Journal of Energy, Heat and Mass Transfer, Vol.15, 165-177 (1993)

Experimental and Theoretical Investigations Concerning Coadsorption of CO_2 and N_2O on Molecular Sieve 5 A

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Abstract

In the present study adsorption of CO_2 and N_2O on molecular sieve with a micropore radius of 5 Angstrom (MS 5A) was investigated experimentally and the results were compared with the results of different models. The measurements showed that the adsorption capacity for N_2O, which is lower than that for CO_2, decreases much more in the case of coadsorption with CO_2 than the capacity for CO_2 does and furthermore the N_2O is displaced by CO_2 in the micropores of the zeolite. At the small partial pressures of max. 72 mbar used in this investigations good agreement was found between the results of measurements and data from various theoretical models. To explain the different adsorption behaviour of N_2O and CO_2, intermolecular potentials between these gas molecules and the ions of the molecular sieve were calculated.

Introduction

More and more molecular sieves are used for air cleaning. The adsorption on these molecularsieves is characterized by their high specific surface, the exactly definable sizes of the pores and the high electrostatic energies, these energies in addition to the van-der-waal-potentials have a strong influence on the adsorption of molecules. The adsorption of polar and polarizable molecules like CO_2 and N_2O shows a specially good effect. The adsorbable molecules are taken up as long as an equilibrium and surface saturation is reached. Then the breakthrough of the fixed bed takes place that means the concentration of gas components which have to be separated attains at the outlet of the adsorber the level of the inlet concentration. Using these breakthrough curves, points of adsorption isotherms can be calculated, which explain the relationship between the quantity of a gas component being taken up by the solid adsorbent and the partial pressure of this gas component in a gas mixture. In the present study the adsorption of CO_2 and N_2O on the molecular sieve 5A was investigated experimentally at a cylindrical adsorption column and the measurement data compared with calculated data from various theoretical models based on equilibrium-thermodynamics and statistical thermodynamics. Furthermore the adsorption of only one component and the interaction of the gas molecules at the two-component adsorption were considered.

Thermodynamic Fundamentals of the One-component Adsorption

For explaining the adsorption equilibrium the adsorptiv is considered as a thermodynamically inert phase which is in equilibrium with the gas phase. For this adsorbed phase consisting of n_{ad} Mol Sorbat und n_s Mol Adsorbens follows:

$$dU = T\,dS - PdV + \mu_s\,dn_s + \mu_{ad}\,dn_{ad} \qquad (1)$$

The internal energy of the unsaturated adsorbens is written by:

$$dU_{Os} = T\,dS_{Os} - PdV_{Os} + \mu_{Os}\,dn_s \qquad (2)$$

By subtraction one obtains:

$$dU_{ad} = TdS_{ad} - PdV_{ad} - \Phi dn_s - \mu_{ad}\,dn_{ad} \qquad (3)$$

$U_{ad} = U - U_{0s}$, $V_{ad} = V - V_{0s}$, $S_{ad} = S - S_{0s}$, $\Phi = \mu_s - \mu_{0s}$. The symbol Φ represents the change in internal energy of the adsorption surface or in micropore volume through adsorption of the components; it may be written by:

$$\Phi=\mu_{Os}-\mu_s=\left(\frac{\partial U_{Os}}{\partial n_s}\right)_{Sos,Vos}-\left(\frac{\partial U}{\partial n_s}\right)_{S,V,n_s}$$

$$=\left(\frac{\partial U_{ad}}{\partial n_s}\right)_{Ss,Vs,ns} \quad (4)$$

In accordance with Gibbs this change can be described by using a two-dimensional spreading pressure π which represents an equivalent of surface tension through adsorbed molecules and influences the surface A. Not to reduce the considerations only to surface adsorption we introduce a three-dimensional spreading pressure ω which is found in micropore volume V_p for example. We may therefore note:

$$\Phi\, dn_s = \pi\, dA = \omega dV_p \quad (5)$$

Analogy to the free energy F is determined by:

$$dF_{ad} = -S_{ad}\, dT - pdV_{ad} - \Phi dn_s + \mu_{ad} \, . \, dn_{ad} \quad (6)$$

Furthermore we define the free energy $F = -\Phi n_s + \mu n_{ad}$ and so it follows:

$$dF_{ad} = -\Phi dn_s - n_s d\Phi + \mu_{ad}\, dn_{ad} + n_{ad}\, d\mu_{ad} \quad (7)$$

By keeping the temperature constant and ignoring the term $p\, dV_{ad}$ it follows from these both equations:

$$n_s d\Phi = A d\pi = V_p\, d\omega = n_{ad}\, d\mu_{ad} \quad (8)$$

In case of equilibrium of two phases their chemical potentials have to be equal. If the gas phase is considered as ideal, one obtains:

$$\mu_{ad} = \mu_g = \mu_g^o + RT \ln\left(\frac{p}{p_r}\right) \quad (9)$$

μ_0 represents the chemical standard potential at the reference pressure $p_r = 1$ bar. We therefore obtain the Gibbian adsorption term of one-component adsorption:

$$A d\pi = R.T.\, n_{ad} \frac{dp}{p} = R.T.\, n_{ad}\, d \ln p \quad (10)$$

Equations of state like $A(\pi,T)$ or $V(\omega,T)$ may be formed for the adsorbed phase analogeous to the gas phase; so adsorption terms may also be defined in case of ignoring the spreading pressure π or ω which can't be measured.

In order to calculate smaller concentrations and saturating grades the adsorption isotherm according Langmuir [5] can be derived from the following equation of state:

$$\pi \, . \, (A - \beta) = n.R.T \quad (11)$$

Using the Gibbian isotherms and the determination $\beta << 2A$ which is correct for small concentrations we obtain:

$$\theta = \frac{b' p}{1+b' p} \quad (12)$$

or by introducing the relative saturating $\Phi = p_i/p_s$ and the monomolecular adsorption X_m

$$X = X_m \, . \, \frac{b.\Phi}{1+b.\Phi} \quad (13)$$

Using this equation it is possible to demonstrate adsorption up to monomolecular covering. It is only valid for adsorption up to $\Phi<0.1$, because the interaction between neighbouring adsorbed molecules isn't considered.

Microporous adsorbents like activated charcoal or molecularsieves are characterised by their high concentration of micropores which are relevant for the adsorption. So physically reasonable for the description not to consider one-or multi-component surface adsorption, but a filling of the pores. According to Dubinin and Radushkevich [3], [4] the difference between the free energy of the adsorbed phase and the free energy of the saturated adsorbate with the adsorption potential ε can be described as follows:

$$\varepsilon = -R.T.\ln\left(\frac{p}{p_s}\right) \quad (14)$$

Assuming homogeneous micropores, the Dubinin-equation can be defined for $T < T_{krit}$:

$$\frac{V}{V_s} = \exp\left[- \left(\frac{R.T}{E}\ln\left(\frac{p_s(T)}{p}\right)\right)^m \right] \quad (15)$$

In the case of higher saturation, molecules are able to adsorb in multimolecular layers on the surface. Brunauer, Emmett and Teller [1] developed a model for multimolecular adsorption, which is a generalisation of Langmuir's isotherm.

The equlibrium in the first layer is determined by equality of condensation rate on the adsorber surface and evaporation rate of the first layer.

$$a_1 . p . s_o = b_1 s_1 \exp(-E_1/RT) \qquad (16)$$

In the second layer four processes take place: condensation on the surface, evaporation from the first layer, condensation on the first layer and evaporation from the second layer.

$$a_2 . p . s_1 + b_1 s_1 \exp(-E_1/RT) = b_2 s_2 \exp(-E_2/RT) + a_1 . p . s_o \qquad (17)$$

One obtains the following isotherm

$$\frac{v}{Av_o} = \frac{v}{v_m} = \frac{s_o \sum_{i=1}^{n} c_i . i . x^i}{s_o \left(1 + \sum_{i=1}^{n} c_i . x^i\right)} \qquad (18)$$

Assuming that adsorption energy in the first layer consists of evaporation energy and binding energy between molecularsieve and adsorbate, in the second and higher layers only of evaporation energy, this well-known form of BET-equation follows

$$\frac{v}{vm} = \frac{cx}{(1-x)} \cdot \frac{1-(n+1)x^n + nx^{n+1}}{1+(c-1)x - cx^{n+1}} \qquad (19)$$

For calculation of adsorption equilibria especially for molecular sieves, Ruthven [7], [9], [10] developed a simplified statistical model. This theory is not based on adsorption on a surface but considers the microscopic pore structure of zeolites. One cage represents an independent subsystem of a grand canonical partition function. The following simplifying assumptions are made: there is no exchange of molecules between neighbouring cages, the molecules within a cage are freely mobile, attractive forces are neglected, repulsive forces between molecules are taken into account by a reduced cage volume.

The whole system consists of M cages, one cage can contain m molecules. The grand canonical partition function is given by

$$F = \left[\sum_{s=o}^{m} q(s)\,\lambda^s\right]^M = \left[\sum_{s=o}^{m} Z(s) . a^s\right]^M = Q^M \qquad (20)$$

with $\lambda = \exp\ (\mu/k.T)$ and $a = p/k.T$.

The average number of molecules per cage is

$$c = \lambda \left(\frac{\partial \ln Q}{\partial \lambda}\right)_T = \frac{\sum_{s=1}^{m} s . Z(s) . a^s}{\left(1 + \sum_{s=1}^{m} Z(s) . a^s\right)} \qquad (21)$$

The configuration integral is defined by

$$Z(s) = \frac{1}{s!} . \int_v \exp[-U_s(r_1, r_2, ... r_s)/(k.T)]\, dr_1 dr_2 ... dr_s \qquad (22)$$

with $U_s(r_1 \cdots, r_s)$ as the potential of the molecules at r_s.

Z(s) can be expressed by

$$Z(s) = \frac{Z_1^s}{s!} . R_s \qquad (23)$$

With K . p for Z_1 . a, one obtains the following simplified description of adsorption equilibrium

$$c = \frac{\left[K.p + (K.p)^2 . R_1 + ... + \frac{(K.p)^m}{(m-1)!} . R_m\right]}{\left[1 + K.p + \frac{1}{2!} . (K.p)^2 . R_1 + ... + \frac{(K.p)^m}{m!} . R_m\right]} \qquad (24)$$

Good agreement with measurements can be obtained if a careful adjustment of the constants K and R to measurements is made.

Considering equations (18) and (21) in detail one receives an interesting result. Two different physical models, the adsorption on a surface and the filling of a micropore lead to isotherms of identical mathematical structure. Both can be transferred to Langmuir-isotherm for small saturation (monolayer (i = 1), one molecul per cage (s = 1)).

Multi-component Adsorption

The free enthalpy G of the adsorbed phase with several components m in an open system depends on temperature T, spreading pressure π and the composition n_i

$$G = G(\pi, T, n_i) \quad i=1.....m \tag{25}$$

with the total differential

$$dG = \frac{\partial G}{\partial T}\bigg|_{\pi,n_i} dT + \frac{\partial G}{\partial \pi}\bigg|_{T,n_i} d\pi + \Sigma \frac{\partial G}{\partial n_i}\bigg|_{T,\pi} dn_i \tag{26}$$

or

$$S\,dT - A\,d\pi + \Sigma n_i\,d\mu_i = 0 \tag{27}$$

The derivations $dG/dn_i\,|(T,\pi)$ are called the chemical potential μ_i of the adsorbed phase. The chemical potential of the adsorbate phase is defined as follows

$$\mu_i = R\,.\,T\,.\ln(\gamma_i x_i) + \mu_i^0 \tag{28}$$

$\mu_{i0} = \mu_{i0}(T,\pi)$ is the free enthalpy of the component i, if the sorbate phase is built only by this component ($x_i = 1$, $\gamma_i = 1$). $p_{i0}(\pi)$ is the equlibrium pressure of the pure component i, that leads to the spreading pressure π and $\mu_i^{0(T)}$ is the free enthalpy of the component i considered as an ideal gas at p = 1 bar. One obtains

$$\mu_i^0(T,\pi) = \mu_i^0(T) + R\,.\,T\ln(p_i^0(\pi)) \tag{29}$$

and for the chemical potential of the adsorbed phase

$$\mu_i^0(T,\pi,x_i) = \mu_i^0(T) + R\,.\,T\ln(p_i^0(\pi)) + R\,.\,T\ln(\gamma_i x_i) \tag{30}$$

For T = const. from equations (30) and (27) it follows

$$A\,.\,d\pi = \Sigma\, n_i\, d\mu_i \tag{31}$$

and

$$A\,.\,d\pi = n_i^0\,.\,R\,.\,T\,.\,d\,[\ln(p_i^0(\pi))] \tag{32}$$

This relation is called the Gibb's adsorption isotherm for multi- component adsorption. The gaseous phase can be considered as an ideal gas with the chemical potential

$$\mu_{i,G} = \mu_i^0(T) + R\,.\,T\,.\ln(y_i\,p) \tag{33}$$

With constant T and π one obtains equality of the chemical potentials of gaseous phase and sorbate phase

$$y_i\,.\,p = \gamma_i\,.\,x_i\,.\,p_i^0(\pi) \tag{34}$$

Combining equations (33) and (34) with equation (30) leads for p = const. to this equation

$$\frac{A\,d\pi}{R\,.\,T} = \Sigma\, n_i\, d\ln y_i \tag{35}$$

The spreading pressure π is the same for all components and one obtains a system of equations which is necessary to calculate multi-component isotherms from data of the adsorption of one component.

The IAS-theory (Ideal Adsorbed Solution Theory) of Myers and Prausnitz [2], [6] is formulated on the equilibrium relations mentioned in cap. 2. Considering the sorbate phase as an ideal gas $\gamma_i = 1$, equation (34) reduces to

$$y_i\,p = x_i\,p_i^0(\pi) \tag{36}$$

If partial pressures are small, interaction between adsorbed molecules can be neglected. From equation (32) follows by interpolation and considering, that $n_{i0}/d\ln p_{i0} = n_{i0}/p_{i0}\,dp_{i0}$

$$\frac{A\,.\,\pi_i^0}{R\,.\,T} = \int_0^{p_i^0} \frac{n_i^0}{p_i^0}\,d\,p_i^0 \tag{37}$$

In equation (37) one can put in the well-known equation for isotherm and one gets the following equations

with Langmuir-isotherm

$$\frac{\pi_i^0\,.\,A}{R\,.\,T} = n_m\,.\ln(1 + b_i\,.\,p_i^0) \tag{38}$$

with BET-isotherm

$$\frac{\pi_i^0 . A}{R . T} = \frac{X_m . V_m . b_i}{M_i} \int_0^{\Phi_i^0} \frac{1}{(1-\Phi_i)} .$$

$$\frac{1-(N+1)\, \Phi_i^N + N . \Phi_i^{N+1}}{1+(b_i-1)\, \Phi_i - b_i . \Phi_i^{N+1}}\, d\Phi \quad (39)$$

with Dubinin-isotherm

$$\frac{\pi_i^0 . A}{R . T} = \int_0^{p_i^0} \exp \left[-\frac{R . T}{E} \ln (p_s/p_i^0)^m \right] dp_i^0 \quad (40)$$

The adsorbed amount of gas component i with the partial pressure p_i in the mixture n_i is given by

$$n_i = x_i\, n_t \quad (41)$$

with

$$\frac{1}{n_t} = \sum_i \frac{x_i}{n_i^0} \quad (42)$$

Furthermore we have

$$\frac{p_1}{p_1^0} + \frac{p_2}{p_2^0} = 1 \quad (43)$$

With the equations (41) - (43) and one of equations (38) - (40) the adsorbed amounts n_i can be calculated at multi-component adsorption.

Ruthven [8] expanded his model for calculation of several gas components. The grand canonical partition function for two components A and B is given by

$$F_{AB} = \left[\sum_j \sum_i q\,(i,j) . \lambda_A^i\, \lambda_B^j \right]^M = Q^M \quad (44)$$

with $q(i,j)\ \lambda_{Ai} \lambda_{Bj} = Z(i,j) . a_{Ai} . a_{Bj}$ und $Z(i,j) = ((Z(1,0)^i . Z(0,1)^j) / i!j!).R_{i,j}$. Further more is

$Z(0,0) = Z(0) = 1$

$Z(1,0) p_A / K \cdot T = Z(1,0) a_A = K_A . p_A$

$Z(0,1) p_B / K \cdot T = Z(0,1) a_B = K_B . p_B$

The configuration integral describes the interactions between adsorbens and sorbate. If these interactions are very small $R_{i,j} = 1$. Otherwise $R_{i,j}$ can be calculated from the data of one- component adsorption.

$$R_{ij} = (R_i^i . R_j^j)^{1/i+j} \quad (45)$$

The relation for coadsorption is given by

$$c_1 = \left[\frac{K_1 . p_1 + \Sigma_j \Sigma_i \frac{(K_1 . p_1)^i . (K_2 . p_2)^j}{i! . j!} . (R_i{}^i . R_j{}^j)^{1/(i+j)}}{1 + K_1 . p_1 + \Sigma_j \Sigma_i \frac{(K_1 p_1)^i . (K_2 p_2)^j}{i! j!} . (R_i{}^i . R_j{}^j)^{1/(i+j)}} \right] \quad (46)$$

The relation for the second component is analogous. The assumption that not more than two molecules are located in one cage leads to following expression

$$c_1 = \frac{K_1 p_1 + (K_1 p_1)^2 . R_{11} + (K_1 p_1) . (K_2 p_2) . R_{12}}{1 + K_1 p_1 + K_2 p_2 + (K_1 p_1^2) . \frac{R_{11}}{2} + (K_2 p_2)^2 . \frac{R_{22}}{2} + (K_1 p_1) . (K_2 p_2) . R_{12}} \quad (47)$$

Using this equation one can achieve good agreement with measurements.

Intermolecular Potentials

The molecules N_2O and CO_2 are regarding molecule size, molecule shape and evaporation enthalpy nearly identical, so that different adsorption behaviour can't be explained by these properties. Therefore intermolecular interactions between these gas molecules and the molecules of the molecularsieve must be considered detailed.

The adsorption of polar and polarisable molecules is strongly influenced by electrostatic forces. This forces exist between the Na^+ and Ca^{++}-ions in the micropores of the molecularsieve which are considered as the preferred places of adsorption and the electric charges, the dipole-, quadrupole- and induced dipole- moments of the gas molecules. The dispersion forces which are caused by the shifting of the electron clouds and do not depend on permanent multipols are calculated with the London-potential

$$\varphi(r) = A \cdot r^{-6} - B \cdot r^{-12} \tag{48}$$

with

$$A = A_L = \frac{3}{2} \cdot \alpha_1 \cdot \alpha_2 \cdot J \,;\, \frac{1}{J} = \frac{1}{J_1} + \frac{1}{J_2} \tag{49}$$

and

$$B = \frac{A \cdot r_0^6}{2} \tag{50}$$

with r_0 as the van-der-Waal's radius. The potential between two electric charges can be calculated with the Coulombian law

$$\varphi_{ab}^{(C,C)} = + \frac{C_a\, C_b}{4\pi\varepsilon_0\, r} \tag{51}$$

Every asymmetrical molecule with a corresponding charge distribution has a permanent dipole moment. The potential between a dipole and an electric charge can be written by

$$\varphi_{ab}^{(C,\mu)} = - \frac{C_a \mu_b}{4\pi\varepsilon_0 r^2} \cos\theta \tag{52}$$

A molecule with more than two charge centers can build a quadrupole moment. It can interact with an electric charge

$$\varphi_{ab}^{(C,Q)} = + \frac{C_a Q_b}{8\pi\varepsilon_0 r^3} (3\cos^2\theta_b - 1) \tag{53}$$

Electrons can be displaced temporarily by an external electric influence and induced dipole results. The potential between an induced dipole and an electric charge is given by

$$\varphi_{ab}^{(C,\mathrm{ind}\,\mu)} = - \frac{C_a^2\, \alpha_b}{32\pi^2 \varepsilon_0^2 r^4} \tag{54}$$

The molecular processes at the adsorption of CO_2 and N_2O can be described by these potentials. Both molecules are polarisable, have a quadrupole moment, N_2O furthermore a dipole moment.

Description of the Experimental Plant

For experimental investigations of one- and multi-component adsorption a cylindrical tube column made of alumina with a length of the fixed bed of 470 mm was built. To be able to take away the adsorption heat sufficiently fast the diameter of the column must be small, on the other side a ratio of particle size to column diameter of 0.05 to 0.1 is worthwhile to avoid disadvantegeous edge effects. As a compromise an inner diameter of 40 mm was determined. The molecular fill is fixed between fine wire nets, to prevent carrying out of molecular sieve particles. In the wall of the adsorber there are cooling and heating channels in longitudinal direction impinged by brine. They are used for adjusting the temperature during the experiment, for removing adsorption heat and for heating during regeneration of the adsorber. The temperature is measured by NiCrNi - thermocouples at the inlet and outlet of the adsorber, as well as at different places along the adsorber and over the cross-section. The accuracy of the used measurement arrangement is +/- 1K.

The gas outlet and inlet is constructed as boreholes in the middle of the caps of the adsorber. To avoid impurities and therefore in accuracies in gas analysis every gas component used in the experiments, oxygen and nitrogen as carrier gas, CO_2 and N_2O, is taken out of gas bottles. The purity of this gases ensures that impurities with water vapor and hydrocarbons are only a few ppm. With the help of electronic mass flow controllers the single gas components are mixed in the desired ratio. In an heat exchanger in front of the adsorption colomn the gas mixture is heated to adsorption temperature.

In figure 1 one can see a scheme of the experimental facility.

To analyse the gas composition gas sampling devices are located in the inlet and outlet of the adsorber as well as along the adsorber. Minimal gasflows are lead to a mass spectrometer for continous gas analysis.

The adsorber is regenerated by a combined temperature- pressure- swing procedure. The molecular sieve is heated up to 90 °C and the desorbed elements are exhausted by a vacuum pump.

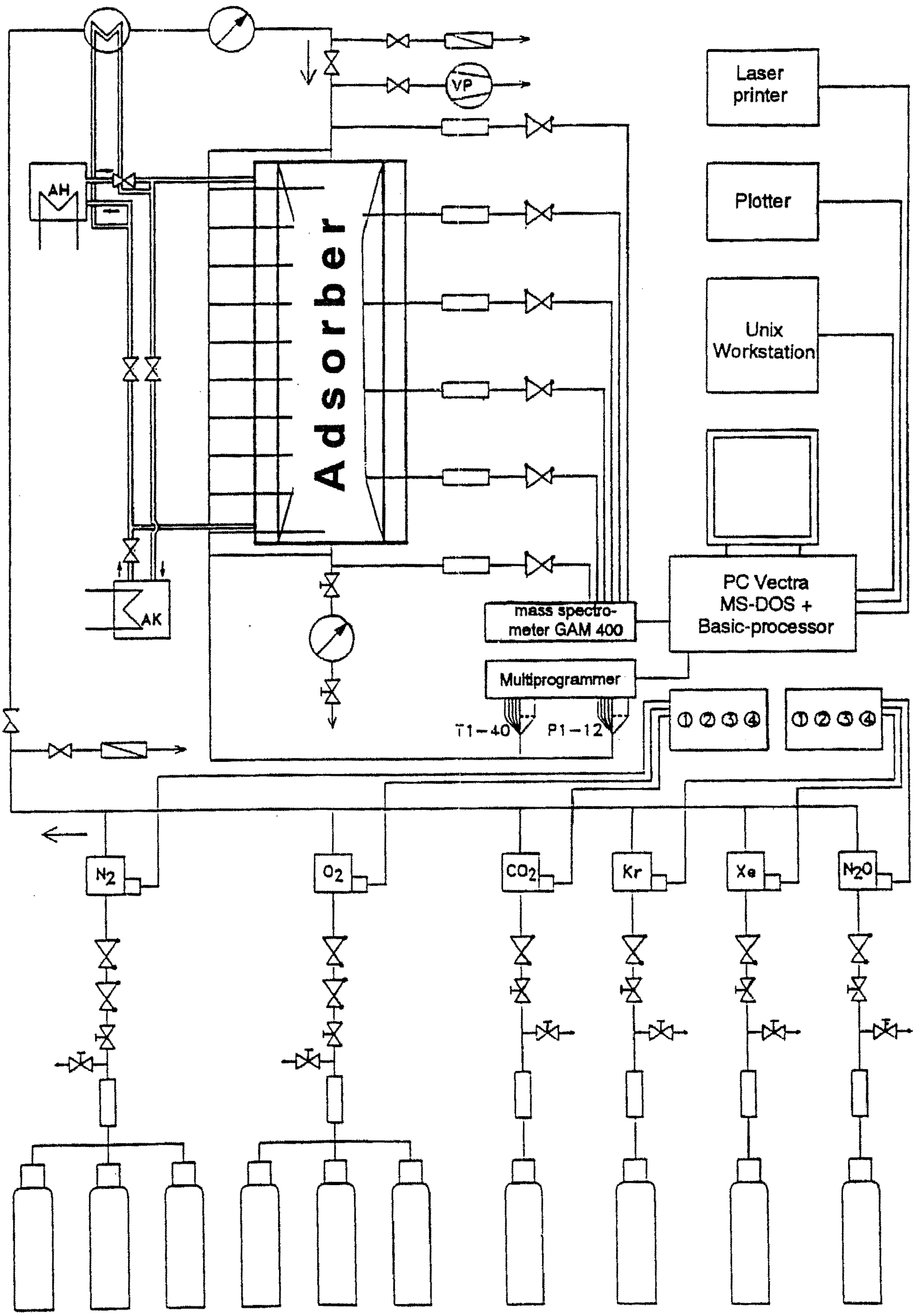

Fig.1: The adsorption facility

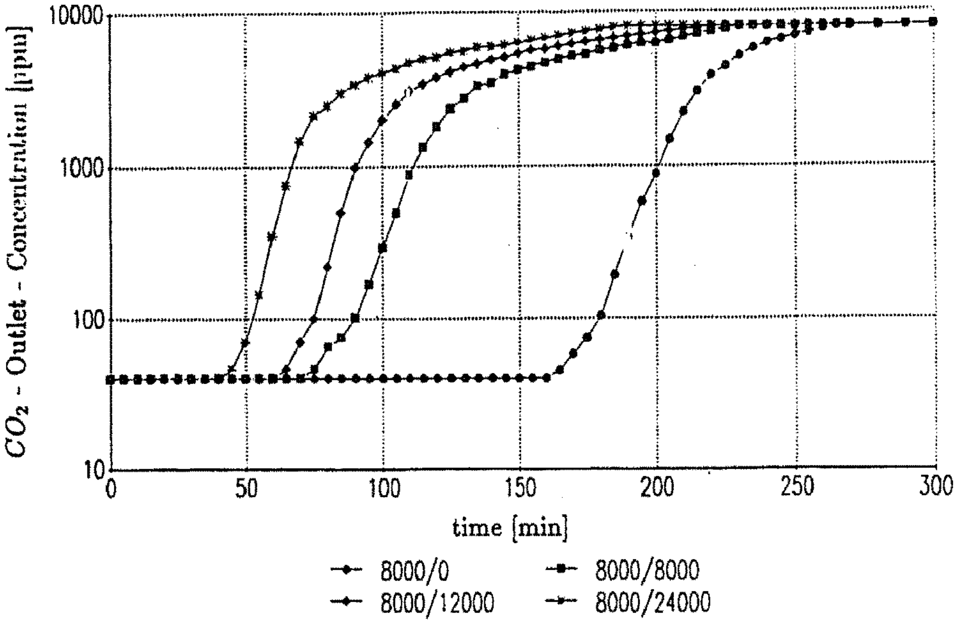

Fig.2: CO_2- Breakthrough - curves for 8000 ppm CO_2 + diff. N_2O - concentration, $-10^{\circ}C$, 3 bar

The remaining adsorbed molecules are washed out by warm nitrogen.

To set up the breakthrough curves and adsorption isotherms temperature was varied between -20 °C and +20 °C, the inlet-concentrations of N_2O and CO_2 between 1800 and 24000 ppm, the volume flow between 1.2 and 3.6 m^3/h. The system pressure was 3 bar.

Results of Measurements and Calculations

Exemplary some results of measurement at a temperature of -10 °C and a volume flow of 1.2 m^3/h are represented in the following.

Figure 2 and 3 show breakthrough curves for CO_2 and N_2O in the case of one- component-adsorption and coadsorption of the second component with different concentrations.

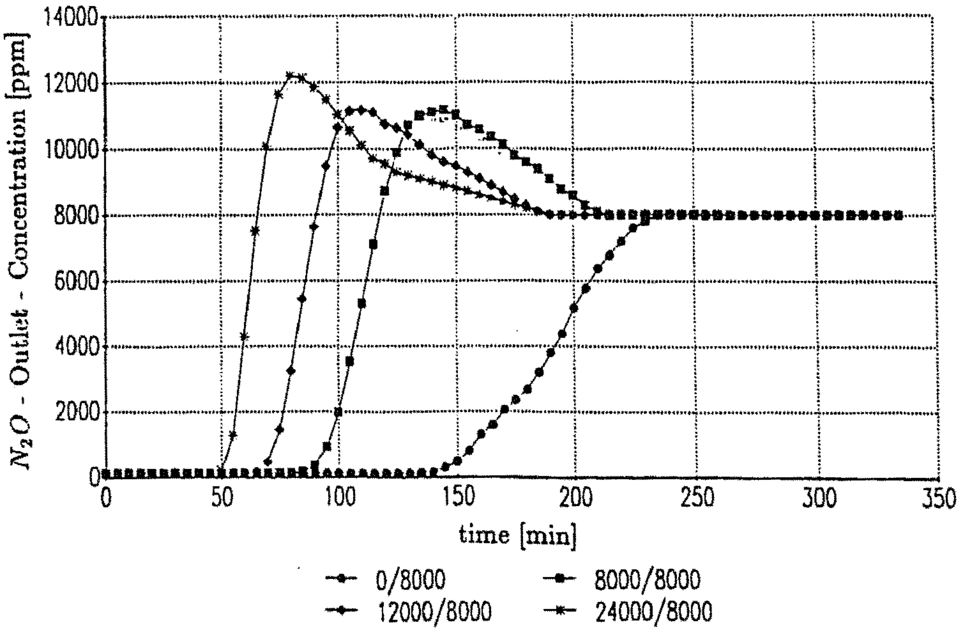

Fig.3: N_2O - Breakthrough - curves for 8000 ppm N_2O + diff. CO_2 - concentration, $-10^{\circ}C$, 3 bar

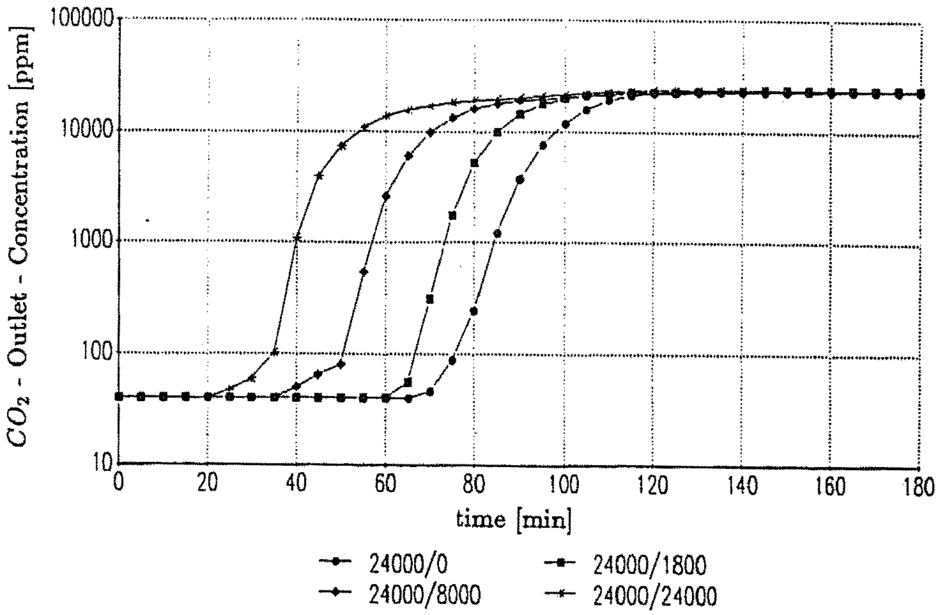

Fig.4: CO_2 - Breakthrough - Curves for 24000 ppm CO_2 + diff. N_2O - concentration, − 10°C, 3 bar

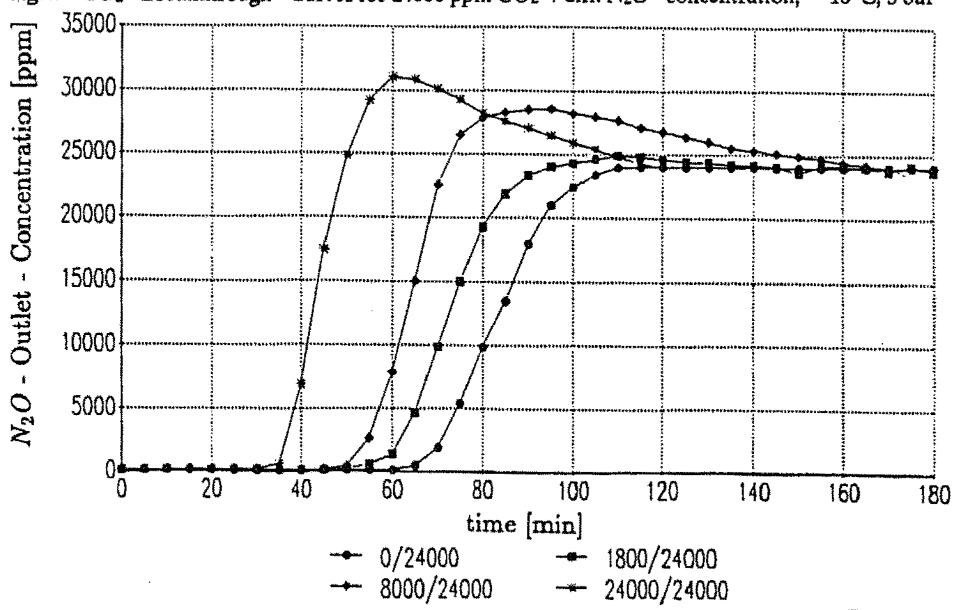

Fig.5: N_2O - Breakthrough - Curves for 24000 ppm N_2O + diff. CO_2 - concentration, − 10°C, 3 bar

It is remarkable that the breakthrough curve of CO_2 is steeper than that of N_2O at one-component adsorption (figure 2). On the other side the breakthrough curves of N_2O in presence of CO_2 are steeper than that of N_2O-one-component adsorption (figure 3). The outlet concentration exceeds the inlet concentration at the breakthrough and then goes back slowly to inlet concentration. This overswing increases with rising CO_2- concentration. The CO_2 drives out already adsorbed N_2O and adsorbes on that places. That is the reason why CO_2-breakthrough curves are flatter whereas the N_2O-breakthrough takes place faster because of this replacement. If the inlet-concentration of a gas component is high in comparison to the other one this effects are not so significant as one can see in figures 4 and 5.

Figure 6 shows both according Langmuir, BET, Dubinin and statistical Thermodynamics calculated isotherms and isotherm determined by measured data for one- and multi- component adsorption,

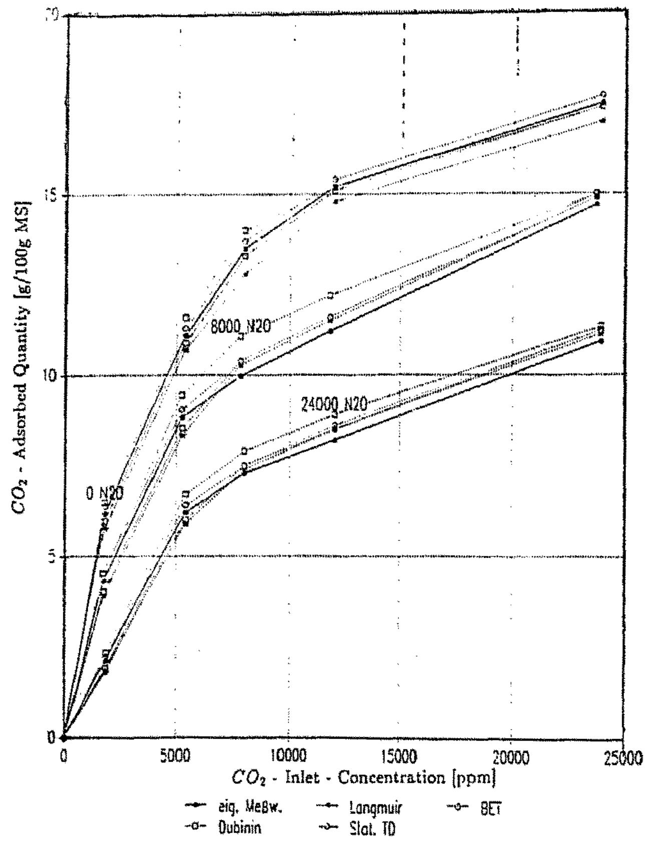

Fig.6: Measured and calculated CO_2 - isotherms (+10°C, 3 bar, 1.2 m^3/h, MS 5A)

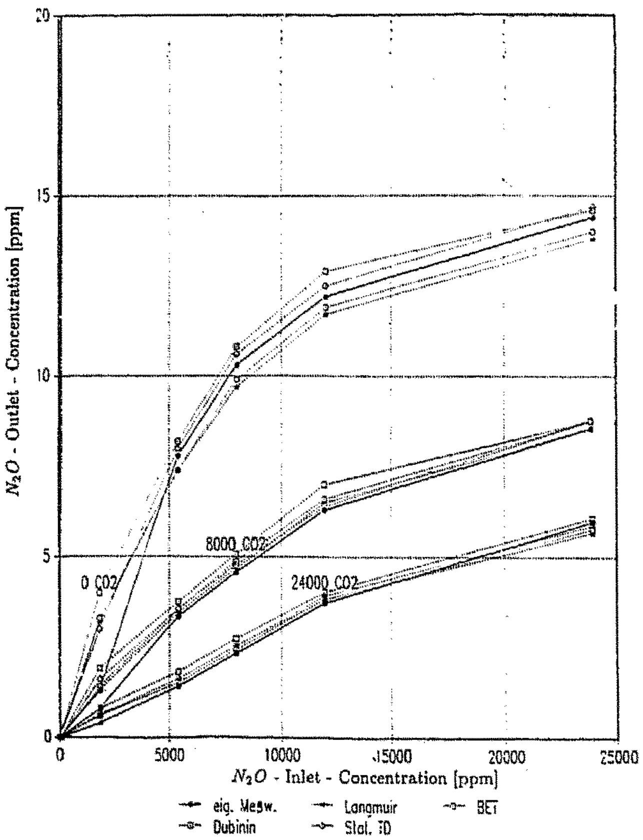

Fig.7: Measured and calculated N_2O - isotherms (+10°C, 3 bar, 1.2 m^3/h, MS 5A)

figure 7 shows analogous plots for N_2O. One can recognize good agreement between all calculation models and data from measurements.

That can be put down to the fact that the isotherms are defined for relative small partial pressures between 0 and 72 mbar, which are sufficient at off-gas cleaning in most cases. On the other side this agreement is obvious, if one considers the mathematical identical structure of the isotherms as shown in cap. 2.

In detail figure 6 shows the adsorption isotherms for the one-component adsorption of CO_2 and for the coadsorption of 8000 and 24000 ppm N_2O. With rising inlet-concentration or partial pressure of CO_2 the adsorption capacity increases. In the cases of coadsorption of N_2O the adsorption capacity decreases with rising N_2O-inlet concentration. The same is valid for the adsorption isotherms of N_2O as shown in figure 7.

Whereas the adsorbed amount of N_2O at one-component adsorption is only slightly smaller than that of CO_2 one can see that at two-component adsorption significantly less N_2O than CO_2 can adsorb. Data received from measurements are assembled in table 1.

Table.1: Comparison of CO2 - and N2O - coadsorption capacities

CO_2-capacities (C_{in} = 8000 ppm) [g/100g molecular sieve]		N_2O- capacities (C_{in} = 8000 ppm) [g/100g molecular sieve]	
+ 0 ppm N_2O	15,2	+ 0 ppm CO_2	13,2
+8000ppm N_2O	11,7	+ 8000 ppm CO_2	5,2
+ 12000 ppm N_2O	10,6	+ 12000 ppm CO_2	4,4
+ 24000 ppm N_2O	7,8	+ 24000 ppm CO_2	2,3

The worse adsorption of N_2O in the presence of CO_2 can be explained partly by the replacing of N_2O with CO_2 as one can see in the breakthrough curves in form of the overswing of N_2O-outlet-concentration. The displaced amount of N_2O depends on the concentration of CO_2. A small CO_2-inlet-concentration of for example 1800 ppm leads only to a small replacement of N_2O whereas at a high concentration of 24000 ppm only à small amount of N_2O remains in the molecular sieve.

The intermolecular forces which are responsible for the adsorption of molecules at molecular sieves are different for CO_2 and N_2O. In this study the potentials between the adsorption relevant charges of the molecular sieve, the Na^+ and Ca^{++}-ions in

Table.2.1: $CO2/Ca^{++}$ - Potential in 10^{20} joule

r_0[Å]	London potential	Charge quadrupole	Charge dipole	Charge ind. dipole	Sum
0	∞	∞	0	∞	
2	+2244.6	−154.8	0	−77.5	
3	+7.8	−45.8	0	−15.3	
3.66	−1.73	−26.06	0	−7.11	−34.90
5	−0.48	−10.490	0	−2.04	−13.02
6	−0.17	−6.09	0	−0.99	−7.25

Table.2.2: N_2O/Ca^{++} - Potentials in 10^{20} joule

r_0[Å]	London potential	Charge quadrupole	Charge dipole	Charge ind. dipole	Sum
0	∞	∞	∞	∞	
2	+2483.4	−130	−4.75	-87.5	
3	+8.63	−38.4	−2.11	−17.29	
3.66	−1.86	−20.37	−1.38	−7.58	−31.19
5	−0.493	−7.95	−0.73	−2.18	−11.39

Table.3.1: CO_2/Na^+ - Potentials in 10^{20} joule

r_0[Å]	London potential	Charge quadrupole	Charge dipole	Charge ind. dipole	Sum
0	∞	∞	0	∞	
2	+ 1786.7	−77.8	0	−19.38	
3	+6.21	−22.9	0	−3.83	
3.66	−1.33	−12.98	0	−1.78	−16.09
5	−0.38	−5.25	0	−0.491	−6.18
6	−0.14	−3.05	0	-0.25	−3.44

Table 3.2: N_2O/Na^+ - Potentials in 10^{20} joule

r_0[Å]	London potential	Charge quadrupole	Charge dipole	Chare ind. dipole	Sum
0	∞	∞	∞	∞	
2	+1981.8	−65.0	−2.38	−21.88	
3	+6.89	−19.2	−1.06	−4.32	
3.66	−1.48	−10.19	−0.75	−1.89	-14.31
5	−0.42	−4.03	−0.37	-0.494	-5.36
6	−0.15	−2.33	−0.26	−0.26	-3.00

the micropores of the adsorbent and a charge, a dipole moment, a quadrupole moment and an induced dipole of the gas molecules are considered.

In table 2 and 3 calculated results for these potentials are summarized. The sum of the potentials considered here is greater for CO_2 than for N_2O and it is especially greater at the equilibrium distance (van-der-Waal's radius). The biggest potential is that between charge and quadrupole moment. Also this potential is greater for CO_2 and furthermore it decreases with the distance less than the others. So the CO_2-molecule is attracted by the ions of the molecular sieve already at bigger distances than the N_2O-molecule. This causes a better adsorption of CO_2 and the CO_2-molecule can replace adsorbed N_2O-molecules because of the higher attractive potential in the equilibrium distance. It is sure that these considerations are simplifying and for a more detailed investigation three-dimensional calculations of all interactions between the gas molecules and the molecules of the molecular sieve and between the CO_2- and N_2O-molecules must be carried out. But these simplifying considerations describe the tendencies of adsorption very well and can be used for an estimation of adsorption capacities. So the difference between adsorption capacity of CO_2 and N_2O and the attractive and repulsive potentials is of the same order, about 12 - 20 %.

Nomenclature

a = activity
A = surface area
b = Langmuir-constant
c = concentration
C = electric charge
E = affinity
F = grand canonical partition function
F_{ad} = free energy
G = free enthalpy
h = Planck-constant
k = Boltzmann-constant
K = Henry-constant
M = molar mass
n = surface concentration
N = number of layers
p = pressure
p_i = partial pressure
Q = canonical partition function
Q = quadrupole moment
S = entropy
T = temperature
U = energy
$U_s(r_1,r_2....)$ = adsorption potential

X_m = constant for monomolecular covering
x = mole fraction in solid phase
y = mole fraction in gaseous phase
Z = configuration integral
γ_i = activity coefficient
μ_i = chemical potential
μ = dipole, induced dipole
Φ = surface potential
ϕ = relative saturation
π = spreading pressure (2-dim.)
ω = spreading pressure (3-dim.)
Θ = adsorption capacity
ε = adsorption potential

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