

## ARTIFICIAL ZEOLITES APPLICATION IN VACUUM TECHNOLOGY

BY I. BARYCKA

Department of Electronics, Institute of Technology, Wrocław\*

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Some sorptive properties of synthetic type *A* and *X* zeolites in various cationic forms are described. The measurements were limited to pressures below 1 Tr and were carried out for nitrogen by means of the volumetric and gravimetric methods at 78°K and for helium by means of the volumetric method at 4.2°K. Besides, the problem is discussed how to get rough vacuum by means of single or double stage sorption pumps filled with synthetic zeolites of different type. Some aspects of the behaviour of zeolite traps cooperating with oil diffusion pumps in laboratory vacuum equipment are also discussed.

*1. Introduction*

The gas sorption by porous materials at low temperatures in the basis of one of the evacuation methods. Synthetic aluminosilicates, alkali or alkali earth metals, known as molecular sieves or artificial zeolites are very good sorptive materials used in vacuum techniques [1-4].

Their good sorptive properties are caused by their specific crystal structure and the energetic heterogeneity of their surface. Zeolites show also a good resistibility against repeated thermal and vacuum regeneration. In consequence of their above-mentioned properties, adsorption of gases occurs even under quite low pressures of the adsorbed gases, and especially for those gases whose molecules are polar or have a free electron pair. The sorptive properties of zeolites are utilized in vacuum techniques in two ways:

1° filling of rough-vacuum sorption pumps in small oil-free vacuum systems operating with sputter-ion pumps,

2° filling of so called zeolite traps put above the oil diffusion pumps in high vacuum parts of the system. Most of residual gases, especially those produced by thermal decomposition of oil, are sorbed by the zeolites, the final pressure being lowered by a factor of 100-1000.

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\* Address: Instytut Technologii Elektronowej Politechniki Wrocławskiej, Wrocław, ul. Smoluchowskiego 11, Polska.

## 2. The isothermes of nitrogen and helium adsorption at low temperatures and low pressures

### 2.1. Materials

Artificial, laboratory-made zeolites were used, corresponding, from the point of view of the structure and chemical composition, to those of Linde's Mol. Sieves NaA and NaX. The ion exchange products, Na-ions being replaced by K, Li, Ca, Mg and Ba, were examined as well. The gases used for the adsorption were spectrally pure.

### 2.2. The apparatus and the measurement methods

The gas adsorption was measured by volumetric and gravimetric methods.

The nitrogen adsorption measurement by means of the gravimetric method was carried out in a glass vacuum apparatus equipped with an electronic balance ( $W$ ) (Fig. 1). 10–30 mg zeolite portions ( $Z$ ) were activated before measurement at 370°C in vacuum, for 5–10 hours. Nitrogen was dosed from an attached gas receptacle ( $C$ ). Equilibrium pressure was measured by an ionization gauge and a Penning gauge ( $S$ ).

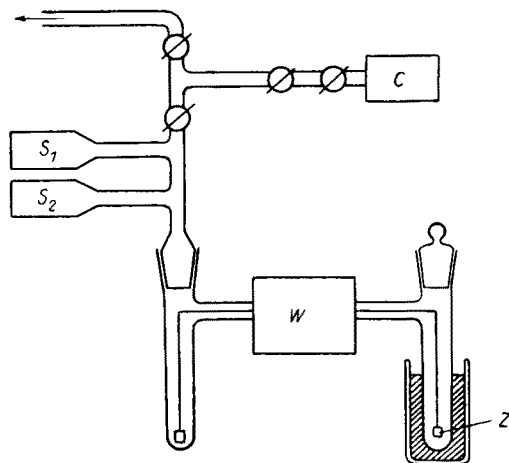


Fig. 1. Schematic diagram of apparatus for gravimetric measurements

Volumetric nitrogen adsorption measurements were carried out in a glass vacuum apparatus having marked chambers ( $B$ ) and a nitrogen filled flask ( $C$ ) (Fig. 2). 200–300 mg zeolite portions ( $Z$ ) were activated as mentioned above, the dosed nitrogen pressure being measured by an oil manometer ( $M$ ) and the equilibrium pressure by a heat conducting gauge and an ionization gauge ( $S$ ). All nitrogen adsorption measurements were carried out at 78°K. The helium adsorption was observed in a simple volumetric system immersed in a cryostat filled with liquid helium (Fig. 3).

5g portions of zeolite were activated as mentioned above. Helium was dosed under atmospheric pressure, the equilibrium pressure being measured by a heat conducting gauge.

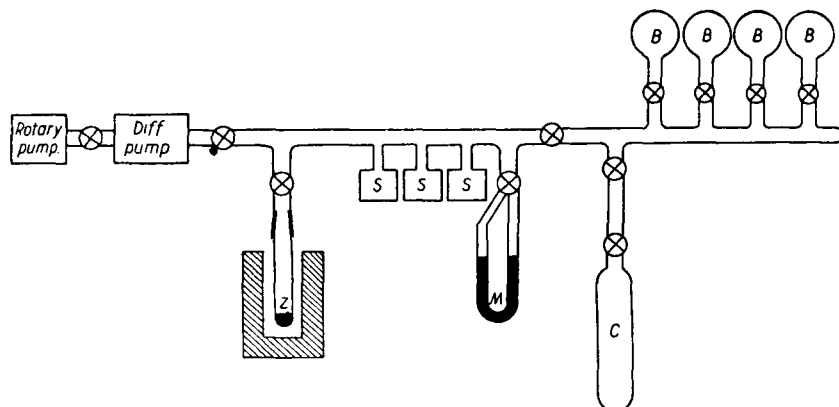


Fig. 2. Schematic diagram of apparatus for volumetric measurements

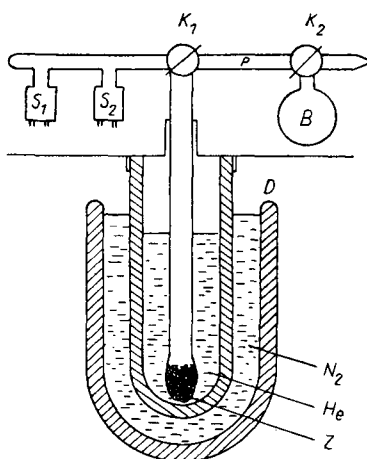


Fig. 3. Schematic diagram of apparatus for volumetric helium adsorption measurements

### 2.3. Results and discussion

All the obtained results are shown in Figs 4–7 as isothermes of sorption.

The high affinity of nitrogen with zeolites (especially type *X*) was confirmed. The saturation state or a state near to it was attained already at  $p \approx 10^{-1}$  Tr *i. e.*  $p/p_0 \approx 10^{-4}$ . It became evident that zeolites with bivalent cations adsorb more gases than those with univalent ones. The interaction of helium with the zeolitic surface may be regarded as a result of the action of its dispersive forces mainly as the polar component gets a very small value for the weak polarizability of helium. On comparing however these results with those of Schaeffer, obtained in his investigations of helium adsorption on Spheron type graphitized carbon black (with typical homogeneous surfaces), some participation of so called specific action in zeolite-helium systems becomes evident [5]. The partial molar heat of helium adsorption on graphitized carbon black ranges from 93–34 cal/mol, depending on the amount of adsorbed helium. The monomolecular layer is attained here at  $p \approx 70$  Tr and the corresponding heat

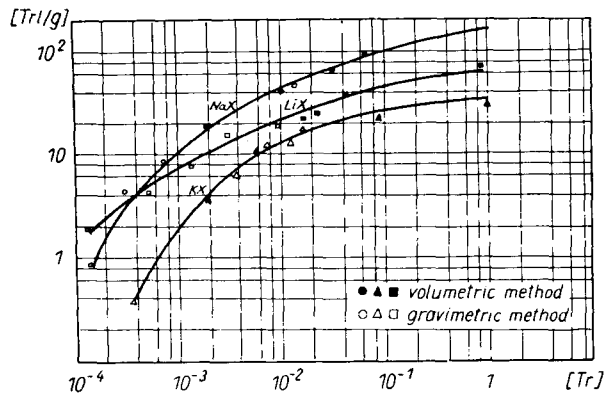


Fig. 4. The isothermes of nitrogen sorption on zeolites NaX, LiX, KX

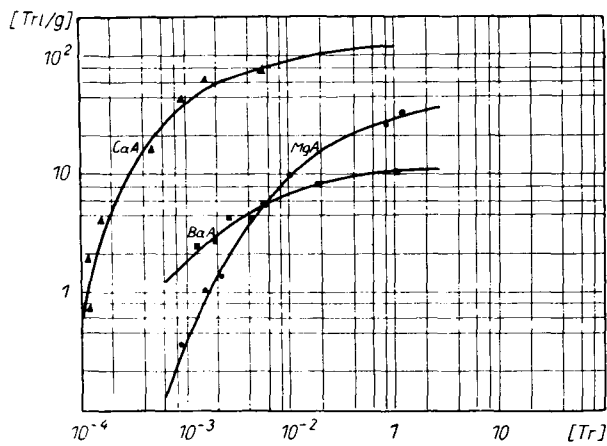


Fig. 5. The isothermes of nitrogen sorption on zeolites CaA, MgA, BaA

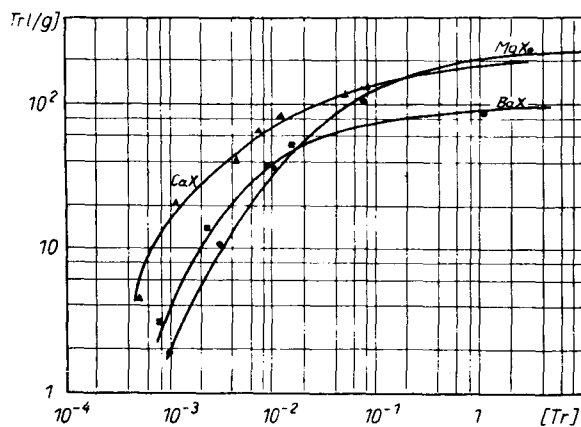


Fig. 6. The isothermes of nitrogen sorption on zeolites MgX, CaX, BaX

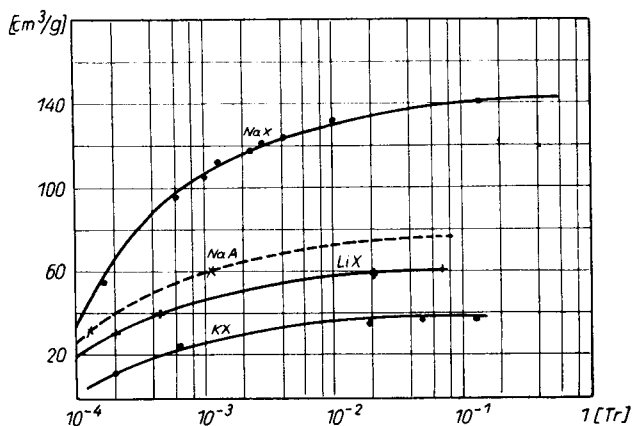


Fig. 7. The isotherms of helium sorption on zeolites NaX, NaA, LiX, KX

amounts then to 60 cal/mol. A similar saturation state for all zeolites is attained at  $p \approx 10^{-4}$ Tr and the calculated adsorption heat for this pressure amounts to about 150 cal/mol. This difference in helium adsorption heat on carbon black and on the zeolites may be treated as a measure of the energetic heterogeneity of zeolite surface.

### 3. Method of obtaining a rough-vacuum by means of sorption pumps filled with artificial zeolites

In this section some possibilities of application of artificial zeolites in rough-vacuum sorption pumps are examined; the characteristic curves of these pumps and the values of equilibrium pressures in two-stage pumps are shown.

#### 3.1. Devices and measurements

The measurements of the isotherms of dry air sorption were carried out in an all-glass sorption pump shown in Fig. 8a. The whole pump volume was 254 cc, the zeolite portions were 4g.

The operation characteristics of two-stage sorption pumps were obtained with the glass pump shown in Fig. 8b. The zeolite portions were 3g and 1g, the pump volumes  $V_1 = 120$ cc,

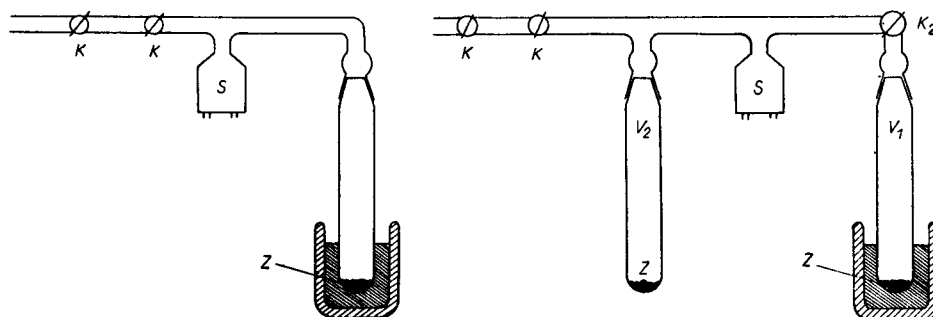


Fig. 8. a) Schematic diagram of a sorption pump, b. Schematic diagram of a two-stage sorption pump

$V_2 = 208\text{cc}$ . In each experiment the zeolite samples were thermally activated at  $370^\circ\text{C}$  for 5 hours; the air, dried above  $\text{P}_2\text{O}_5$ , was dosed by a calibrated vessel  $K-K$ . During the measurement the adsorption tubes were immersed in liquid nitrogen. The equilibrium pressure was measured by means of a heat conducting gauge. The following artificial zeolites were tested: NaX, KX, CaX, MgX, BaX, CaA and BaA.

### 3.2. Results

The measurement results are shown in Figs. 9a, 9b, 9c in the form of air adsorption isothermes. The operation characteristics of two stage sorption pumps can be seen in Table I. A closer interpretation of the results presented above is impossible owing to the large va-

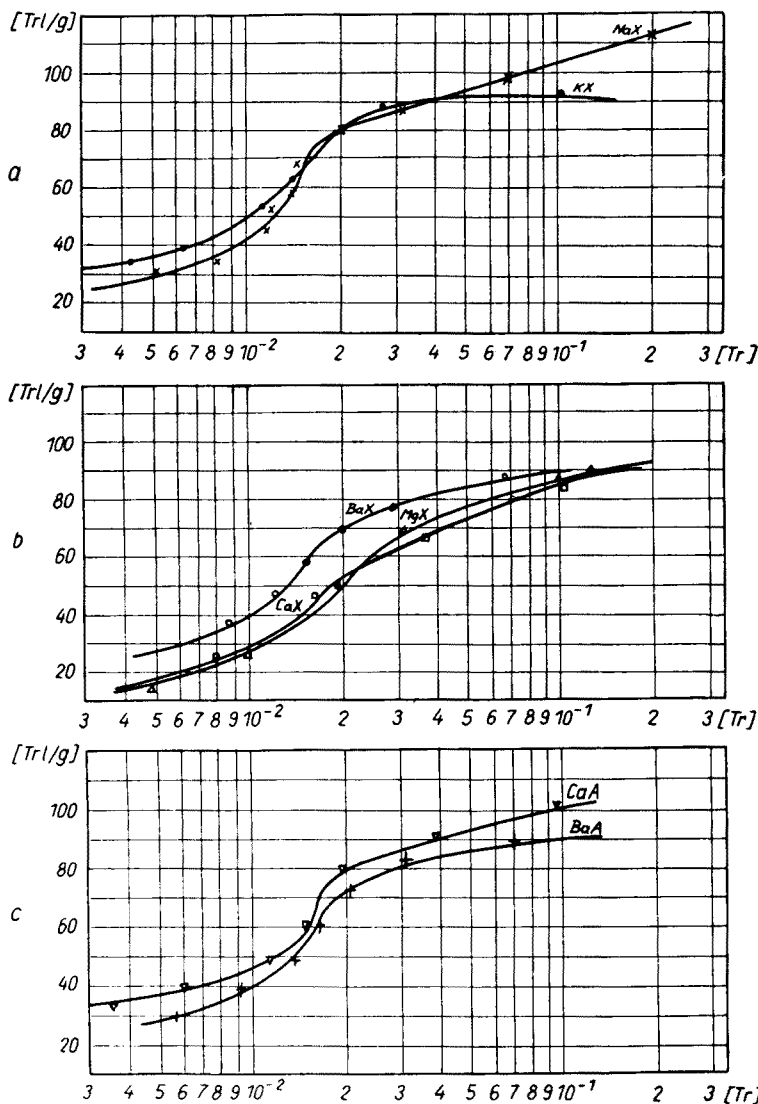


Fig. 9. The isothermes of dry air adsorption on zeolites: a. KX, NaX; b. BaX, CaX, MgX; c. BaA, CaA

TABLE I

Zeolite type	Stage I $p_1$ Tr	Stage II $p_2$ Tr
CaA	$4 \times 10^{-2}$	$4 \times 10^{-3}$
MgA	$9 \times 10^{-2}$	$1 \times 10^{-2}$
CaX	$1 \times 10^{-1}$	$5 \times 10^{-3}$
MgX	$1 \times 10^{-1}$	$9 \times 10^{-3}$
BaX	$8 \times 10^{-2}$	$5 \times 10^{-3}$
KX	$8 \times 10^{-2}$	$3 \times 10^{-3}$
NaX	$3.8 \times 10^{-2}$	$3 \times 10^{-3}$

riety of properties of the air components. Generally, one can state that the sorptive properties of the different zeolite types in relation to air, change similarly as for pure nitrogen. In view of the results obtained by utilizing the one stage sorption pump it is reasonable to use the latter only for pressures greater than  $1 \times 10^{-2}$  Tr, whereas a further pressure lowering can be attained by using the two stage system. The second stage of sorption pumping is much less efficacious because of the noble gases preponderance in the residual gas and its low initial pressure. Some improvement of the two stage sorption pump parameters was attained in a mixed system, where in the first pumping stage a NaX zeolite was applied with a higher sorptive capacity while in the second stage KX or NaA zeolites, having the best activity at the lowest initial pressures [6].

#### 4. Utilization of artificial zeolites in high vacuum systems

Some improvement in high vacuum systems operating with oil diffusion pumps can be attained by removing the most part of the residual gases, especially those arising from thermal decomposition of oil. This is brought about by freezing these gases or their adsorption at room temperature by traps. The role of such adsorbent is played by artificial zeolites. Previous reports [7], [8] concerned only the NaX (13X) type zeolite, cooperating with Convoil 20 and Octoil S type oils. In this study some aspects of the action of these zeolite traps are dealt with.

##### 4.1. Devices and measurements

All the measurements were carried out in a glass vacuum system equipped with a rotary pump and an oil diffusion pump *PDO60*, filled with silicon oil *DC 703*, the pressure being measured by an ionization gauge and a mass spectrometer-omegatron. Granulated zeolite was placed in a simple glass trap above the diffusion pump in the baked part of the system (Fig. 10).

##### 4.2. Results

All the conditions of measurement and results of the investigations carried out with the NaX zeolite filled traps are listed in Table II.

The results of the studies have revealed that in the described conditions the final pressure can be easily lowered below  $1 \times 10^{-7}$  Tr ( $10^{-8}$  Tr, even to  $10^{-9}$  Tr). No influence

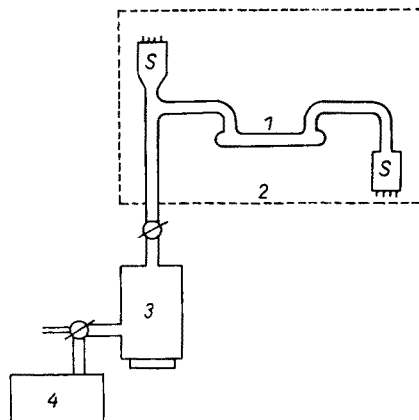


Fig. 10. Schematic diagram of a vacuum system zeolite trap. 1. trap, 2. furnace, 3. diff. pump., 4. rotary pump

of the trap construction, nor of the amount of zeolite used on the final pressure have been observed here. It was noticed that a zeolite sample activated in high vacuum and exposed to air for 5 min. underwent some deactivation necessitating to be anew shortly activated thermally in vacuum conditions.

TABLE II

Pressure attained without using zeolite trap	$8 \times 10^{-6}$ Tr
NaX zeolite amount	30 g
Activation temperature	$350^{\circ}\text{C}$
Activation time	10 hours
Final pressure above the trap	$< 1 \times 10^{-7}$ Tr

The main cause of the deactivation is moisture adsorption, becoming irreversible at low pressures.

In further experiments the behaviour of various zeolite types in traps above diffusion pumps was tested. The conditions as well as the results are shown in table III.

TABLE III

Zeolite type	Activation time (h)	Final pressure (Tr)
NaX	6	$< 1 \times 10^{-7}$
MgX	6	$< 1 \times 10^{-7}$
CaX	6	$1 \times 10^{-7}$
BaX	6	$< 1 \times 10^{-7}$
NaA	6	$< 1 \times 10^{-7}$
NaY	6	$< 1 \times 10^{-7}$
NaB	6.5	$< 1 \times 10^{-7}$
NaKL	5	$< 1 \times 10^{-7}$



It has been stated that for all zeolite species, neither the cation type, nor the crystal structure type do influence the final pressure value achieved in this system. Some insignificant differences in the resistance to a short air influence is in each particular case directly connected with the zeolite affinity to water, thus, *e.g.* the CaX zeolite type shows a strong water adsorption in low pressure conditions, causing in consequence some difficulties with activation after exposition to the air whereas the BaX type zeolite, having the lowest affinity to water, easily returns to its active form. The fact that the final pressure obtained was less than  $1 \times 10^{-7}$ , as when using 13 X type zeolite, having the largest windows leading to adsorptive cells, as when using NaB type, having the finest windows, proves that the primary catalytic decomposition of the oil vapours precedes the proper adsorption. Residual gases have been analyzed by means of an omegatron gauge. Some gase analyses have performed both in the glass vacuum system with empty trap above oil diffusion pump (Figs. 11 *a, b, c*), and with trap filled with 20 g NaX zeolite (Figs. 11 *d, e, f*) as well.

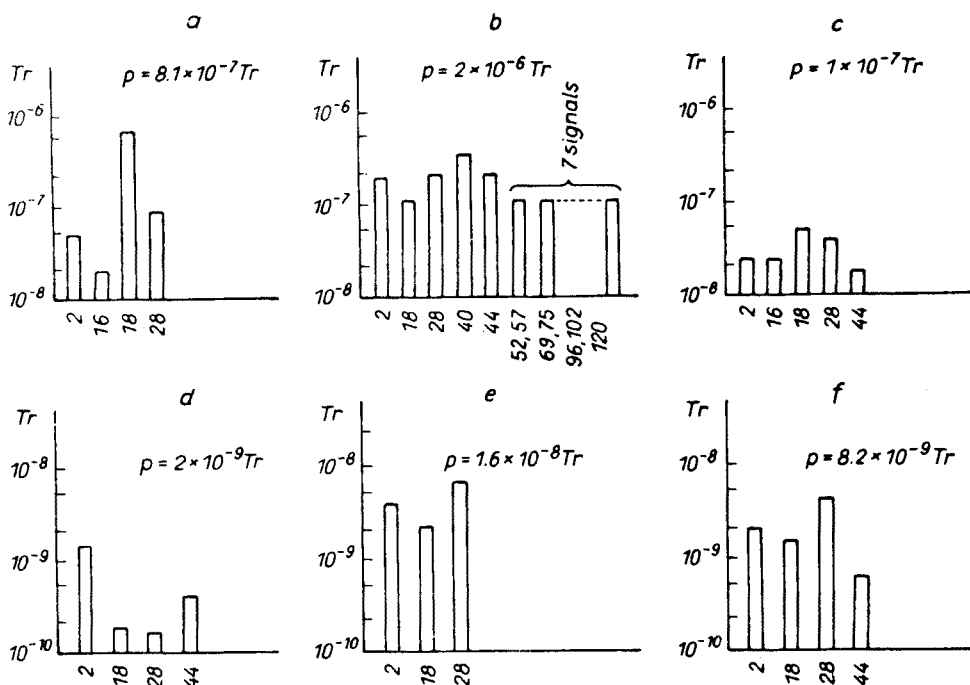


Fig. 11. Mass spectrometer analysis of residual gases

In any case one could observe that the switching on of the ionization gauge changed the composition of the residual gas phase, raising thereby the total pressure. All analyses were carried out with the ionization gauge being switched off. The results of the analyses can be seen in Fig. 11. The conditions of all the experiments were as follows:

a) the high vacuum part of the system was baked for 4 hours at  $400^\circ\text{C}$ . The analyses were made immediately after the heating was finished,

b) the same experiment — on the next day after baking and after pumping for 5 hours.

Signals characteristic for oil vapour have appeared,

c) the same experiment, with the use of liquid nitrogen trap,

d) the high vacuum part of the system with zeolite trap was baked for 5 hours at 400°C.

The analysis was made immediately after the baking was finished,

e) the same experiment — on the next day after baking and after pumping for 5 hours,

f) the same experiment, four days after the baking; the diffusion pump was working about 20 hours.

It is evident that the role of the zeolites as trap filling consists not only in oil vapour adsorption, but also in a distinct decrease in the partial pressure of the gases. The gas most resistant to zeolite traps appeared to be hydrogen due to its physico-chemical properties.

During these experiments it has been observed that in systems equipped with zeolite traps there was a very slow increase in pressure after cutting them off from the pumps. In practice, in glass-apparatus with glass valve (greased with apiezon) the  $1 \times 10^{-6}$  Tr pressure was maintained for several weeks. From the aforesaid statements one can conclude the existence of a dynamic equilibrium between the desorption process of the residual gases from the apparatus walls and the diffusion through the walls and the leakings on the one hand, and a strong sorption of those gases through the mass of the active zeolites, on the other.

In experimental conditions it was not possible to observe the changes in the static vacuum value because every switching on of ionization gauge caused substantial differences in the gaseous phase being in equilibrium with the zeolite. Some of these values are given in Table IV.

TABLE IV

Zeolite type	The final pressure in the cut-off instant (Tr)	Cut-off time (h)	The final pressure after the time $t$ (Tr)
NaX	$2.7 \times 10^{-6}$	120	$6.7 \times 10^{-6}$
NaX	$9 \times 10^{-7}$	15	$5.8 \times 10^{-6}$
MgX	$9 \times 10^{-7}$	120	$4 \times 10^{-6}$
BaX	$6 \times 10^{-7}$	15	$9 \times 10^{-7}$
BaX	$7 \times 10^{-7}$	60	$2 \times 10^{-6}$
without zeolite trap	$1 \times 10^{-6}$	24	$5 \times 10^{-4}$
without zeolite trap	$1 \times 10^{-6}$	48	$1 \times 10^{-3}$

After 200–300 hours of operation of the zeolite trap above the oil diffusion pump there appears on the surface of the granules a black-coloured efflorescence caused by the carbonization of organic molecules. This further observation confirms that the supposition of the catalytic decomposition of oil vapours on the zeolite surface is correct. During about 500 hours utilization of the vacuum zeolite-trap-system which has been periodically regenerated by heating in vacuum, no zeolite deactivation was seen.

A general comparison of the results obtained by means of the zeolite trap with those

obtained with liquid nitrogen points out clearly the superiority of the first system, both from the point of view of ultimate pressure and easy handling.

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