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Separation of Gases by Zeolites

In "Electrostatic aspects of physical adsorption: Implications for molecular sieves and gaseous anesthesia," (*1*) Benson and King correctly state that the adsorptive properties of zeolites can be modified by exchanging the mobile cations for different ones. However, exception must be taken to their conclusion that the separation of gases by zeolites is due primarily to adsorption on the external surface of the crystal, rather than to adsorption in the internal cavities of the zeolite.

When a zeolite is outgassed at elevated temperature under vacuum and then cooled to a lower temperature, the zeolite crystals will occlude in their cavities, molecules of any gas to which they are exposed (subject to molecular-size restrictions). Barrer and Gibbons (*2*) have shown that the saturation sorption capacity of synthetic faujasite for CO_2 corresponds quite well to the volume of the large cages in this zeolite. They have also shown that the amount of NH_3 occluded by synthetic faujasite corresponds quite well to that predicted by assuming that the large cages and sodalite cages in this zeolite are filled (*3*). Rees and Williams have similarly shown that the saturation sorption capacity of synthetic faujasite for krypton is equal to that calculated by assuming the large cages are filled with krypton atoms (*4*). These studies have shown how the sorptive properties of the zeolite depend on the kind of exchangeable cation which is present in the zeolite.

In the investigation of NH_3 sorption (*3*) it was shown that the temperature dependence of the saturation sorption value was quite similar to the temperature dependence of the density of liquid NH_3. In a previous study of the occlusion of hydrocarbons by synthetic faujasite (*5*), Barrer and co-workers showed that, near saturation of the crystals, the thermal expansivity of the occluded hydrocarbons was quite similar to the thermal expansivities of the liquid hydrocarbons. The occluded sorbate was likened to a "capillary condensate." Quoting the authors further: "Unlike usual micropore systems, however, we are now considering a regular intersecting channel system, with uniform alternations between a widest diameter of only ~12A and a narrowest diameter of only ~9A. Because of this, capillary condensation and occlusion merge, and no hystereris is observed. No part of any channel is wide enough to escape the field of sorption potential due to the surrounding lattice." It should be pointed out that the zeolite faujasite, which Barrer was studying, is one of the most open zeolite structures. It is still more certain that in other zeolites the occluded gas molecules are under the influence of a sorption potential.

Since the crystal structure of many zeolites is known, Barrer and co-workers have made some efforts to calculate the sorptive potentials. They have considered guest molecule interactions with both the mobile cations and the anionic lattice (2–4,6). Thus, it is quite certain that the gas molecules adsorbed by a zeolite are occluded in the cavities and that it is the internal surface that is responsible for this sorption. Certainly the external surface area could not be responsible for the large sorption capacities that have been observed.

The positions of the exchangeable cations are known for many zeolites (*1*). They are certainly within the interior of the crystal and not on the surface. Thus exchanging cations should modify the sorption potential at the exterior of the crystal very little. Sorption of gas molecules at the crystal faces most probably depends primarily on their interaction with hydroxy groups on the crystal faces (*8*). The weakly acidic protons in these groups should not exchange for other cations at the *p*H used to exchange the exchangeable cations that are in the zeolite. Adsorption on the exterior surface of the crystal should be a relatively constant factor. The action of a sorption potential in the interior of the zeolite will also explain why Benson and King find a linear correlation between retention volumes for nonpolar molecules and atoms and their polarizability, when it is realized that all the molecules and atoms used could penetrate the Linde 5-A (Ca-A) sieve used. No investigator of zeolites today believes that the adsorption and separation of gas molecules on zeolites is determined primarily by the relative size of the adsorbate molecules and the channels in the zeolite. Benson and King cite Barrer in 1949 (*9*) as believing this. What Barrer said was, "The molecular-sieve property of zeolites would suggest that clear-cut separations could be obtained in molecular mixtures of which one constituent was freely occluded by the zeolite, while the other constituent, having the wrong molecular dimensions, was not occluded." Barrer was only pointing out that the most striking separations that can be made on zeolites do depend on the relative sizes of the gas molecules and the channels in the zeolite. For instance, the synthetic zeolite Linde 4-A (sodium form of Linde A) will not sorb normal paraffins, isoparaffins, and N_2 (*10*). If about one-third of the sodium ions are replaced with calcium ions, by ion exchange, normal paraffins and N_2 are sorbed in large quantities, but no isoparaffins are sorbed. This phenomenon does, indeed, depend on the relative minimum cross-sections of the gas molecules for diffusion and the size of the zeolitic channel. Many other examples can be found in the literature.

Ion exchange can change the sorptive properties of zeolites for two reasons. In the first case, ion exchange changes the sorption potential in the interior of the zeolite cavities causing the kinds of subtle changes in selectivity that are normally seen in sorption on conventional adsorbents. Once it is realized that gas molecules must diffuse through narrow openings to gain access to the cavities of a zeolite, it then becomes reasonable that, if cations are located in the channels of a zeolite, there is some molecule which, although it is small enough to diffuse through the empty channel, is excluded from the partially blocked channels. If the blocking cations are removed by ion exchange, this molecule can now freely diffuse through the channel. This is what happens in the case of calcium exchange of Linde 4-A. Two sodium cations are replaced by one calcium cation and the channels become unblocked, giving normal paraffin and nitrogen molecules access to the cages in the interior of the crystal.

In summary, it can be safely concluded that occlusion of guest molecules in the cavities is responsible for the sorptive properties of zeolites. Because the internal cavities or pores are so small, all the guest molecules are under the influence of the sorption potential of the host structure. Exchanging the cations, which are also located in the interstices of, and are really part of, the hose structure, modifies the sorption potential; but it can also modify the effective channel size. Sorption studies on zeolites are, therefore, in agreement with the conclusions of Benson and King that electrostatic interactions play a major role in gas adsorption on zeolites. However, these interactions occur in the cavities of the zeolites. Separations can be made using zeolites because of intrinsic differences in molecules and therefore in their interactions with the sorption potential in the interior of the zeolite. More spectacular separations based on molecular sieving can also be made, but less frequently, because it is possible either to choose a zeolite with a suitable channel size or to modify the effective channel size of a particular zeolite, by ion exchange, so that it has a suitable effective channel size for accomplishing a separation based on true molecular sieving.

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Molecular sieves (*1*) bear a relation to many biological systems in containing centers of localized polarity or charge arising from the distribution of the opposing polarity or charge over a macromolecular structure. These systems can therefore sorb nonpolar molecules both through attractive dispersion and through ion-induced dipole interactions. Because the latter, electrostatic interactions were recently suggested to play a major role (*2*), it is of interest to compare the known importance of both in the environments of molecular sieves (zeolites) and of certain biological systems (proteins).

For zeolites, which occlude in quantity only those molecules small enough to penetrate the intracrystalline free volume (*3*), electrostatic forces enter to the extent that the sorbed molecules possess permanent electric moments. This is shown by the energetics of occlusion of molecules of varying polar character:

1) Molecules having no permanent electropoles (noble gases) are sorbed with energies which are in reasonable agreement with those calculated for dispersion interactions alone, even though they exceed appreciably those for simple condensation (*4, 5*). Ion-induced dipole interactions ordinarily play only a minor role, but become significant when the counter-ion-exchange sites are occupied by strongly polarizing ions (*4*) or when these sites are peculiarly exposed (*5*).

2) Molecules having permanent dipoles (NH_3, H_2O) (*6*) or quadrupoles (N_2, CO, CO_2) (*4, 5, 7*) are sorbed with energies even further exceeding those accountable by dispersion forces alone.

In both cases, however, the electrostatic contributions to the differential heats of sorption decline rapidly with increasing concentration of the intracrystalline sorbate. At higher concentrations, the energy of sorption may include an appreciable contribution from sorbate-sorbate interactions (*8*).

That the sorption of nonpolar gases by biological systems can also be due mainly to dispersion forces has been shown by x-ray diffraction analyses of the association of xenon with myoglobin and hemoglobin:

1) In myoglobin (*9*) it was found that xenon is bound to one specific site which is buried in the interior of the molecule and is nearly equidistant from one of the pyrrole rings in the heme group and the ring of the heme-linked histidine. The xenon atom therefore lies between a nonpolar area and an area which is partially polar and indeed, slightly charged. The calculated dispersion interaction potential is 10.2 kcal/mole of xenon atoms. Potentials due to the dipole-induced dipole interactions and to the net charge-induced dipole interactions cannot be accurately determined since it is not yet known how the charge on the heme group is distributed. However, the maximum net charge that can be located on the pyrrole group in question is 0.5 *e*. Even if all this charge were located on the atom closest to the xenon, the interaction energy would only amount to 0.7 kcal/mole. Actually, because of the distribution of this charge on the pyrrole ring, this term will be less than 0.2 kcal/mole, or about 2 percent of the estimated total binding energy.

2) In hemoglobin (*10*) it was found that the binding site is near no charged amino acids, and therefore that net charge-induced dipole interactions are absent. A calculation of the dispersion energy is not possible because the atomic coordinates in hemoglobin are not yet known precisely enough; but it has again been shown that xenon lies in a cavity with a number of nonpolar neighbors favoring strong dispersion interactions.

While electrostatic forces play at most only a minor part in these two systems, it is not impossible that they are of more importance in certain other cases. However, it is apparent that in both inorganic and biological macromolecular environments, dispersion, and not electrostatic forces, play the universal role.

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