905. *Water in Hydrates. Part II.* Light and Heavy Water and Sulphur Dioxide in Synthetic Zeolites.*

By R. M. BARRER and A. F. DENNY.

Sorption of light and heavy water and of sulphur dioxide by a number of synthetic zeolites was studied. Sorption of water was reversible in zeolites Na-X and Na-A (sample 2); it was irreversible in Na-A (sample 1), Ca-A (sample 1), Na-Y and basic sodalite, revealing hysteresis effects of considerable complexity. Sorption of sulphur dioxide was reversible on the X, Y, and A zeolites, but on basic sodalite sorption was very slow and also a side reaction yielded some sulphur on outgassing. When reversible sorption of water occurred it was found that the differences in sorption of liquid D_2O and H_2O in Na-X and Na-A were negligible; but that small differences existed for uptake of the vapours. This is in line with results previously observed for chabazite, gmelinite, and heulandite.[1]

THERMODYNAMIC studies of zeolitic water [1-3] and other zeolitic species [4-7] have given considerable information regarding the physical state of these species. Such studies may be complemented by optical,[3,8-10] nuclear magnetic resonance,[11] and diffusion measurements,[1] by differential thermal analysis,[2,12] and by investigation of dielectric relaxation.[11]

* Part I, preceding Paper.

[1] Barrer and Fender, *J. Phys. and Chem. Solids*, 1961, **21**, 1, 12.
[2] Barrer and Bratt, *J. Phys. and Chem. Solids*, 1959, **12**, 130, 146, 154.
[3] Frohnsdorff, Ph.D. Thesis, University of London, 1959.
[4] Barrer and Sutherland, *Proc. Roy. Soc.*, 1956, *A*, **237**, 439.
[5] Barrer and Reucroft, *Proc. Roy. Soc.*, 1960, *A*, **258**, 431, 449.
[6] Barrer and Stuart, *Proc. Roy. Soc.*, 1959, *A*, **249**, 464, 484.
[7] Barrer and Wasilewski, *Trans. Faraday Soc.*, 1961, **57**, 1140, 1153.
[8] Eitel, " The Physical Chemistry of the Silicates," University of Chicago Press, 1954, p. 989.
[9] Rinne, *Neues Jb. Mineral. Mh.*, 1897, **1**, 41; 1899, **1**, 1.
[10] Slawson, *Amer. Mineralogist*, 1925, **10**, 305.
[11] Ducros, *Bull. Soc. franc. Mineral. Crist.*, 1960, **83**, 85.
[12] Barrer and Langley, *J.*, 1958, 3804, 3811, 3817.

Recently,[1] isotope effects were also considered by sorbing D_2O and H_2O in the naturally-occurring zeolites chabazite, gmelinite, and heulandite. At a fixed relative humidity the number of moles of pure D_2O and of pure H_2O sorbed were very nearly the same, while at a particular vapour pressure the uptake of D_2O slightly exceeded that of H_2O. It was of interest to extend these measurements to some synthetic zeolites in order to compare them with the naturally-occurring species. One may also compare isotopic fractionations by sorption of water in zeolites with those occurring when H_2O–D_2O mixtures distribute themselves between a saturated solution and crystallising stoicheiometric salt hydrates.[13-16] The new measurements revealed hysteresis in some instances and led to a study of the intracrystalline sorption of another polar molecule, sulphur dioxide, which is less reactive towards its intracrystalline environment than water. In this way it was hoped to throw further light on the hysteresis.

Experimental

The zeolitic sorbents examined were basic sodalite, and Linde Sieves A, X, and Y. Basic sodalite [17] has the ultramarine structure [18] whereas Sieves X and Y have the faujasite structure.[19] Sieve A is of known structure but is without a natural counterpart.[19-21] The A, X, and Y molecular sieves are of a particularly open character which can be expected to influence considerably the behaviour of zeolitic guest molecules. The samples used had the compositions given below (in which n, the number of moles of zeolitic water, is variable):

Basic sodalite	$Na_2O, Al_2O_3, 2SiO_2, 0.36NaOH, nH_2O$
Zeolite A, sample 1	$Na_2O, Al_2O_3, 2SiO_2, 0.17NaAlO_2, nH_2O$
Zeolite A, sample 2	$Na_2O, Al_2O_3, 2SiO_2, 0.07NaAlO_2, nH_2O$
Zeolite X	$Na_2O, Al_2O_3, 2.67SiO_2, nH_2O$
Zeolite Y	$Na_2O, Al_2O_3, 4.45SiO_2, nH_2O$

Zeolites X and Y differ not in structure but in the alumina–silica ratio and hence in the number of exchangeable cations. The sodium hydroxide in the basic sodalite and the sodium aluminate in the A zeolite are guest molecules, like the water molecules, within the sodalite cages that are present in the structures.[17, 21]

Water isotherms were measured gravimetrically, using a silica spring balance, at 30, 45, 55, and 70°, the balance case and manometer being immersed in a water thermostat. Sulphur dioxide isotherms were determined in a standard volumetric apparatus at temperatures near -51 and $-33°$. Calcium chloride–water and magnesium chloride–water eutectics were used to maintain these temperatures. Equilibrium sorption pressures were read with a cathetometer. Freshly distilled and degassed H_2O, or D_2O of 99.98% purity, were used to study the isotope effect. Sulphur dioxide was obtained from a cylinder, dried by passage through phosphoric oxide, condensed, degassed, and then fractionally distilled under vacuum. The middle fraction only was used. In the volumetric apparatus the temperature of the sorption cell was measured using a sulphur dioxide vapour pressure thermometer.

The zeolites were outgassed in a vacuum by slowly raising their temperature to 350° and maintaining them thereat for 8—10 hr. It was expected, however, that a small amount of water would remain in the zeolite. Accordingly, to avoid contamination of D_2O, residual H_2O in the zeolite was replaced by D_2O. This was done by degassing the zeolite at 70°, about 70% of its water content being removed. The zeolite was then saturated with D_2O and the process repeated several times. It was finally degassed, as described above, at a final temperature of 350°. Any residual water should then be D_2O.

Isotherms and Hysteresis.—Reversible sorption isotherms were obtained for water in Na-X and in sample 2 of NaA (Figs. 1a and b). Reversible sorption was also observed for sulphur

[13] Day, Hughes, Ingold, and Wilson, *J.*, 1934, 1593.
[14] Uusitalo, *Suomen Kem*, 1958, B, **31**, 362.
[15] Teis, *Doklady Akad. Nauk. S.S.S.R.*, 1954, **99**, 585.
[16] Barrer and Denny, preceding Paper.
[17] Barrer and White, *J.*, 1952, 1561.
[18] Barth, *Z. Krist.*, 1932, **83**, 405.
[19] Broussard and Shoemaker, *J. Amer. Chem. Soc.*, 1960, **82**, 1041.
[20] Reed and Breck, *J. Amer. Chem. Soc.*, 1956, **78**, 5972.
[21] Barrer and Meier, *Trans. Faraday Soc.*, 1958, **54**, 1074.

dioxide in Na-X, Na-Y, and Na-A (sample 1) (Fig. 1c). On the other hand hysteresis was observed when water was sorbed by Na-Y, Na-A (sample 1), Ca-A (from sample 1), and basic sodalite. The hysteresis loops were narrow and continued down to the lowest relative pressures at which measurements were made. The hysteresis behaviour differed in the individual systems, as described below.
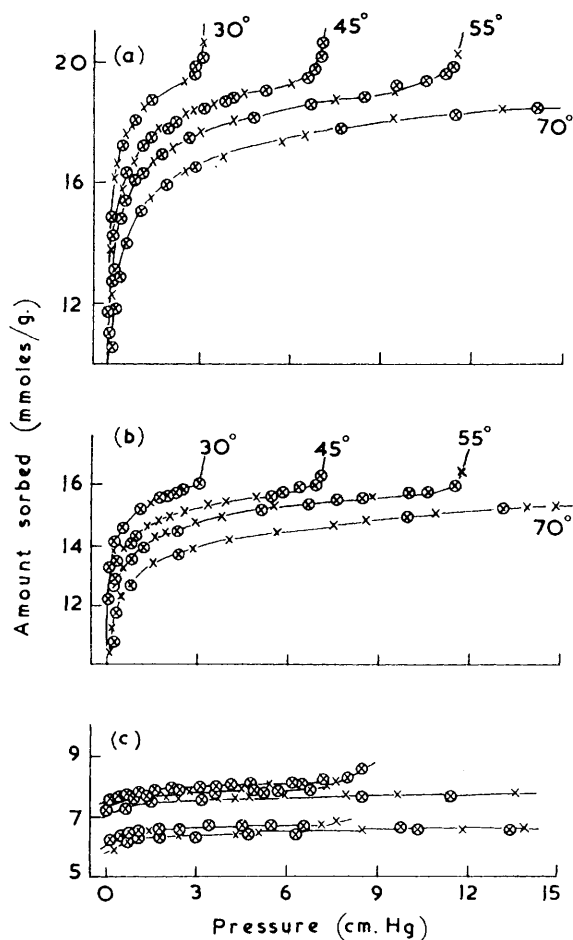

FIG. 1. Families of isotherms of water and of SO_2 in several zeolites at various temperatures.

(a) Water in Na-X.
(b) Water in Na-A(II).
(c) SO_2 in Na-Y at $-49.5°$ (top curve); in Na-X at -51 and $-33.6°$ (in descending order); and in Na-A(I) at -51 and $-33.6°$ (in descending order).

Sorption points: $\times$.
Desorption points: $\otimes$.

(a) *Basic sodalite.* The isotherm is shown in Fig. 2a. The first desorption curve lay above the first adsorption curve and was coincident with the second adsorption curve. The second desorption curve lay above the three previous ones. Attainment of a final state was very slow and the isotherm was completed over a period of seven months. In basic sodalite, the water molecules, having a van der Waals diameter of about 2·8 Å, have to diffuse through six-membered ring windows of about 2·2 Å free diameter in order to permeate the structure. It is of interest that the still larger sulphur dioxide molecule was not sorbed at room temperature although at 200° a very slow, non-equilibrium uptake of about 5 cm.³ at S.T.P. was observed in two days. When the system was outgassed after the sulphur dioxide sorption, a little sulphur was obtained. The sulphur dioxide may react with the intracrystalline sodium hydroxide in basic sodalite to form sodium hydrogen sulphite which disproportionates on heating:

$$6Na HSO_3 \longrightarrow 2Na_2SO_4 + 2NaHSO_4 + 2H_2O + 2S$$
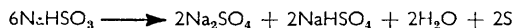
The non-equilibrium sorption of carbon dioxide in basic sodalite was also briefly investigated. This linear molecule has a smaller cross-section than the non-linear sulphur dioxide molecule

and at room temperature about 4 cm.³ at S.T.P. were sorbed in one day while at 120° another 5 cm.³ at S.T.P. were sorbed overnight.

(*b*) *Zeolite Na-Y.* This structure is very open, and sorption even of large molecules is rapid. However, the water–zeolite system gave the most complicated hysteresis behaviour observed. The isotherm is shown in Fig. 2*b*. Each desorption curve was higher than the previous sorption curve and the total uptake of water increased in successive sorption–desorption cycles, with no outgassing between cycles. It is possible that the system might have settled down to a final maximum water uptake but there was no evidence of a closing of the hysteresis loops for any given sorption–desorption cycle. The experimental points were usually obtained every hour but in some cases longer periods, of up to one day, were involved. When, after the fourth of the sorption–desorption cycles, shown in Fig. 2*b*, the water was removed by degassing at 350°,
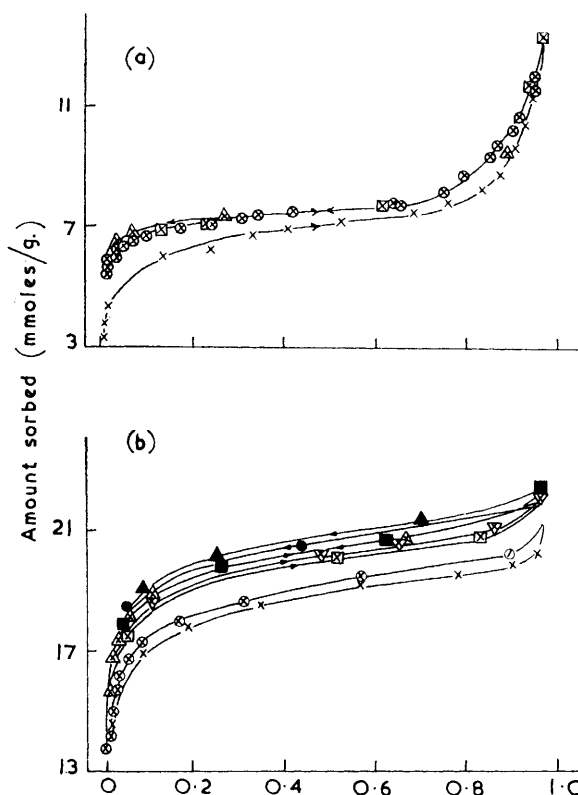

FIG. 2.   The hysteresis behaviour ob-
              served for water.

(*a*) In basic sodalite at 30°.

     × = 1st sorption.
     ⊗ = 1st desorption.
     ⊠ = 2nd sorption.
     ⬲ = 2nd desorption.

(*b*) In Na-Y at 30°.

     × = 1st sorption.
     ⊗ = 1st desorption.
     ⊠ = 2nd sorption.
     ▲ = 2nd desorption.
     ▽ = 3rd sorption.
     ● = 3rd desorption.
     ■ = 4th sorption.
     ▲ = 4th desorption.

the next set of sorption isotherms were all in the region of cycle 1 of Fig. 2*b*, but they showed no regular progression. After a third outgassing the pattern of behaviour was that shown after the second outgassing. Similar behaviour was observed with Pb-A (this work) and Sr-A [2] which were known to suffer structural damage as a result of outgassing and water uptake. *X*-Ray and optical examination of the Na-Y sample after these experiments provided no evidence of decomposition of the crystals, although up to 15% decomposition might not be detected by *X*-ray methods. Zeolite Y, as far as the aluminosilicate framework is concerned, is isostructural with zeolite X, which however gave reversible water isotherms (Fig. 1; also ref. 2).

(*c*) *Zeolite Ca-A (sample* 1). The isotherms are shown in Fig. 3*a*. The zeolite sample was outgassed at 350° between the measurements at 30° and those at 70° and this caused a small decrease in the sorptive capacity, such as could result from a partial breakdown in the structure. At any temperature, the first desorption curve lay above the first sorption curve and was virtually coincident with the second sorption curve. The second desorption curve lay above the preceding curves, but the system was not investigated further. The time intervals between the

measurement of the isotherm points were comparable with those allowed for the Na-Y–water system.

(*d*) *Zeolite Na-A* (*sample* 1). The isotherms are shown in Fig. 3*b*. Both for H_2O and D_2O only the first adsorption curve involved hysteresis and subsequent sorption and desorption curves always coincided. Also hysteresis did not occur in the first sorption–desorption cycle unless a certain relative pressure had been exceeded. No sharp threshold for hysteresis need have been involved, but the necessary pressures to produce hysteresis decreased with increasing
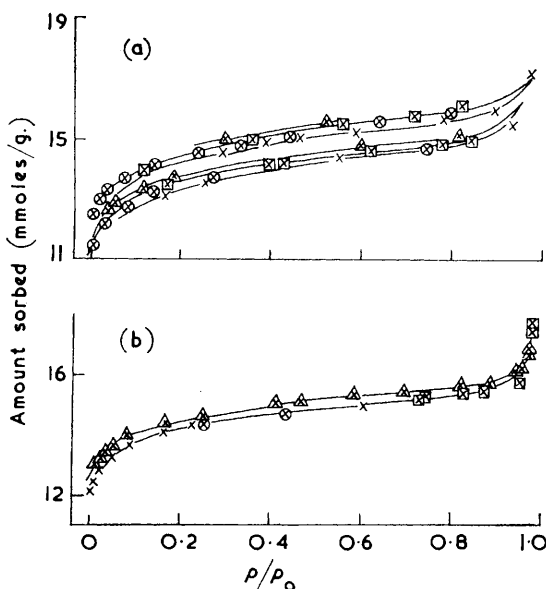

FIG. 3. Hysteresis observed.

(*a*) In D_2O–Ca-A(I) at 30° (upper group of curves) and 70° (lower group).

$\times$ = 1st sorption.
$\otimes$ = 1st desorption.
$\boxtimes$ = 2nd sorption.
$\triangle$ = 2nd desorption.

(*b*) In H_2O–Na-A(I) at 30°.

$\times$ = 1st sorption.
$\otimes$ = 1st desorption after reaching p/p_0 of only 0·63.
$\boxtimes$ = 2nd sorption.
$\triangle$ = 2nd desorption.

temperature and were above 0·75 and 0·63 relative humidity for D_2O and H_2O, respectively, at 30°, while for D_2O at 70° they were below 0·45 relative humidity. The presence of a possible threshold range of pressures was not investigated in the other zeolite–water systems. The time allowed between experimental points was again similar to that for the Na-Y–water system.

Explanations of the hysteresis based on capillary condensation,[22, 23] surface irregularities,[24] nucleation,[25] microscopic metastability,[26] and swelling and shrinking of the aluminosilicate matrices,[23] all appear inappropriate for intracrystalline sorption in rigid, non-swelling crystals such as those examined here. As stated above, Na-Y and Na-A (sample 1) have the same aluminosilicate framework structures as Na-X and Na-A (sample 2), respectively, but only the first two zeolites exhibited hysteresis. Furthermore, the sorption of sulphur dioxide was fully reversible in Na-X, Na-Y, and Na-A (sample 1). The hysteresis is therefore a function of the sorbate, and can be specific even to a given sample of zeolite.

No positive identification of the origin of this behaviour can be given, but the following consideration may be relevant. All the zeolites investigated contain sodalite cages (*i.e.*, cubo-octahedral cavities) in differing co-ordinations. These cavities are known to be able to scavenge, by inclusion, not only water but also sodium hydroxide, salts, and sodium aluminate during crystal growth from the mineralising solutions. The hysteresis may be associated with hydration or hydrolysis of the included molecules such as aluminate or silicate. In support of this argument, it was known from the analysis that Na-A, sample 1, contained more included sodium aluminate than Na-A, sample 2. Sample 1 showed a small hysteresis, but any hysteresis associated with sample 2 was within the error of the measurements. Hysteresis exhibited by Ca-A (from Na-A, sample 1) is likely to resemble that in the same specimen of Na-A.

[22] Barrer and McLeod, *Trans. Faraday Soc.*, 1955, **51**, 1290.
[23] Hirst, *Discuss. Faraday Soc.*, 1940, No. 3, 22.
[24] Holmes and Beebe, *J. Phys. Chem.*, 1957, **61**, 1684.
[25] Barrer, Drake and Whittam, *Proc. Roy. Soc.*, 1953, *A*, **219**, 32.
[26] Everett, *Trans. Faraday Soc.*, 1955, **51**, 1557.

A further factor involves the progressive changes in sorptive capacity during successive sorption–desorption cycles and on de-gassing, changes which are sometimes increases (Na-Y) and sometimes decreases (Ca-A). While decreases are reasonably understood as a tendency to decomposition of the aluminosilicate, the increase is more puzzling.

Other examples of lattice breakdown of specific cation-exchanged forms of a zeolite have been recorded. One such is Sr-X; [2] in this work breakdown was noted with Sr-A (from sample 1 of Na-A) and with Pb-A from the same sample. Breakdown involves hydrolysis of Si–O–Si or of Si–O–Al bonds, and re-formation of bonds with different atomic partners, to yield either glassy [12] or new crystalline [12] phases.

Finally, in basic sodalite, a very slow diffusion throughout the crystals may be the most logical cause of part at least of the hysteresis. It may not be possible to give sufficient time per point to be certain with all points that true equilibrium is established (as in adsorption curve 1, Fig. 3a). However, a true equilibrium must have been very closely approached for the upper curves of Fig. 3a, where for instance at one point the system, having reached apparent equilibrium, showed no change during a further interval of 17 days; and where residual hysteresis at smaller relative pressures is seen from the Figure to be small.

Reversible Isotherms.—The reversible sorption of water in Na-X and in Na-A (sample 2), and of sulphur dioxide in zeolites X, Y, and A (sample 1) permitted several equilibrium aspects of the process to be considered.

(a) *Apparent intracrystalline saturation capacities.* Intracrystalline sorption capacities of the zeolites were estimated in several ways: (i) by extrapolation of nearly flat central sections of graphs of x (x = amount sorbed) against p to $p=p_0$; (ii) by extrapolation of the linear sections of the graphs of log x against log p to log p_0; and (iii) by the B-point method of Emmett and Brunauer.[27] The results are in Table 1. As expected, small differences arise between those from

TABLE 1.

Apparent intracrystalline sorption capacities of zeolites in millimoles of sorbate per g. of outgassed zeolite.

		H$_2$O			D$_2$O		
		(i)	(ii)	(iii)	(i)	(ii)	(iii)
Na-X	30°	19.5$_6$	19.7$_3$	18.9$_3$	19.5$_8$	19.7$_9$	19.0$_1$
	45	19.4$_1$	19.4$_9$	18.8$_6$	19.2$_5$	19.4$_6$	18.8$_6$
	55	19.2$_3$	19.3$_3$	18.5$_6$	19.2$_1$	19.3$_9$	18.6$_0$
	75	19.0$_6$	19.1$_6$	18.3$_1$	19.0$_2$	19.1$_4$	18.4$_0$
Na-A(II)	30	15.8$_3$	15.9$_4$	15.3$_9$	15.7$_8$	15.9$_6$	15.2$_6$
	45	15.8$_4$	15.9$_1$	15.4$_2$	15.7$_8$	15.9$_3$	15.3$_6$
	55	15.7$_9$	15.8$_9$	15.4$_6$	15.7$_4$	15.8$_1$	15.2$_6$
	70	15.6$_2$	15.7$_2$	15.2$_0$	15.6$_2$	15.7$_2$	15.0$_8$

		SO$_2$		
		(i)	(ii)	(iii)
Na-A(I)	−33.6°	6.6$_6$	6.7$_0$	6.5$_9$
	−51.0	6.7$_0$	6.6$_7$	6.6$_2$
Na-X	−33.6	7.7$_9$	7.7$_9$	7.7$_1$
	−51.0	7.8$_6$	7.8$_6$	7.8$_2$
Na-Y	−33.3	8.0$_8$	8.0$_8$	8.0$_3$
	−49.6	8.1$_1$	8.1$_2$	8.0$_6$

the several procedures, but no measurable difference exists between the saturation values for D$_2$O and H$_2$O. The saturation values decrease slowly with increasing temperature. Saturation values are much smaller for sulphur dioxide than they are for water, approximately in the inverse ratios of the molecular volumes.

(b) *Isotope effect.* When the amounts of D$_2$O and of H$_2$O sorbed are expressed as mmoles per g. of outgassed zeolite, and are plotted against the relative humidity, the isotherms for Na-X and Na-A (sample 2) coincide, as is shown in Fig. 4a. On the other hand, when the sorption is plotted against the actual vapour pressure, the uptake of D$_2$O exceeds that of H$_2$O for Na-X (Fig. 4b). The sorption obtained for the present sample of Na-X is appreciably larger, at a

[27] Emmett and Brunauer, *J. Amer. Chem. Soc.,* 1937, **59**, 1553.

given pressure, than that observed with another sample [2] from the same bulk batch, perhaps due to less residual water or to greater purity of the zeolite specimen (Fig. 4b).

(c) *Thermodynamic aspects of sorption.* The isotherms were plotted in the form log p against amount sorbed and the isosteric heat was obtained from such isotherms, using the Clausius–Clapeyron equation. Since the isotherms are rectangular, these heats can be found only over a limited range in the quantities sorbed. The isosteric heat, q_{st}, is given by

$$q_{st} = -\Delta \tilde{H} = (\tilde{H}_g - \tilde{H}_s)$$

where $\tilde{H}_g$ is the molar enthalpy of the sorbate in the gas phase and $\tilde{H}_s$ is the mean molar enthalpy in the sorbed phase. The error in q_{st} is about 500 cal. for the sorption of water on Na-X and
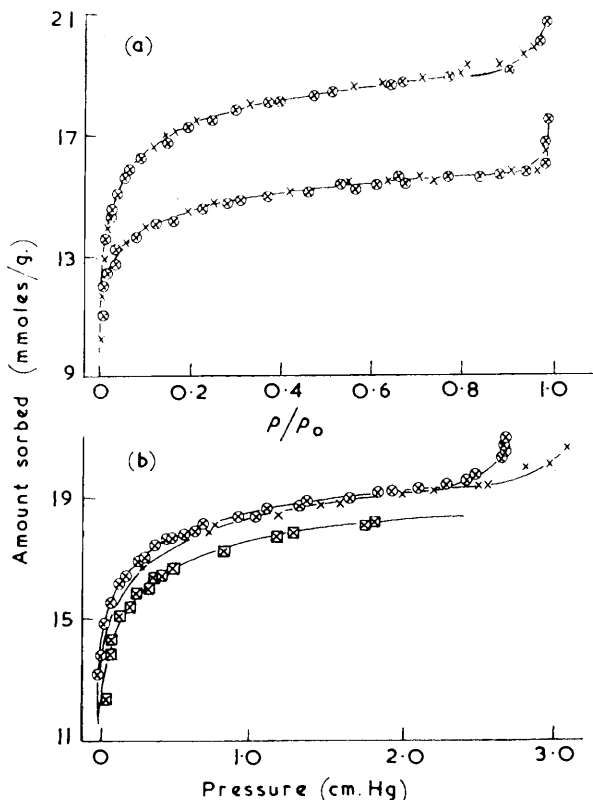

Fig. 4. (a) Comparison, on a relative pressure scale of abscissae, of sorptions of H_2O and D_2O in Na-X (upper curve) and Na-A(II) (lower curve) at 55°.

$\times = H_2O.$
$\oplus = D_2O.$

(b) Comparison, on a pressure scale of abscissae, of isotherms for D_2O ($\otimes$) and H_2O ($\times$) in Na-X at 30°. The lowest curve ($\boxtimes$) shows the corresponding isotherm for H_2O in another sample of Na-X obtained by Barrer and Bratt.[2]

1 kcal. for the water on Na-A (sample 2). The error in q_{st} for the sorption of sulphur dioxide on the zeolites Na-Y, Na-X, and Na-A (sample 1) is also about 1 kcal.

The curves of q_{st} for sulphur dioxide against θ, for −33°, are shown in Fig. 5a for the A, X, and Y zeolites. They are of characteristic form, q_{st} dropping rather sharply to the value of the heat of vaporization of sulphur dioxide as θ approaches and passes through unity. There is some evidence of a flat maximum as θ * decreases below 0·9. Similarly, in Fig. 5b curves of q_{st} against θ, for 55°, are given for the sorption of light and heavy water by Na-X and Na-A (sample 2). The curve for light water in Na-A (sample 2) is of the same form, and q_{st} has a similar magnitude to that measured calorimetrically by Frohndsdorff.[3] The curve for light water in Na-X is the same, within experimental error, as that obtained by Barrer and Bratt [2] in the range $0·80 < θ < 1·00$ but is appreciably larger for smaller values of θ. There is also a difference in the adsorption isotherms, as shown in Fig. 4b. The heats of sorption of D_2O are, within the experimental error, the same as those of H_2O.

* θ is defined as the ratio amount sorbed/intracrystalline sorption capacity. Since extracrystalline sorption and capillary condensation can occur at high relative pressures, θ can exceed unity.
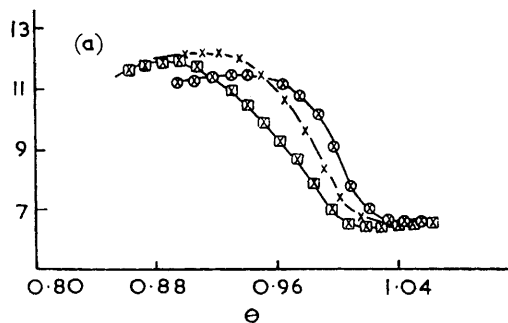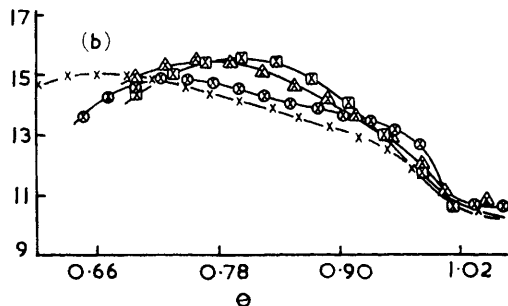
FIG. 5.   Isosteric heats of sorption of sulphur dioxide and water in the region near saturation of the sorbent.

(a) SO$_2$ in Na-A(I) (×); Na-X (⊗); and Na-Y (⊠).

(b) H$_2$O in Na-X(×); D$_2$O in Na-X (⊗); H$_2$O in Na-A(II) (⊠); and D$_2$O in Na-A(II) (▲).

DISCUSSION

It has been established from this work and from that of Barrer and Fender[1] that for the zeolites Na-X, Na-A (sample 2), heulandite, gmelinite, and chabazite there is little selectivity as between D$_2$O and H$_2$O when sorption occurs from the pure liquids, but that from the vapours D$_2$O is preferentially sorbed.   If liquid D$_2$O–H$_2$O mixtures behaved ideally then it could be predicted that little fractionation of such mixtures would be observed.   A minimal separation of H$_2$O and D$_2$O from the liquid mixtures was detected by a chromatographic procedure, in which the liquid was passed slowly upwards through a column of out-gassed zeolite Ca-A.   Heavy water was preferentially retained on the column, as shown by a small enrichment in the leading boundary in light water.   However, as far as liquid mixtures are concerned it can be said that the change in environment when sorption occurs virtually fails to distinguish between D$_2$O and H$_2$O.   This is probably representative of the more open zeolites as a class.

On the other hand we have found [16] that a significant enrichment of the aqueous phase in heavy water occurs when any one of six typical crystallohydrates are grown from their saturated solutions in D$_2$O–H$_2$O mixtures.   Here the effect is in the opposite sense to that observed with Ca-A and is much larger.   The hydrate water in such stoicheiometric crystallohydrates is distinguished from zeolitic water in that hydrate water is much less mobile and, therefore, considerably further removed in properties from liquid water.

Although zeolitic water is comparatively fluid[1] and hydrogen bonds occur in it between

TABLE 2.

Sorbent	Ref.	q_{st} (kcal./mole) $\theta = 0.88$	$\theta = 0.94$	Sorbent	Ref.	q_{st} (kcal./mole) $\theta = 0.88$	$\theta = 0.94$
Li-X	2	15·2	14·8	Na-A	This work	14·5	12·9
Na-X	2	13·5	13·5	Na-A	3	13·7	11·5
Na-X	This work	13·5	13·0	Chabazite ...	1	14·5	14·4
K-X	2	18·8	17·8	Gmelinite ...	1	14·7	14·3
(Ca, Cs)-X	2	14·2	14·0	Heulandite	1	13·7	13·0
Ca-X	2	14·2—14·8	12·2				

pairs of water molecules and between water and the anionic oxygens of the aluminosilicate frameworks, both differential and integral heats of sorption exceed the heats of condensation of water vapour to its liquid or of water vapour into concentrated electrolyte solutions.[2] However, this is due, in part, to a difference in the nature of the vaporization process.[2,12] The magnitudes of some differential heats of sorption of zeolitic water for θ values approaching unity are summarized in Table 2. Perhaps their most striking feature is a general similarity in magnitude.

PHYSICAL CHEMISTRY LABORATORIES,
    IMPERIAL COLLEGE, LONDON S.W.7.