

Values of entropy calculated from experimental data

t [°C]	Θ	a _e [g/100 g]	p_{e} [torr]	—⊿H [cal mol ⁻¹]	$-\varDelta G$ [cal mol ⁻¹]	$-\Delta S_{e}$ [cal mol ⁻¹ K ⁻¹]
150	0.05	0.557	0.54	13 410	6096	17.3
	0.15	1.671	1.78	12 700	5093	18.0
	0.3	3.343	4.58	12 780	4298	20.1
	0.5	5.572	18.32	13,400	3133	24.3
220	0.5	0.523	2.82	13 450	5485	16.2
	0.15	1.568	12.00	12 700	4065	17.5
	0.3	3.136	32.80	12 710	3080	19.5
	0.5	5.227	131.55	13 400	1719	23.7
280	0.05	0.473	8.90	13 520	4888	15.6
	0.15	1.418	41.00	12 850	3029	17.4
	0.3	2.835	141.50	12 700	1848	19.6
	0.5	4.725	470.00	13 315	528	23.1
340	0.05	0.487	32.2	13 520	3852	15.8
	0.1	0.995	73.8	13 000	2843	16.6
	0.2	1.989	190.00	12 700	1689	18.0
380	0.05	0.577	83.00	13 380	2874	16.1
	0.1	1.153	189.60	12 900	1802	17.0
	0.2	2.306	490.00	12 700	570	18.6

We expressed the quantity of adsorbate on the surface of adsorbent by means of Θ in the range from 0.05 to 0.5 and used the temperature of experiment as standard temperature. We determined the isosteric heat of adsorption for a certain concentration Θ from experimental data. This heat of adsorption corresponded to the total change in enthalpy ΔH . We calculated the change in free enthalpy from the pressure of gaseous phase which is a function of concentration Θ . By using these two quantities we estimated the decrease in entropy accompanying adsorption ΔS_e on the basis of experimental data. The calculated values are listed in Table 1.

Calculation of entropy according to models

We calculated the theoretical values of entropy of the gaseous and adsorbed amount of n-pentane as a sum of the contributions of translational, rotational, and vibrational entropy.

Translational entropy

The translational entropy of ideal gas is given by the Sackur-Tetrode's equation

$$_{0}S_{t} = R \left(\ln M^{3/2} \cdot T^{5/2} \right) - 2.30$$
 (1)

valid at the pressure of 760 torr.

For the entropy with two degrees of translational freedom we used the expression put forward by *Kemball* [2]

$$_{2}S_{t} = R \ln M T a + 65.8, \qquad (2)$$

where a was the specific area in the region of intracrystalline cavities appertaining to one molecule at standard occupation in cm².

The specific volume v of intracrystalline cavities appertaining to one molecule of adsorbate, the specific area a, and the linear distance l available for the free motion of one molecule of adsorbate were determined from the total volume of big cavities in molecular sieve Calsit 5 (21.5 cm³/100 g of adsorbent) [3] and the number of molecules at standard occupation. The calculated values are presented in Table 2.

In order to derive the expression for the entropy of a gas with one translational degree of freedom ${}_{1}S_{t}$, we applied the partition function for the free motion of a particle of mass *m* along the linear section *l*[4]

$$f = \frac{(2\pi m \, kT)^{1/2} \, l}{h},\tag{3}$$

where m is the mass of molecule, k is the Boltzmann's constant, and h is the Planck's constant. For a molecule of gas the partition function has the following form

$$f = \frac{(2\pi m kT)^{1/2}}{h} l e, \qquad (4)$$

Table 2

Properties of the adsorbate caught on molecular sieve as a function of temperature and degree of occupation

t [°C]	Θ	$v\cdot 10^{24}$ [cm ³]	$a\cdot 10^{16}$ [cm ²]	<i>l</i> · 10 ⁸ [cm]
150	0.05	4569.9	277.5	16.7
	0.15	1522.9	136.1	11.7
	0.3	770.4	84.0	9.2
	0.5	462.2	59.8	7.7
220	0.05	4870.1	289.6	17.0
	0.15	1623.4	138.1	11.8
	0.3	821.3	87.7	9.4
	0.5	492.7	62.4	7.9
280	0.05	5387.5	307.3	17.5
	0.15	1816.9	148.9	12.2
	0.3	908.5	93.8	9.7
	0.5	545.1	66.7	8.2
340	0.05	5285.9	303.4	17.4
	0.1	2589.8	188.6	13.7
	0.2	1294.9	118.8	10.9
380	0.05	4467.0	271.2	16.5
	0.1	2233.8	170.9	13.1
	0.2	1168.9	111.0	10.5

where e is the base of natural logarithms.

If the partition function of the molecules is known, one can calculate their entropy by means of the relation

$$S = R\left(\ln f + \frac{\partial \ln f}{\partial T}\right).$$
(5)

By inserting (4) into (5) and rearranging the equation we obtained the following relation

$$_{1}S_{t} = R \ln (M T)^{1/2} l + 38.72,$$
 (6)

where l is the linear distance appertaining to one molecule in cm.

Vibrational entropy

Vibrational motions of a polyatomic molecule may be in good approximation transformed into the so-called normal vibrations of individual atoms of the molecule which are characterized by fundamental frequencies and are independent of each other. Then the vibrational entropy may be calculated from the following relation [5]

$$S_{\text{vib.}} = R \sum_{i=1}^{N-n_1-n_1} \left[\frac{h\nu/kT}{e^{-h\nu/kT} - 1} - \ln \left(1 - e^{-h\nu/kT}\right) \right], \tag{7}$$

Table 3

Vibrational entropy of gaseous n-pentane at 220°C

	Kind of vibration	Wave- number of vibrations [cm ⁻¹]	Frequency of vibration [s ⁻¹ • 10 ⁻¹³]	$S_{ m vib.}$ [cal mol ⁻¹ K ⁻¹]
n-1	Stretching vibration C-C	1000	2,9972	1.7
2n + 2	Stretching vibration C-H	3000	8.9937	0.03
n+4	Deformation vibration H-C-H	1400	4.1797	1.5
3n-2	Deformation vibration $H-C-C$	1000	2.9979	5.6
$n-2 \\ n-1$	Deformation vibration C-C-C Botational swings from restricted	350	1.0493	6.0
<i>n</i> – 1	internal rotation	250	0.7495	5:3
Contra Tra	degrees of freedom		2.50	
	Σ	20		20.13

Table	4

rotational energy of <i>n</i> -pentano at 220 0						
Rotation	σ	${I}_{ m A} \cdot 10^{39} \ [{ m g~cm^2}]$	$I_{ m B} \cdot 10^{39}$ [g cm ²]	$I_{ m C} \cdot 10^{39}$ [g cm ²]	$I_{ m red.} ~~ 10^{39} \ [{ m g~cm^2}]$	S _{rot.} [cal mol ⁻¹ K ⁻¹]
External Internal	2 3	4.42	42.87	45.76	0.5 [7]	26.0 3.04

Rotational entropy of n-pentane at 220°C

where N is the total number of degrees of freedom, n_1 is the number of translational degrees of freedom, n_2 is the number of degrees of freedom of external rotation, and ν is the frequency of vibration.

The frequencies of vibration are most frequently determined from spectral data. According to Volkenštejn [6] a molecule of normal paraffin of formula C_nH_{2n+2} has 9n + 6 degrees of freedom from which n_1 is the number of translational freedom, n_2 is the number of degrees of freedom for external rotation of the molecules, n - 1is the number of degrees of freedom for internal rotation and the rest is the number of degrees of freedom for normal vibrations. The distribution of individual vibrations is presented in Table 3. The calculation of the vibrational contribution to entropy is based on the assumption that the frequencies of vibration are independent of the degree of occupation Θ . For an adsorbed phase with mobile molecules this idea is to be expected.

Rotational entropy

The symmetrical nonlinear molecule of n-pentane has three degrees of freedom for external rotation around three mutually perpendicular axes going through the centre of the molecule gravity and four degrees of freedom for internal rotation of different parts of the molecule. For calculation of the entropy for external rotation we used the following relation [5]

$$S_{\rm rot. \ ext.} = R \left\{ \ln \left[\frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 \ kT}{h^2} \right)^{3/2} (I_{\rm A} \ I_{\rm B} \ I_{\rm C})^{1/2} \right] + 3/2 \right\}, \tag{8}$$

where σ is the number of symmetry and I_A , I_B , I_C are the moments of inertia around the coordinate axes. For the entropy of internal rotation we derived the following equation from the partition function [6]

$$S_{\text{rot. int.}} = R \left\{ \ln \left[\frac{1}{\sigma} \left(\frac{8\pi^3 I_{\text{red.}} kT}{h^2} \right)^{1/2} \right] + 1/2 \right\},\tag{9}$$

where $I_{red.}$ is the reduced moment of inertia.

We calculated the entropy of internal rotation of two methyl end groups and included the remaining two degrees of freedom of internal rotation into the calculation in the form of rotational swings. The values of the moments of inertia, symmetry numbers, and rotational entropy are given in Table 4.

The theoretical values of entropy at standard occupation $\Theta = 0.05$, 0.15, 0.3, and 0.5 were calculated for 150, 220, and 280°C and those at $\Theta = 0.05$, 0.1, and 0.2 for 340 and 380°C. The difference between the entropies of molecules in the gaseous state and in the adsorbed phase gives the change in entropy due to adsorption. As an example of calculation we present Table 5 in which the decrease in entropy accompanying the adsorption of *n*-pentane is calculated for the temperature of 220°C and standard state $\Theta = 0.5$. The decrease in entropy found from experimental data for 220°C and standard state $\Theta = 0.5$ is 23.7 cal mol⁻¹ K. This value is in good agreement with the theoretical value of the decrease in entropy calculated for one-dimensional gas with total rotation (23.4 cal mol⁻¹ K). The degrees of translational freedom determined by comparing the theoretical value of entropy with the value calculated from experimental data are listed in Table 6.

Table 5

Decrease Entropy [cal mol⁻¹ K⁻¹] Description of phase in trans. ext. rot. int. rot. vibr. together entropy Three-dimensional 41.3 26.0 6.1 20.0 93.4 0 Two-dimensional with total rotation 21.6 26.0 6.1 20.7 74.4 19.0 Two-dimensional with internal rotation 21.6 0 6.1 28.6 56.3 37.1 Two-dimensional without rotation 21.6 0 0 33.8 55.4 37.9 One-dimensional with total rotation 16.6 26.0 6.1 21.3 70.0 23.4 **One-dimensional** with internal rotation 16.6 0 6.1 29.2 51.9 41.5 **One-dimensional** without rotation 16.6 34.4 51.142.3 0 0 Localized 0 0 0 35.1 35.1 58.3

Adsorption entropy of *n*-pentane at 220°C and standard occupation $\Theta = 0.5$

Table 6

Values of entropy as a function of temperature, degree of occupation (Θ) and degree of translational freedom of *n*-pentane (n_1)

t [°C]	Θ	n_1	$\frac{-\Delta S_t}{[\operatorname{cal} \operatorname{mol}^{-1} \mathrm{K}^{-1}]}$	−ΔS _e [cal mol ⁻¹ K ⁻¹]
150	0.05	2←3	15.8	17.3
	0.15	2	17.2	17.8
	0.3	1 2	18.3; 22.8	20.1
	0.5	1	23.2	24.3
220	0.05	2	16.0	16.2
	0.15	2	17.4	17.5
	0.3	1 2	18.3; 23.0	19.5
	0.5	1	23.4	23.7
280	0.05	2	16.0	15.6
	0.15	2	17.5	17.4
	0.3	1 2	18.4; 23.1	19.6
	0.5	1	23.5	23.1
340	0.05	2	16.3	15.8
	0.1	2	17.4	16.6
	0.2	2	18.3	18.0
380	0.05	2	16.5	16.1
	0.1	2	17.5	17.0
	0.2	2	18.3	18.6

Discussion

In the introduction the factors influencing the mobility of molecules have been given and now we are going to confront them with the results of calculations. The effect of intracrystalline structure on the number of degrees of freedom may be

estimated at such low concentrations of adsorbate that the probability of occurrence of a molecule in two neighbouring cavities is negligible. At low concentrations the relative error of measurement is relatively great and for this reason we chose the value $\Theta = 0.05$ for the lowest degree of occupation used for the calculation of entropy. The intracrystalline cavities of molecular sieve Calsit 5 show cubic--octahedral shapes but with good approximation their volume may be regarded as the volume of a sphere with the diameter of 11.28×10^{-8} cm, *i.e.* 750×10^{-24} cm³. Every cavity is connected with six adjacent cavities by the openings the effective diameter of which is 5×10^{-8} cm. A molecule of adsorbate can move from the cavity in three directions. The probability of motion of a molecule in arbitrary direction is limited and of all attempts to move only a certain percentage is successful. For the molecules of adsorbate at standard occupation $\Theta = 0.05$ the number of degrees of freedom $2 \leftarrow 3$ is close to two. The missing degree of translational freedom expresses the limitation of the motion of adsorbate molecules in molecular sieve with respect to the number of degrees of freedom which the adsorbate molecules would have in the gaseous state. At standard occupations $\Theta = 0.1, 0.15$, and 0.2 the number of translational degrees of freedom is equal to 2. If we assume the most probable distribution of the adsorbate molecules in cavities, then at the concentration $\Theta = 0.1$ one molecule may be assigned to three cavities, at $\Theta = 0.15$ one molecule corresponds to 2-2.4 cavities according to temperature, and at $\Theta = 0.2$, one molecule appertains to 1.5–1.7 cavities. The degree of occupation $\Theta = 0.2$ at which one molecule corresponds to 1.5-3 cavities affects very little the mobility of molecules. At the degree of occupation $\Theta = 0.3$ one molecule of adsorbate corresponds to 1-1.2 cavities and the number of degrees of freedom is 1-2. At this occupation the molecules begin to prevent each other in motion. At the concentration $\Theta = 0.5$ one cavity contains 1.3-1.6 molecule of adsorbate. The number of degrees of freedom equals 1. The effect of the degree of occupation on the number of translational degrees of freedom manifests itself in the region where one cavity contains 0.84 - 1.6 molecules of adsorbate and involves the loss of one degree of freedom.

In the investigated temperature range from 150 to 380°C the effect of temperature on the number of translational degrees of freedom is not conspicuous. It appeared merely at the concentration $\Theta = 0.3$. At 150°C the number of degrees of freedom 1-2 is approximately equal to 1.5 while it approximates 1 at 220 or 280°C. The opposite tendency at $\Theta = 0.05$ may be attributed to the worse accuracy of calculation in the region of small concentrations.

The theoretical calculation of entropy confronted with the values of entropy calculated from experimental data provides valuable information on the mechanism of adsorption and completes the testing of experimental data for the equation of adsorption isotherm. The study of the degree of freedom of adsorbate shows us how it is possible to a certain degree and with an accuracy suitable for technical purposes to predict an equilibrium quantity of adsorbate as a function of temperature, and the sizes of the adsorbate molecules of certain kind, *e.g.* paraffin hydrocarbons on a given type of adsorbent provided the adsorption heat is known.

Symbols

- *a* specific area corresponding to one molecule of adsorbate
- $a_{\rm e}$ mass of the adsorbate caught on adsorbent at the equilibrium pressure $p_{\rm e}$

a_0	mass of the adsorbate on adsorbent corresponding to the pressure of saturated					
	vapour of adsorbent p_e at room temperature					
e	base of natural logarithms					
f	partition function					
h	Planck's constant					
k	Boltzmann's constant					
l	linear distance for free motion of a molecule					
m	mass of a molecule of adsorbate					
n	number of carbon atoms in a chain of normal paraffin					
n_1	number of translational degrees of freedom					
n_2	number of degrees of freedom for external rotation of molecule					
p^0	standard pressure, 760 torr					
Pe	equilibrium pressure					
t	temperature [°C]					
v	specific volume of intracrystalline cavities corresponding to one molecule					
	of adsorbate					
⊿G	change in free enthalpy due to adsorption					
ΔH	change in enthalpy due to adsorption					
$I_{\rm A}, I_{\rm B}, I_{\rm C}$	moments of inertia of a molecule around coordinate axes					
Ired.	reduced moment of inertia					
M	molecular weight of adsorbate					
\boldsymbol{N}	total number of degrees of freedom					
\boldsymbol{R}	gas constant					
ΔS_{e}	change in entropy calculated from experimental data for adsorption					
ΔS_t	change in entropy obtained by theoretical calculation for adsorption					
3St	translational entropy of ideal gas					
2.St	translational entropy of two-dimensional ideal gas					
$_1S_t$	translational entropy of one-dimensional ideal gas					
Sext. rot.	entropy of external rotation of molecules					
Sint. rot.	entropy of internal rotation of molecules					
Svib.	vibrational entropy of molecules					
T	temperature [K]					
$\Theta = \frac{a_{\rm e}}{a_0}$	degree of occupation of adsorbent by adsorbate					
ν	frequency of normal vibration					
σ	symmetry number					

References

1. Šefčíková, M., Havalda, I., Kossaczký, E., and Bobok, D., Chem. Prům., in press.

- 2. Kemball, C., Proc. Roy. Soc. (London) A187, 73 (1946).
- 3. Sitnai, O., Thesis. Slovak Technical University, Bratislava, 1966.
- 4. Moelwyn-Huges, E. A., Physical Chemistry, I. Pergamon Press, London, 1961.
- 5. Hála, E. and Boublík, T., Úvod do statistické termodynamiky. (Introduction to Statistical Thermodynamics.) Prague, 1969.
- 6. Volkenštejn, M. V., Struktura a fysikální vlastnosti molekul. (Structure and Physical Properties of Molecules.) Prague, 1962.
- 7. Pitzer, K. S., J. Chem. Phys. 8, 711 (1940).

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