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*Studies on the zeolites. Part VIII. A theory of the vapour pressure of the zeolites, and of the diffusion of water or gases in a zeolite crystal.*¹

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THE behaviour of the zeolites on dehydration, and their capacity for absorbing other gases and vapours in place of the water removed, have formed the subject of numerous investigations, qualitative and quantitative, of various degrees of accuracy. In only a few cases have attempts been made to fit an equation² to the experimental data. Of these equations, those proposed by O. Weigel, G. F. Hüttig, and O. Schmidt³ are quite inadequate, as is readily seen by a trial with the more extensive data now available. On the other hand, E. Rabinowitsch⁴ derived an equation which proved capable of reproducing the experimental data and is very similar to the equation now proposed, but derived in a quite different way.⁵

¹ Parts I-VII, *Min. Mag.*, 1930-1934, vols. 22-23.

² Other than a Freundlich isotherm, an empirical type of equation which will almost always represent the data over a limited range.

³ O. Weigel, *Sitzungsber. Gesell. Naturwiss. Marburg*, 1924, p. 107 [M.A. 4-373]; G. F. Hüttig, *Fortschr. Chem. Phys. und Physikal. Chem.*, 1924, vol. 18, no. 1, and *Kolloid-Zeits.*, 1924, vol. 35, p. 337 [M.A. 5-82]; O. Schmidt, *Zeits. Physikal. Chem.*, 1928, vol. 133, p. 263 [M.A. 5-81].

⁴ E. Rabinowitsch, *Zeits. Physikal. Chem., Abt. B*, 1932, vol. 16, p. 50 [M.A. 5-355].

⁵ The similarity is not immediately apparent, but is readily disclosed by substituting $(1-x)$ for Q/Q_m and writing the equation logarithmically.

Rabinowitsch's equation is not, however, perfectly satisfactory, as it is found impossible, on applying it to the newer experimental data, to uphold either of the interpretations he suggests for the constant b .

The equation now proposed is based on the assumption that the water in the zeolites occupies a definite integral number of lattice positions per unit cell, which need not all be filled; the water is, however, readily mobile, since the binding energy in the lattice is not very large. The grounds on which it is held that such a view best represents the condition of the water in the zeolites will be discussed below.

The theory here developed applies not only to the zeolites, but to any crystalline compound of a volatile and non-volatile component the crystal-structure of which is such that the whole or a part of the volatile component can be removed without the structure collapsing. At present there is no comprehensive term for such compounds, and they are often referred to as 'zeolitic' compounds, after the best-known examples of the class, but a more satisfactory term is desirable. Although in most of what follows only zeolites or 'zeolitic' hydrates are referred to, it should be emphasized that the arguments and equations apply equally to all 'zeolitic' compounds, including, for example, the systems FeS-S, FeO-O₂, Pd-H₂, &c.

Theoretical.

For a primary treatment, it will be assumed that the volatile component does not undergo any change in molecular complexity (e.g. dissociation) in passing from crystal to vapour or the reverse; and that in the crystal all the molecules (or atoms) of the volatile component are structurally of the same kind, occupying one set of equivalent positions.

Consider a plate of the zeolite so cut and mounted that the free surface exposed to the vapour is of unit area, and is normal to the channels along which the water migrates, and which form so notable a feature of the structure of the zeolites. When the zeolite is partially dehydrated, let x be the fraction of water molecules that have been removed.

If p is the pressure of water vapour above the crystal, the number of water molecules striking the surface in unit time is $Np/\sqrt{2\pi MRT}$, where N is the Avogadro number, M the molecular weight of the volatile component (water), R the gas constant, and T the absolute temperature. But only a part of the surface of the

crystal consists of vacant lattice positions in which the water might condense; if there are ν lattice positions for water per sq. cm. in the surface layer,¹ the number of vacancies will be νx . Further, in order to condense in a given vacant position, a water molecule must strike the proper channel centrally, within a limited area a . For a spherical molecule of radius ρ entering a channel of effective radius r the area will be $a = \pi(r - \rho)^2$. For a non-spherical molecule it is probably permissible to use a mean radius unless one or more dimensions of the entrant molecule exceed the diameter of the channel; in the latter case the expression for a will be complex, involving an orientation factor. Lastly, it may be necessary for the incident molecule to possess a component of kinetic energy normal to the crystal surface greater than some value η (the activation energy of condensation) if it is to condense. Of the incident molecules, only a fraction $ax\nu$ per sq. cm. will strike vacant lattice positions within the 'condensation area', a , and only a fraction $e^{-N\eta/RT}$ of these will have the requisite activation energy η . Hence the number of water molecules condensing in unit time will be $ax\nu N p e^{-N\eta/RT} / \sqrt{2\pi MRT}$.

Of the $\nu(1 - x)$ water molecules in the surface layer, only a fraction $e^{-N\epsilon/RT}$, having a component of kinetic energy normal to the free surface greater than ϵ (the activation energy of evaporation), will have sufficient energy to overcome the forces holding them to the lattice; and only half of these will be moving in the right direction at any moment. In an equilibrium state, the number of molecules escaping is balanced by those condensing, and it is therefore permissible to determine the number of molecules escaping in unit time by dividing the number in a position to escape at any instant by the average time required for escape.

The existence of an activation energy of condensation, η , implies a potential hump between the free vapour and the potential trough corresponding to the structural water lattice position.² Let the distance from the summit of the potential hump to the lattice position be $\frac{1}{2}D$, and from the hump to a point at which the escaping (or entering) molecule may just be regarded as free $\frac{1}{2}D'$. The distance $\frac{1}{2}D$ will be

¹ It is not necessary to consider more than the surface layer, since, in equilibrium, the influence of deeper layers on condensation and on evaporation must necessarily balance.

² That is, a molecule approaching a given vacant lattice position is at first repelled, and only on reaching a certain point (which it will not reach, against the repulsion, unless it has the necessary energy η) is it attracted into the lattice position.

approximately equal to half the distance between equivalent water lattice positions, along the channels. Provided $N\epsilon/RT$ is large, which will normally be the case, the great majority of the escaping molecules will have energies but little greater than ϵ , and hence their mean velocity as they leave the lattice positions may be taken¹ as $\sqrt{2N\epsilon/M}$; this velocity is all lost as the summit of the potential hump is reached, after which the repulsion accelerates them again, so that on reaching the free vapour state their mean velocity is $\sqrt{2N\eta/M}$. Nothing is known of the law governing the acceleration and deceleration of the molecules, but as an approximation the time of escape may be taken to be χ times the value calculated on the assumption that both portions ($\frac{1}{2}D$ and $\frac{1}{2}D'$) of the path of escape are traversed in simple harmonic motion;² the factor χ should be greater than 1, but numerically small, and it may also be allowed to correct for any difference between D and the distance between equivalent water lattice positions. The time of escape is then

$$\pi\chi D\sqrt{M/4\sqrt{2N\epsilon}} + \pi\chi D'\sqrt{M/4\sqrt{2N\eta}}.$$

To a first approximation, it is probably permissible to assume that $D':D::\eta:\epsilon$; and the error introduced by this assumption is the less since η is probably much less than ϵ . Substituting $D\eta/\epsilon$ for D' , and approximating $(1 + \sqrt{\eta/\epsilon})/\sqrt{\epsilon} = 1/\sqrt{\epsilon - \eta}$, since $\epsilon \gg \eta$, the time of escape becomes $\pi\chi D\sqrt{M/4\sqrt{2N(\epsilon - \eta)}}$, and the number of molecules escaping in unit time is:

$$2\nu(1-x)\sqrt{2N(\epsilon - \eta)} \cdot e^{-N\epsilon/RT} / \pi\chi D\sqrt{M}.$$

Equating the number of molecules escaping and condensing, the equilibrium equation is:

$$p = [4(1-x)\sqrt{NRT(\epsilon - \eta)} \cdot e^{-N(\epsilon - \eta)/RT}] / aNDx\chi\sqrt{\pi},$$

or $\log_e p =$

$$\log_e 4\sqrt{NR(\epsilon - \eta)} / aNDx\chi\sqrt{\pi} + \frac{1}{2} \log_e T - \log_e x / (1-x) - N(\epsilon - \eta) / RT.$$

In this equation, all the quantities must be expressed in comparable units— p in dynes per sq. cm., R , ϵ , and η in ergs, a and D in cm. It is more convenient in practice to use common logarithms, to have p in mm. Hg, the energies in calories, and a and D in Å., and to replace the activation energy difference per molecule of water, $(\epsilon - \eta)$,

¹ Strictly, the mean velocity is $\sqrt{2N\epsilon/M} + e^{N\epsilon/RT} \cdot \sqrt{\pi RT/2M} \cdot \Phi(\sqrt{N\epsilon/RT})$, where Φ denotes the Gaussian error function. If $N\epsilon/RT$ is large, the second expression is negligible.

² Compare J. E. Lennard-Jones, *Trans. Faraday Soc.*, 1932, vol. 18, p. 351, who concludes, in a very similar problem, that the factor χ can be neglected.

by the difference per gram-mol., $E = N(\epsilon - \eta)$. The equation then becomes :

$$\log p = C + \frac{1}{2} \log T - \log x/(1-x) - E(\log e)/RT,$$

where $C = 5.22 + \log \sqrt{E/aD\chi}$.

The heat of hydration,¹ $Q_x = -R\partial \log_e p/\partial(1/T) = E + \frac{1}{2}RT$. The variation in Q_x with T is so small that when isohydric curves are plotted in the form $\log p$ against $1/T$ they are reduced to straight lines within the experimental error; this is in agreement with all the experimental results.

So far the equation has only been derived for a very special case, and it remains to generalize it. It was assumed that the whole free surface of the zeolite was normal to one particular direction. Now ϵ , η , a , and D certainly vary markedly with direction in the crystal, but, since neither the equilibrium pressure nor the heat of hydration can so vary, the difference $\epsilon - \eta = E/N$ and the product aD must be constant. The equation is therefore independent of direction.

It was assumed that the volatile component did not undergo any change in molecular complexity in vaporization. This is true when the volatile component is water, but in several systems the volatile component is incorporated in the crystal as atoms, while in the vapour phase it is present as polyatomic molecules. The systems PdH-H_2 , FeS-S_2 , and $\text{Sb}_2\text{O}_{4-5}\text{-O}_2$ are examples of such systems, and recent work tends to show that they are fairly numerous, especially among sulphides and selenides, though the range in composition of the solid phase may be fairly small. In such cases atomic oxygen, sulphur, &c., in the crystal may probably be regarded as being in equilibrium with the minute equilibrium fraction of dissociated molecules in the vapour phase, and the total pressure may then be calculated with the aid of the dissociation equation of the volatile component.

Thirdly, it was assumed that the water molecules are all structurally of the same kind. Among zeolites in particular this is rarely the case, the water occupying two, three, or more sets of lattice positions. In equilibrium, each set of water molecules can be considered independently, and the water distributes itself among the several sets, each of which will have its own value for E , and possibly for a also, in such a way that the equilibrium pressure is the same for each set. If two sets of water molecules have very similar values for the

¹ That is, the heat evolved when one gram-mol. of water vapour combines with an infinite amount of zeolite of degree of dehydration x , exclusive of the external work involved.

constants E and a , water will be lost from both sets to much the same degree during dehydration, but if the constants differ markedly for the two sets but little water will be lost from one set of positions until the other set is almost empty. But it is characteristic of zeolitic hydrates (if the above equation is correct) that in the partially dehydrated compound no set of water positions will be completely full, nor any quite empty. Indeed, it is impossible for any set of equivalent positions to be quite fully occupied, even when the zeolite is in contact with liquid water, for this would require $p = \infty$. But very little water need be lost to bring the dissociation pressure of the zeolite below the vapour pressure of water—something of the order of 0.01 % will often suffice, so that the deficit will often be quite impossible of direct detection. When the loss of water is small, the relative accuracy with which it can be determined falls sharply, and vapour pressure observations in this region become of little value.

In many zeolite structures there are cavities which might be occupied by water molecules but are not. Presumably the heats of hydration for these groups of lattice positions would be so small that at all accessible water vapour pressures the positions must remain practically empty. It is possible that a small degree of occupation of such 'forbidden' positions may account for the slight excess of water often found in zeolites after exposure to nearly saturated atmospheres, which excess is usually attributed wholly to adsorption. And it is always possible that another volatile component might prove able to occupy these positions, though this is not likely to occur, as the affinity of a zeolite for water is generally greater than for any other vapour, except perhaps ammonia.

On applying the above equation to the experimental data, it is found that in many cases E varies markedly with x , and often C also varies with x to a greater extent than the variation of its constituent factor, $\log \sqrt{E}$, would account for. The variation in E may be formally recognized by replacing it by $E_0\{1+f(x)\}$, where E_0 is the value of E for $x = 0$, and $f(x)$ some unknown function of x ; in practice $f(x)$ often proves to be approximately linear, and is invariably positive. The origin of this variation in E is fairly readily understood; as the water is removed, the whole distribution of affinity in the crystal is necessarily disturbed, and the more water is removed the more firmly bound is what remains, leading to an increase in E with increase of x , i.e. a positive value of $f(x)$.

The variation in C , in so far as it is not solely due to a variation

in E , is found to be always an increase with increase of x , and is almost certainly to be attributed to lattice shrinkage.¹ As the water is removed the lattice tends to shrink, particularly in directions normal to the water-bearing channels; this shrinkage normally² decreases the area of the channels, and hence the 'condensation area', a . The variation in a may be formally expressed by writing $a = a_0\{1 + \phi(x)\}^2$, where a_0 is the value of a for $x = 0$; then taking $a = \pi(r - \rho)^2$, as above, $\phi(x) = (r - r_0)/(r_0 - \rho)$, so that if the lattice shrinkage and consequent decrease in r are linear functions of x , as is often the case to a first approximation, $\phi(x) = -x(r_0 - r_1)/(r_0 - \rho)$.

When the lattice shrinkage is very marked it often departs from the linear approximation, and there sometimes seems to be a tendency for the shrinkage to regulate itself so that the vapour pressure remains constant over a fairly wide range of x -values; such pseudo-univariant equilibria, exemplified by natrolite, the palladium-hydrogen system, and probably also by calcium sulphate hemihydrate, have hitherto remained unexplained.

Thus, eliminating all dependent variables,³ the equation may be written:

$$\log p = C_0 + \frac{1}{2} \log T - \log x/(1-x) - 2 \log \{1 + \phi(x)\} + \frac{1}{2} \log \{1 + f(x)\} - E_0\{1 + f(x)\}(\log e)/RT,$$

where $C_0 = 5.22 + \log \sqrt{E_0}/a_0 D \chi$.

The interpretation of the existing experimental data.

Edingtonite (figs. 1 and 2) shows fairly simple behaviour, and its vapour pressure surface can be readily formulated if it is assumed that the water is divided between two groups of four equivalent positions per unit cell each, which may be indicated conveniently by writing the unit cell formula: $\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{20} \cdot (4 + 4)\text{H}_2\text{O}$. This division of the water into two groups is in agreement with the X-ray work of W. H. Taylor and R. Jackson.⁴ The X-ray work would also lead

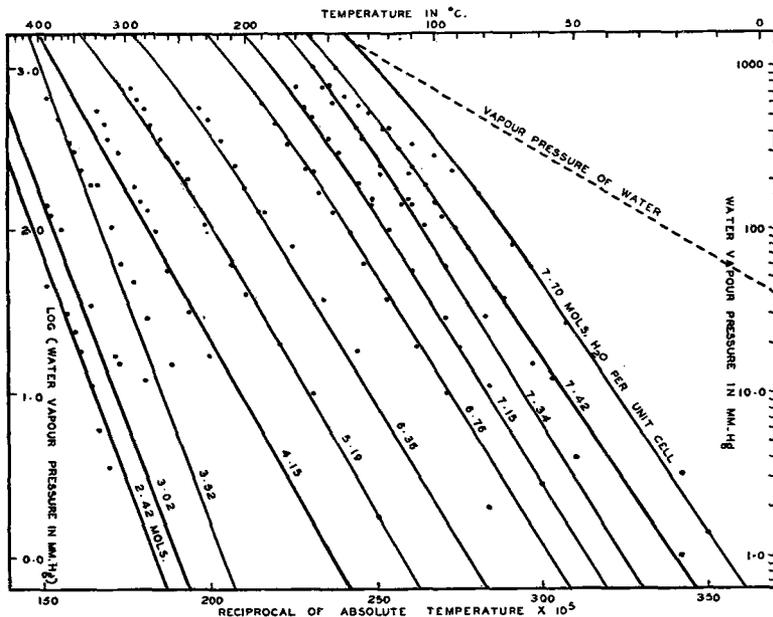
¹ The reality of lattice shrinkage has been repeatedly demonstrated by X-ray and specific gravity measurements.

² In some types of structure (e.g. chabazite) lattice shrinkage does not appear to affect the water-bearing channels.

³ Strictly, both E_0 and a probably vary slightly with temperature, but the variation is in general too small to be detected with the range of experimental temperatures normally available. The variation in D due to thermal expansion is negligible.

⁴ W. H. Taylor and R. Jackson, *Zeits. Krist.*, 1933, vol. 86, p. 53 [M.A. 5-354].

one to expect that the two groups of water molecules will have appreciably different volatilities, since their surroundings in the crystal are different, and this is found to be the case. The more volatile group of water molecules have $E = 1.35(1 + 0.22x) \times 10^4$



temperature. The calorimetrically determined figure was 17,000 cal. The experimental vapour pressure data for edingtonite are given in table I, which also shows the agreement between the observed and calculated values of $\log p$.

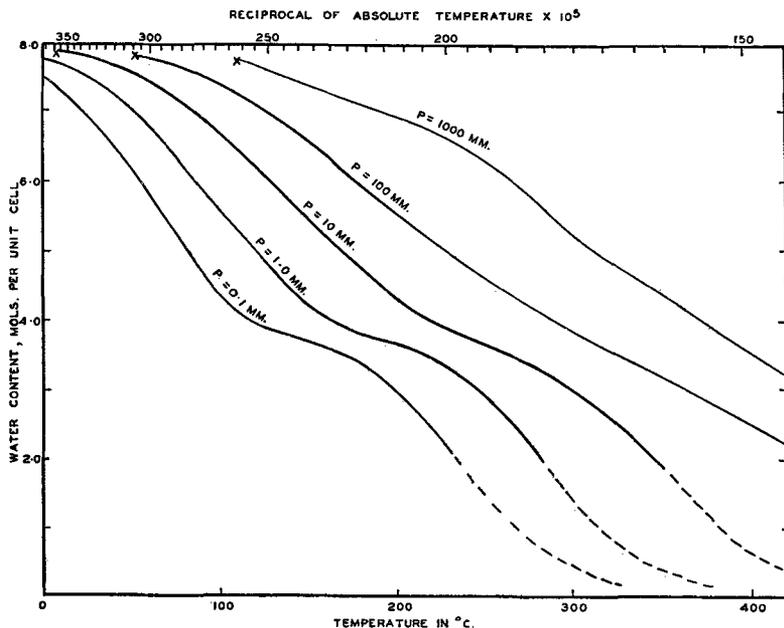
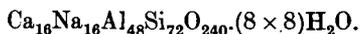


Fig. 2. Calculated isobaric dehydration curves for edingtonite. A typical example of subdivision of the water into two groups. In this and other isobaric graphs the curves terminate towards low temperatures at saturation points, where liquid water condenses.

Mesolite crystallizes in the space-group C_{2v}^3 , which has, in the face-centred aspect adopted, sets of four or eight equivalent positions in the unit cell. The water is almost certainly in general positions, and the unit cell formula may therefore be written



The task of working out vapour pressure constants for such a case would in general be almost impossible, but fortunately the relation of this zeolite to natrolite and scolecite assists. The formula amounts to one natrolite and two scolecite unit cells combined, and there is reason to believe that this represents the actual structure rather

TABLE I. Observed and calculated water vapour pressures of edingtonite from Böhlet, Sweden (B.M. 81049), for various water contents and temperatures.

<i>Series 1.</i> $c = 7.70$ mol.			<i>Series 4.</i> $c = 7.15$ mol.		
$x_1 = 0.075$ to 0.095 .			$x_1 = 0.21$ to 0.23 .		
$x_2 = 4 \times 10^{-9}$ to 7×10^{-7} .			$x_2 = 4 \times 10^{-7}$ to 3×10^{-6} .		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
19	0.49	0.38	114	2.26	2.18
53	1.41	1.45	80	1.46	1.35
64	1.76	1.75	96	1.88	1.75
71	1.90	1.93	105	2.02	1.96
77	2.10	2.12	110	2.16	2.08
83	2.22	2.21	112	2.19	2.11
92	2.33	2.43	124	2.34	2.41
100	2.45	2.58	125	2.39	2.42
109	2.53	2.73	133	2.56	2.56
119	2.63	2.90	138	2.63	2.63
130	2.70	3.04	149	2.79	2.83
			155	2.88	2.90
<i>Series 2.</i> $c = 7.42$ mol.			<i>Series 5.</i> $c = 6.76$ mol.		
$x_1 = 0.145$ to 0.165 .			$x_1 = 0.31$ to 0.33 .		
$x_2 = 10^{-8}$ to 10^{-6} .			$x_2 = 10^{-6}$ to 10^{-4} .		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
19	0.00	1.92	128	2.18	2.12
57	1.08	1.10	79	1.04	0.98
74	1.58	1.56	90	1.28	1.27
92	2.00	2.00	95	1.46	1.41
97	2.08	2.12	120	2.00	1.96
104	2.27	2.28	129	2.16	2.12
110	2.39	2.40	134	2.28	2.26
116	2.50	2.52	146	2.48	2.45
123	2.62	2.68	150	2.56	2.53
135	2.76	2.85	160	2.71	2.66
142	2.82	2.97	163	2.75	2.72
140	2.88	3.06	170	2.88	2.81
<i>Series 3.</i> $c = 7.34$ mol.			<i>Series 6.</i> $c = 6.36$ mol.		
$x_1 = 0.155$.			$x_1 = 0.41$ to 0.43 .		
$x_2 = 10^{-7}$ to 10^{-6} .			$x_2 = 2 \times 10^{-6}$ to 2×10^{-4} .		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
50	0.6	0.85	160	2.36	2.34
64	1.18	1.25	94	1.0	1.00
78	1.63	1.61	80	0.3	0.62
87	1.88	1.82	108	1.28	1.33
100	2.16	2.11	122	1.57	1.63
111	2.35	2.35			

TABLE I (continued).

<i>Series 6 (continued).</i>			<i>Series 9. c = 4.15 mol.</i>		
$t^{\circ}\text{C.}$	Log p (mm. Hg)		$t^{\circ}\text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
134	1.79	1.87	275	2.13	2.00
141	1.98	2.00	228	1.23	1.34
148	2.11	2.16	242	1.50	1.57
156	2.23	2.28	258	1.75	1.78
165	2.38	2.41	270	2.00	1.93
175	2.53	2.57	282	2.18	2.08
183	2.66	2.69	289	2.27	2.15
191	2.78	2.81	304	2.48	2.34
199	2.88	2.97	313	2.57	2.45
<i>Series 7. c = 5.39 mol.</i>			319	2.66	2.48
$x_1 = 0.65$ to $0.67.$			326	2.74	2.55
$x_2 = 5 \times 10^{-5}$ to $10^{-3}.$			<i>Series 10. c = 3.52 mol.</i>		
$t^{\circ}\text{C.}$	Log p (mm. Hg)		$1 - x_1 = 0.01$ to $0.04,$		
	Obs.	Calc.	$x_2 = 0.13$ to $0.10.$		
192	2.20	2.12	$t^{\circ}\text{C.}$	Log p (mm. Hg)	
137	1.26	1.14		Obs.	Calc.
154	1.57	1.48	328	2.28	2.00
172	1.90	1.79	255	1.18	0.82
187	2.11	2.05	276	1.46	1.20
199	2.26	2.26	290	1.68	1.40
207	2.40	2.36	301	1.79	1.61
219	2.56	2.53	313	2.02	1.80
228	2.68	2.63	335	2.20	2.10
235	2.76	2.73	343	2.37	2.28
<i>Series 8. c = 4.72 mol.</i>			352	2.48	2.38
$x_1 = 0.82$ to $0.84.$			357	2.54	2.43
$x_2 = 5 \times 10^{-4}$ to $0.01.$			372	2.69	2.63
$t^{\circ}\text{C.}$	Log p (mm. Hg)		385	2.82	2.80
	Obs.	Calc.	<i>Series 11. c = 2.82 mol.</i>		
160	1.00	0.94	$1 - x_1 = 0.001$ to $0.01.$		
180	1.30	1.30	$x_2 = 0.30$ to $0.31.$		
200	1.61	1.66	$t^{\circ}\text{C.}$	Log p (mm. Hg)	
210	1.79	1.80		Obs.	Calc.
230	2.04	2.08	385	2.16	2.10
243	2.32	2.27	280	1.08 ?	0.47
250	2.42	2.37	306	1.18	0.94
265	2.57	2.52	310	1.23	1.00
272	2.65	2.62	335	1.54	1.40
280	2.75	2.68	370	2.01	1.88
286	2.81	2.76	380	2.10	2.04
293	2.88	2.82	390	2.16	2.15

TABLE I (continued).

Series 12. $c = 2.42$.			Series 12 (continued).		
$1 - x_1 = 4 \times 10^{-4}$ to 4×10^{-3} .			$t^\circ \text{C.}$	$\text{Log } p \text{ (mm. Hg)}$	
$x_2 = 0.40$.				Obs.	Calc.
$t^\circ \text{C.}$	$\text{Log } p \text{ (mm. Hg)}$				
	Obs.	Calc.			
387	1.66	1.78	332	1.05	1.05
314	0.54	0.76	345	1.26	1.22
325	0.78	0.98	351	1.38	1.34
			360	1.49	1.45

closely. Now scolecite, as will be shown later, has three groups of eight molecules each per unit cell, and one group is much more volatile than the other two,¹ which appear to have almost, if not quite, the same volatility. As a first trial, therefore, an attempt was made to interpret the mesolite data on an assumption of $16\text{H}_2\text{O}$ of high and equal volatility, and $48\text{H}_2\text{O}$ of lower and again equal volatility. This treatment proved fully satisfactory. The more volatile group of 16 water molecules was found to have $E = 2.11 \times 10^4$ cal., and $C = 9.17$. The constants for the less volatile group of 48 water molecules could not be fixed with the same degree of accuracy, but are near $E = 2.52 \times 10^4$ cal. and $C = 8.85$. The mean heat of hydration of mesolite over the range 33.7 to 64 mols. H_2O per unit cell, computed from the vapour pressure data, is 23,300 cal. per gram-mol. of water. Calorimetrically, a figure of 18,000 cal. was obtained, but it is quite possibly low. It was not shown that the whole of the water expelled was reabsorbed, and any failure to reabsorb part of it would lead to a low value for the heat of hydration. This explanation is supported by X-ray examination of a partially dehydrated mesolite containing about 30 mols. H_2O per unit cell, which showed considerable lattice breakdown.

The heats of hydration for the two groups of water molecules differ much less for mesolite than they do for edingtonite, and this is reflected in the isobaric curves, which show much less of a 'step' for mesolite than for edingtonite. While with edingtonite almost the whole of the more volatile group of water molecules can be removed before the less volatile ones begin to be removed to any appreciable extent, with mesolite, at 227°C. and 10 mm. Hg, when only 10.6 mols. H_2O have been lost from the more volatile group ($x = 0.66$),

¹ More strictly, this applies to the high-temperature modification, metascolecite; scolecite itself has a more volatile group of 16 and a less volatile group of 8 molecules.

the loss of the less volatile group is already appreciable, being 0.8 molecule ($x = 0.016$). The observed and calculated values of $\log p$ for mesolite are shown in table II.

TABLE II. Observed and calculated water vapour pressures of mesolite from Bhole Ghaut, Syhadree Mts., Bombay (B.M. 33868), for various water contents and temperatures.

<i>Series 1. c = 59.8 mols.*</i>			<i>Series 3. c = 55.1 mols.</i>		
$x_1 = 0.26.$			$x_1 = 0.53 \text{ to } 0.47.$		
$x_2 = 0.001 \text{ to } 0.006.$			$x_2 = 0.01 \text{ to } 0.03.$		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
238	1.95	2.01	291	2.41	2.32
153	0.14	0.23	298	2.50	2.42
164	0.49	0.46	312	2.60	2.68
170	0.61	0.60	320	2.70	2.78
188	0.94	1.02	332	2.80	2.93
195	1.16	1.21	334	2.89	2.99
200	1.33	1.30	344	2.95	3.13
206	1.38	1.40	352	3.04	3.23
218	1.62	1.64	330	2.94	2.93
229	1.76	1.88	324	2.89	2.83
238	2.01	2.01	315	2.85	2.72
245	2.23	2.16	313	2.76	2.71
256	2.39	2.36	299	2.56	2.50
259	2.45	2.40			

<i>Series 2. c = 57.6 mols.</i>			<i>Series 4. c = 53.2 mols.</i>		
$x_1 = 0.40 \text{ to } 0.38.$			$x_1 = 0.65 \text{ to } 0.56.$		
$x_2 = 0.002 \text{ to } 0.008.$			$x_2 = 0.01 \text{ to } 0.04.$		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
180	0.38	0.46	297	2.16	2.22
168	0.23	0.18	300	2.27	2.30
160	1.78	0.00	314	2.42	2.53
170	0.00	0.23	326	2.55	2.68
180	0.23	0.46	333	2.67	2.78
200	0.83	0.93	346	2.87	2.95
200	1.03	0.93	355	2.94	3.11
210	1.21	1.12	361	2.99	3.10
222	1.32	1.36	366	3.04	3.20
235	1.62	1.60	370	3.08	3.24
254	2.01	1.94	210	0.62	0.64
264	2.12	2.12	195	0.38	0.35
277	2.27	2.30	221	0.88	0.84
			233	1.00	1.10
			240	1.16	1.25

* There is some uncertainty as to this water content.

TABLE II (continued).

<i>Series 4 (continued).</i>			<i>Series 6 (continued).</i>		
$t^{\circ}\text{C.}$	Log p (mm. Hg)		$t^{\circ}\text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
268	1.71	1.77	386	2.95	2.99
242	1.23	1.31	395	2.99	3.09
246	1.36	1.36	352	2.54	2.55
266	1.77	1.72	320	2.42 ?	2.06
279	2.04	1.97			
 <i>Series 5. $c = 52.2$ mols.</i>			 <i>Series 7. $c = 41.1$ mols.</i>		
$x_1 = 0.68$ to 0.63 .			$x_1 = 0.96$ to 0.89 .		
$x_2 = 0.02$ to 0.04 .			$x_2 = 0.15$ to 0.18 .		
$t^{\circ}\text{C.}$	Log p (mm. Hg)		$t^{\circ}\text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
215	0.00 ?	0.64	328	1.79	2.04
220	0.46 ?	0.74	240	0.30	0.21
233	0.94	1.00	255	0.61	0.55
245	1.24	1.25	280	1.28	1.00
249	1.38	1.36	300	1.72 ?	1.32
259	1.56	1.52	300	1.62 ?	1.32
280	1.90	1.88	295	1.56 ?	1.22
294	2.06	2.08	315	1.79	1.62
310	2.41	2.34	340	2.17	2.01
324	2.54	2.55	371	2.63	2.46
340	2.72	2.80	385	2.72	2.58
358	2.94	3.06	398	2.88	2.74
369	3.03	3.19			
 <i>Series 6. $c = 47.5$ mols.</i>			 <i>Series 8. $c = 36.1$ mols.</i>		
$x_1 = 0.88$ to 0.79 .			$1 - x_1 = 0.07$ to 0.03 .		
$x_2 = 0.05$ to 0.08 .			$x_2 = 0.25$ to 0.26 .		
$t^{\circ}\text{C.}$	Log p (mm. Hg)		$t^{\circ}\text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
224	0.23	0.32	285	0.95	0.80
237	0.69 ?	0.60	319	1.56	1.44
270	1.28	1.24	344	1.98	1.84
279	1.34	1.40	356	2.13	2.02
299	1.70	1.72	287	0.83	0.81
315	1.99	2.00	270	0.60	0.59
255	0.95	0.97	307	1.48	1.24
292	1.50	1.62	344	1.95	1.84
310	1.81	1.90	331	1.84 ?	1.60
331	2.28	2.22	360	2.13	2.08
352	2.45	2.55	365	2.21	2.12
361	2.65	2.66	376	2.35	2.31
380	2.86	2.93	387	2.45	2.43
382	2.90	2.90	401	2.60	2.59

TABLE II (continued).

<i>Series 9.</i> $c = 32.5$ mols.			<i>Series 12.</i> $c = 23.0$ mols.		
$1 - x_1 = 0.03$ to 0.05 .			$1 - x_1 = 0.01$ to 0.02 .		
$x_2 = 0.33$ to 0.34 .			$x_2 = 0.52$.		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
290	0.23 ?	0.74	290	$\bar{1}.3 ?$	0.4
295	0.70	0.80	325	0.23 ?	0.96
311	0.86 ?	1.14	336	0.70 ?	1.20
325	1.20	1.32	330	0.48 ?	1.07
352	1.59	1.79	380	1.52	1.82
376	1.93	2.13	351	1.15	1.42
380	2.00	2.19	380	1.54	1.82
391	2.16	2.30	401	1.78	2.05
			358	1.43	1.54
<i>Series 10.</i> $c = 30.7$ mols.			<i>Series 13.</i> $c = 16.0$ mols.		
$1 - x_1 = 0.04$ to 0.02 .			$1 - x_1 = 0.006$ to 0.013 .		
$x_2 = 0.35$.			$x_2 = 0.66$.		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
328	0.42 ?	1.30	390	1.23 ?	1.70
340	0.86 ?	1.54	338	0.26 ?	1.01
346	1.32	1.60	353	1.02	1.24
338	1.32	1.48	357	1.34	1.42
370	1.80	2.00	385	1.61	1.64
346	1.49	1.60	390	1.84	1.90
378	1.97	2.08			
395	2.22	2.28			
<i>Series 11.</i> $c = 25.6$ mols.			<i>Series 14.</i> $c = 9.7$ mols.		
$1 - x_1 = 0.02$ to 0.03 .			$1 - x_1 = 0.003$ to 0.008 .		
$x_2 = 0.48$.			$x_2 = 0.80$.		
$t^\circ \text{C.}$	Log p (mm. Hg)		$t^\circ \text{C.}$	Log p (mm. Hg)	
	Obs.	Calc.		Obs.	Calc.
336	0.64 ?	1.30	290	$\bar{1}.58$	$\bar{1}.90$
350	0.95 ?	1.46	316	0.00	0.38
360	1.23 ?	1.65	350	0.64	0.88
373	1.53	1.82	377	1.04	1.32
395	1.81	2.05	392	1.28	1.48
345	1.16	1.42	399	1.46	1.58
321	1.07	1.01			
340	1.32	1.36			

Natrolite (fig. 3) also crystallizes in space-group C_{2v}^3 , and in the face-centred aspect has a unit cell formula $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80} \cdot (8+8)\text{H}_2\text{O}$, with the water in two sets of eightfold positions. But there is an extremely close approximation of the related space-group C_{2v}^{19} ; if the space-group were truly C_{2v}^{19} , the water would all be in one set of 16

equivalent positions. Hence it is not surprising that no difference in volatility could be detected between the two groups of water molecules. However, the behaviour is by no means simple. As X-ray work showed, dehydration results in a small degree of lattice shrinkage; as the condensation area, a , is already small in fully hydrated natrolite, a small shrinkage produces a relatively large decrease in a , and consequently the shrinkage factor $\log \{1 + \phi(x)\}$ is very considerable. If the decrease in the channel radius, r , is assumed linear to x , the constant $(r_0 - r_1)/(r_0 - \rho)$ is found by a process of trial and error to be approximately 0.90. Then $C_0 = 8.63$, while E is not even approximately linear to x ; assuming the above values of the other constants, E may be calculated for each series of experimental data. These 'observed' values of E (table III) are plotted,

TABLE III. 'Observed' values of E for natrolite derived directly from the vapour pressure data, for various degrees of dehydration, and 'calculated' values taken from a smoothed curve.

Dehydration fraction, x .			$E \times 10^{-4}$, cal.		Dehydration fraction, x .			$E \times 10^{-4}$, cal.		
			Obs.	Calc.			Obs.	Calc.		
0.044	...	1.70	}	1.70	0.125	...	2.34	}	2.34	
0.044	...	1.75			0.125	...	2.37			
0.048	...	2.22		1.78	0.14	...	2.37	}	2.35	
0.050	...	1.99		1.83	0.14	...	2.39			
0.052	...	1.78	}	1.86	0.155	...	2.38	}	2.36	
0.052	...	1.86			0.155	...	2.44			
0.058	...	1.96	}	1.96	0.21	...	2.44	}	2.36	
0.058	...	2.05			0.21	...	2.49			
0.062	...	2.07		2.02	0.50	...	2.36		2.36	
0.069	...	2.24		2.09	0.88	...	2.43	}	2.36	
0.071	...	2.27		2.11	0.88	...	2.25			
0.11	...	2.32	}	2.31	0.95	...	2.23	}	2.36	
0.11	...	2.35			0.95	...	2.47			
0.11	...	2.40								
0.11	...	2.43								

a smooth curve laid through them, and 'calculated' values of E taken from this. From these constants, calculated values of $\log p$ are then obtained. The agreement between the experimental and calculated values of $\log p$ is relatively poor (the difference averages 0.4) for water contents above 15 mols. per unit cell ($x < 0.07$), owing mainly to the unavoidable inaccuracies in the determination of x , which increase the smaller x is. For water contents below 15 mols. per unit cell, $\log p_{\text{obs.}} \sim \log p_{\text{calc.}}$ averages 0.22. Space does not permit of a detailed comparison of the observed and calculated values, either graphically or in tabular form.

The above vapour pressure constants for natrolite cannot be regarded as final. The assumption of a linear form for $\phi(x)$ is probably incorrect, and it is certain that, with more extensive data, much better agreement and more satisfactory vapour pressure constants could be obtained.

The mean heat of hydration of natrolite, estimated from the vapour

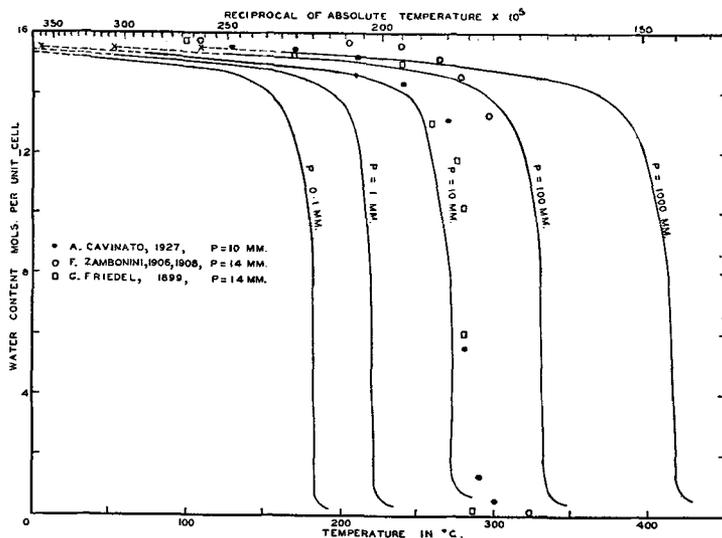


FIG. 3. Calculated isobaric dehydration curves for natrolite. An example of pseudo-univariant behaviour due to lattice shrinkage.

pressure data, is 23,300 cals., while a figure of 22,800 cals. was found calorimetrically.

The apparent step in the isobaric and isothermal dehydration curves of natrolite is seen to be due, in all probability, to lattice shrinkage. Careful search was made for any evidence of discontinuity in the vapour pressure surface, but none could be found; the former conclusion that natrolite and metanatrolite are not distinct phases is confirmed, and natrolite must be really monoclinic. The intersection of the isohydric curves noted and discussed in part III of this series now proves to be spurious, and due to unavoidable inaccuracies in the isohydric curves for small degrees of hydration.

Analcime, unit cell formula near $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{96}\cdot 16\text{H}_2\text{O}$, is probably really orthorhombic or perhaps tetragonal, but is very markedly

pseudo-cubic, and all its water is likely to have nearly the same volatility, though strictly it should be divided into two or four groups. It is therefore a simple case, since the dehydration fraction x is simply calculable. Two good isobaric dehydration curves have been obtained by G. Friedel.¹ Plotting $\log x/(1-x)$ against $1/T$, the graphs of these two series are a parallel pair of practically straight lines, indicating that E and a probably do not vary with x . The difference between the two series is probably within the experimental error, and may be attributed to small errors in the determination of the water content; it may, however, be real, and due to a small difference in composition. That E and a do not vary with x is confirmed by Friedel's finding that near 250°C ., where the water loss at 12 mm. Hg. is about 4%, a change in the water vapour pressure of 2 mm. causes a change of 0.25% in the water content; that is, for $\delta \log p = 0.06$ to 0.08 , $\delta \log x/(1-x) = 0.06$, or

$$\delta \log p / \delta \log x/(1-x) = -1 \text{ (approx.)},$$

as it should if E and a do not vary with x . The constants $E = 1.80 \times 10^4$ cal., $C = 7.25$, give a good representation of the data.

Chabazite, with a unit cell formula $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$, crystallizes in space-group D_{3d}^5 , or rather in a related group of lower symmetry, but with a very close approximation to the rhombohedral group. According to J. Wyart,² the water occupies two sets of equivalent positions with different environments, but the structure proposed is not conclusively proved, and the vapour pressure data shows no indication of any such division. D. Chilton and E. Rabinowitsch³ regard the existence of two distinct bands in the absorption spectrum of chabazite-iodine as evidence of the existence of two absorption regions of different potential, without continuity between them, that is, of the division of the volatile component between two sets of lattice positions. But chabazite-iodine is known to be pleochroic,⁴ and it is probable that the two absorption bands observed are oppositely polarized, pleochroic bands. F. Simon⁵ found a discontinuity

¹ G. Friedel, Bull. Soc. Franç. Min., 1896, vol. 19, p. 363.

² J. Wyart, Recherches sur les zéolites. Thèse Fac. Sci. Univ. Paris, 1933 [M.A. 5-354]; Bull. Soc. Franç. Min., 1933, vol. 56, p. 103.

³ D. Chilton and E. Rabinowitsch, Zeits. Physikal. Chem., Abt. B, 1932, vol. 19, p. 107 [M.A. 5-356].

⁴ F. Grandjean, Bull. Soc. Franç. Min., 1910, vol. 33, p. 5.

⁵ F. Simon, Zeits. Physikal. Chem., 1928, vol. 132, p. 456 [M.A. 5-81]; also Zeits. Elektrochem., 1928, vol. 34, p. 528 [M.A. 5-82].

in the absorption of argon and of nitrogen by dehydrated chabazite (the latter not confirmed by E. Rabinowitsch, see below), and J. Aharoni and F. Simon¹ found discontinuities in the curve of magnetic susceptibility against oxygen absorbed by dehydrated chabazite. These results tend to indicate that vapours absorbed by chabazite occupy more than one set of lattice positions, but they cannot be regarded as very definite evidence, and it appears best to accept the clear indication of the dehydration data that the lattice positions in chabazite for absorbed gases and vapours are probably all structurally of one set.

G. Friedel's isobaric dehydration data² are best represented by taking $E = 1.52(1 + 0.53x) \times 10^4$ cals., $C_0 = 9.61$. With these constants, the isobar computed for a vapour pressure of 10.5 mm. Hg agrees reasonably with Friedel's measurements, the average difference between the observed and calculated values of $\log x/(1-x)$ being 0.06. For the two isolated observations, at p 244 mm., x 0.042, and p 710 mm., x 0.066, temperatures of 71° C. and 101° C. respectively are computed, against 71° C. and 98° C. observed.

Shortly after these calculations had been completed, A. Tiselius and S. Brohult³ published a further study of the vapour pressure of an analysed specimen of chabazite. They found Q_x to vary with x , from 1.51×10^4 cals. near full hydration, through a maximum of 1.85×10^4 cals. at $x = 0.3$, to about 1.75×10^4 cals. at $x = 0.5$. The agreement with the values calculated from Friedel's data is gratifying, but the maximum in Q_x appeared so remarkable that the author undertook a re-computation of the data; a good representation (average difference between $\log p_{\text{obs.}}$ and $\log p_{\text{calc.}}$, 0.07) is given by taking $C_0 = 8.71$ and $E = 1.51(1 + 0.258x) \times 10^4$ cals. No evidence of a maximum in E (and Q_x) could be found, but it is probable that the linear relation of E and x is not maintained beyond about $x = 0.6$. The new constants do not cover the data of Friedel so well as the old; the discrepancy is probably to be assigned to a difference in the composition of the specimens, since E. Rabinowitsch⁴ has shown that the vapour pressure of chabazite varies very appreciably

¹ J. Aharoni and F. Simon, Zeits. Physikal. Chem., Abt. B, 1929, vol. 4, p. 175 [M.A. 5-81].

² G. Friedel, Bull. Soc. Franç. Min., 1899, vol. 22, p. 5.

³ A. Tiselius and S. Brohult, Zeits. Physikal. Chem., Abt. A, 1934, vol. 168, p. 248 [M.A. 6-126].

⁴ E. Rabinowitsch, Zeits. Physikal. Chem., Abt. B, 1932, vol. 16, p. 50 [M.A. 5-355].

with the composition of the anhydrous mineral. The same cause may account for a failure to correlate the data of G. Tammann¹ and of E. Löwenstein² with those of Friedel or of Tiselius and Brohult.

Many workers have studied the absorption by dehydrated chabazite of vapours other than water, but many of the studies were only qualitative, and for others the data were not sufficiently extensive for computation. The only adequate data appear to be those of E. Rabinowitsch (loc. cit.) for chabazite-nitrogen and chabazite-hydrogen. For *chabazite-nitrogen*, the constants $E = 2.60(1 + 1.46x) \times 10^3$ cal., $C_0 = 6.11$ give good agreement, the average difference between $\log p_{\text{calc.}}$ and $\log p$ as measured from Rabinowitsch's graphs being 0.20. Each nitrogen molecule was assumed to occupy two lattice spaces.

For *chabazite-hydrogen*, good agreement is obtained by taking $E = 100 + 2550x$ cal., $C_0 = 5.16$, each hydrogen molecule occupying one lattice space. The average agreement is 0.27. Since E is so small, of the same order as the average kinetic energy of the molecules at the temperatures of experiment, the approximations dependent on $N\epsilon/RT$ being large will not hold, and these constants can only be regarded as a rough approximation. Nevertheless, the remarkably low value of E for chabazite-hydrogen near complete saturation, and its marked increase as the hydrogen is removed, are reasonably well established.

The vapour pressure data for *heulandite* and for *stilbite* proved impossible of interpretation, the former because the water is divided into at least three, possibly six sets, and only isobaric data are available, the latter because the true saturation water content of stilbite and the possible grouping of the water remain quite unknown.

Very few 'zeolitic' compounds other than the zeolites themselves have been examined in sufficient detail to deduce the vapour pressure constants. The system *palladium-hydrogen* has been the subject of numerous studies, and it has proved possible to explain the behaviour of this system fairly satisfactorily on the new theory, but the results will not be discussed here, as the treatment is more complex, owing to the dissociation of the hydrogen.

¹ G. Tammann, Zeits. Physikal. Chem., 1897, vol. 27, p. 325; Ann. Phys. Chem. (Wiedemann), 1897, vol. 63, p. 16.

² E. Löwenstein, Zeits. Anorg. Chem., 1909, vol. 63, p. 69.

D. Balarew¹ has made some observations on the vapour pressure of *calcium sulphate hemihydrate*, $12\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$, which he interprets as indicating a truly univariant equilibrium in a substance which optical and X-ray data show² is definitely zeolitic in nature. His data are not very accurate, but it is easily shown that they are reasonably reproduced by taking $E = 2.15 \times 10^4$ cal., and $C = 12.13 - 2 \log(1 - 0.94x)$. These constants are necessarily very approximate as the data are so few.

A series of very valuable data has been obtained by W. Lange, working with the benzene sulphonates of potassium, rubidium, and caesium.³ Unfortunately, much of the data consists of isothermal curves only, which are inadequate for the deduction of vapour pressure constants, and X-ray work is lacking. But experimental data consisting of both isothermal and isobaric curves were obtained for *potassium benzene sulphonate* with H_2S , N_2O , CO_2 , NH_3 , CH_3Cl , and argon. From these results, the following constants were calculated, and reproduce the experimental figures very well: N_2O , $E = 8.75 \times 10^3$ cals., $C = 8.48$; CO_2 , $E = 7.18 \times 10^3$ cals., $C = 7.30$; H_2S , $E = 8.33 \times 10^3$ cals.,⁴ $C = 7.19$; CH_3Cl , $E_0 = 1.19 \times 10^4$ cals., $C_0 = 9.60$, while $\{1 + f(x)\}$ is almost but not quite linear, approaching $(1 + 0.15x)$. All these four gases occupy one lattice position each, so that the saturated compounds have formulae analogous to that of the zeolitic hydrate $-4(\text{C}_6\text{H}_5\text{SO}_3\text{K}) \cdot \text{G}$, where G represents one molecule of the gas. For ammonia, the data proved barely adequate to compute constants, but $E = 8.93 \times 10^3$ cals., $C = 6.65$ gave a fairly good reproduction of the experimental data for compositions up to $4(\text{C}_6\text{H}_5\text{SO}_3\text{K}) \cdot \text{NH}_3$; the data are insufficient to give any indication whether the ammonia

¹ D. Balarew, *Zeits. Anorg. Chem.*, 1926, vol. 156, p. 238; *ibid.*, 1927, vol. 163, p. 137; *Kolloid-Zeits.*, 1929, vol. 48, p. 63.

² G. Linck and H. Jung, *Zeits. Anorg. Chem.*, 1924, vol. 137, p. 407; H. Jung, *ibid.*, 1925, vol. 142, p. 73; W. Feitknecht, *Helv. Chim. Acta*, 1931, vol. 14, p. 85; E. Onorato, *Periodico Min. (Roma)*, 1932, vol. 3, p. 73; P. Gallitelli, *ibid.*, 1933, vol. 4, p. 132; W. A. Caspari, *Nature*, 1934, vol. 133, p. 648. The objections of P. Gaubert (*Bull. Soc. Franç. Min.*, 1934, vol. 57, p. 252) cannot be accepted as valid [*M.A.* 6-58].

³ W. Lange and G. Lewin, *Ber. Deut. Chem. Gesell.*, 1930, vol. 63B, pp. 2156, 2954; W. Lange and G. Krueger, *Zeits. Anorg. Chem.*, 1933, vol. 216, p. 49; W. Lange, *ibid.*, 1934, vol. 219, p. 305.

⁴ The isothermal data for H_2S for -60.6°C . are not in agreement with the isotherm for 0°C . and the isobar for 760 mm., the observed pressures being much too high; they have therefore been rejected. Calorimetric measurements gave for H_2S , $Q_x = 9.94 \times 10^3$ cals., or $E = 9.9 \times 10^3$ cals.

absorbed in excess of this composition occupies a second set of lattice positions, or whether there is a polymorphic change.

Lange's data with argon are particularly interesting, proving the existence of the definite 'zeolitic' compound $4(\text{C}_6\text{H}_5\text{SO}_3\text{K})\cdot\text{Ar}$, with a low heat of formation. With $E = 400$ cal., $C = 3.6$, the experimental data are represented, but an impossible value of the condensation area a is found. It is true that the constants are only approximate, since $N\epsilon/RT$ is not large, E being so small, but it does not seem probable that correction for this would resolve the discrepancy. This is the only serious discrepancy so far encountered, and it is not clear how far it arises from the deficiencies of the equation, and how far from inadequacy of the data. It is also possible that E and a may vary with x , which might make a considerable difference, though it has not been possible to prove any such variation.

The dimensions of the water-bearing channels in the zeolites.

The constants $C (= 5.22 + \log \sqrt{E/aD\chi})$ and E have now been derived for several zeolites and related compounds, and in most cases the crystal structure is sufficiently known to fix the value of D , the spacing of the water molecules along the channels. Hence, by assuming $\chi = 1$, a maximum value of the 'condensation area', a , can be calculated; and as $a = \pi(r - \rho)^2$, the difference, $r - \rho$, between the effective radii of the molecules of the volatile component and of the channels can be obtained. Assuming a value for the molecular diameter of water, the diameters of the channels are found (table V). In the case of chabazite, there are also data for hydrogen and nitrogen, and the lattice shrinkage is negligible. Hence, accepting the channel diameter, the effective molecular diameters of nitrogen and hydrogen are found, and agree well with the commonly accepted values. The agreement is, perhaps, somewhat fortuitous, as an appreciable change could be made in E and C without greatly altering the average agreement between $\log p_{\text{obs.}}$ and $\log p_{\text{calc.}}$

For Lange's potassium benzene sulphonate compounds, X-ray data to fix D are lacking; but assuming $D = 10 \text{ \AA.}$, which cannot be far out, and $r = 2.14 \text{ \AA.}$ (a value selected to give optimum agreement), satisfactory values of the molecular radii are found for all the gases studied (except argon).

The generally reasonable values of the channel and molecular radii

found for all the zeolitic compounds studied furnishes further evidence in favour of the vapour pressure equation here proposed.

TABLE IV. Observed and accepted values for the radii of the water-bearing channels in several zeolitic compounds, and for the molecular radii of several gases.

Non-volatile component.	Volatile component.	Spacing, D , of the volatile component.		Channel radius, r .	Molecular radius, ρ , of the volatile component.	
		$r - \rho$.	(obs.)		Observed.	Accepted.
Edingtonite	Water	6.53 Å.	0.070 Å.	1.52 Å.	—	1.45 Å. †
Mesolite	Water	6.53	0.028	1.48	—	1.45 †
Natrolite	Water	6.60	0.049*	1.50	—	1.45 †
		6.60	0.005 †	1.46	—	1.45 †
Analcime	Water	5.89	0.26	1.71	—	1.45 †
Chabazite	Water	7.47	0.014 §	1.46 ¶	—	1.45 †
			0.04	1.49 ¶	—	1.45 †
Chabazite	Nitrogen	7.47	0.59	1.49**	0.90 Å.	1.02 † †
Chabazite	Hydrogen	7.47	0.69 † †	1.49**	0.80	0.94 † †
CaSO ₄	Water §§	6.3 ?	0.001 ?*	1.45	—	1.45 †
		6.3 ?	0.0006 ? †	1.45	—	1.45 †
C ₆ H ₅ SO ₃ K	N ₂ O	10**	0.04	2.14**	2.10	2.03 † †
C ₆ H ₅ SO ₃ K	CO ₂	10**	0.15	2.14**	1.99	1.99 † †
C ₆ H ₅ SO ₃ K	CH ₃ Cl	10**	0.012	2.14**	2.13	2.0–2.1
C ₆ H ₅ SO ₃ K	NH ₃	10**	0.33 † †	2.14**	1.81	1.80 † †
C ₆ H ₅ SO ₃ K	H ₂ S	10**	0.17	2.14**	1.97	2.04 † †

* At full hydration.

† Completely dehydrated.

‡ L. Pauling, Zeits. Krist., 1930, vol. 72, p. 485.

§ From Friedel's data.

|| From Tiselius and Brohult's data.

¶ J. Wyart (loc. cit.) found 1.35 Å. approximately from X-ray data; O. Schmidt (loc. cit.), from a consideration of the largest molecules absorbed by dehydrated chabazite, found 1.75 Å. approximately.

** Assumed.

† † Approximately.

‡ ‡ Chem. Soc., Annual Reports, 1931, p. 303.

§ § Hemihydrate.

The condition of the water in the zeolites.

The question, whether the water in zeolites occupies definite lattice positions or no, has been the subject of some controversy. At one extreme, it has been supposed that the water occupies definite, fixed lattice positions, while, at the other extreme, the water is supposed merely to fill in the empty spaces in the structure, packing irregularly into them, and taking no real part in the crystal structure.

The latter view would imply that the water or other volatile component present at saturation need not always be an integral number of molecules per unit cell. Evidence in this direction has been advanced by E. Rabinowitsch (*loc. cit.*); chabazite absorbed 300 c.c. water vapour, 350 c.c. H_2 , 270 c.c. NH_3 , 175 c.c. N_2 , 170 c.c. CO_2 , and over 400 c.c. He per gram, all calculated to normal temperature and pressure. The calculated volume of gas absorbed per gram chabazite if there are 12 lattice positions per unit cell is 335 ± 10 c.c. Now all the above figures are obtained by extrapolation, and for NH_3 and He the extrapolation was very considerable and the result correspondingly open to doubt; moreover J. Sameshima¹ found that the ammonia absorbed by dehydrated chabazite is molecularly equivalent to the water removed. The figures for H_2 and H_2O are clearly within the experimental error of the calculated 335 c.c., while N_2 and CO_2 evidently occupy two lattice positions per molecule.

There is very little other data available as to saturation values, but it may probably be assumed that the values obtained by O. Weigel and E. Steinhoff² for ethyl and methyl alcohols at atmospheric pressure and temperatures near their boiling points are not far from saturation values. These figures, 110 c.c. C_2H_5OH and 165 c.c. CH_3OH per gram anhydrous chabazite, agree well with the conclusion that in thomsonite one molecule of ethyl alcohol replaces three, and one of methyl alcohol two molecules of water, in accordance with their molecular dimensions.

A quantity of other experimental data has been held to support the view that the water (or other volatile component) in zeolites does not occupy definite lattice positions, but in large measure it does not lead unequivocally to this conclusion. Thus E. Rabinowitsch (*loc. cit.*) regarded a failure to catalyse the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ by dehydrated chabazite as evidence against the theory of definite lattice positions, but although this catalysis failed, O. Weigel and E. Bezner³ and T. Baba⁴ have shown that chabazite catalyses the reaction $CS_2 + 3H_2O \rightleftharpoons 2H_2S + H_2CO_3$, and W. Lange and G. Lewin (*loc. cit.*) have shown that potassium benzene sulphonate catalyses the reaction $C_2H_4 + H_2S \rightleftharpoons C_2H_5SH$.

¹ J. Sameshima, *Bull. Chem. Soc. Japan*, 1929, vol. 4, p. 96 [M.A. 5-79].

² O. Weigel and E. Steinhoff, *Zeits. Krist.*, 1925, vol. 61, p. 125 [M.A. 2-528].

³ O. Weigel and E. Bezner, *Sitzungsber. Gesell. Naturwiss. Marburg*, 1927, vol. 62, p. 57 [M.A. 5-78].

⁴ T. Baba, *Bull. Chem. Soc. Japan*, 1930, vol. 5, p. 190 [M.A. 5-79].

F. Simon¹ has found a value of approximately 3 cal. per gram for the specific heat of hydrogen absorbed on chabazite at -240 to -230° C., but the data do not appear adequate to justify his conclusion that the molecules do not occupy definite lattice positions.

The problem has been attacked by X-ray methods, but here again the results are not quite conclusive. Some workers² have supposed that because no very marked differences were observed between the X-ray photographs of zeolites before and after dehydration, the water cannot occupy definite lattice positions. Others³ have observed changes, in approximate agreement with those expected on theoretical grounds for fixed water molecules. But in no instance has any attempt been made to calculate the changes to be expected, firstly on the assumption of fixed water molecules, and secondly on the assumption that the water molecules are irregularly distributed over all the space not occupied by other atoms. Much the most effective evidence on the question is to be found in the crystal structures proposed by W. H. Taylor for analcime, thomsonite, edingtonite, natrolite, and scolecite; in these structures there are several spaces into which water molecules could enter, but the saturation water content does not by any means correspond to the complete filling of them all, and it is difficult to see, on the extreme 'sponge' theory, why they should not all be filled.

Further support for the idea of definite lattice positions for the water is provided by the calorimetric measurements of the heats of hydration of natrolite, edingtonite, and mesolite, and by the data of A. Tiselius (see below) on the rate of diffusion of water in heulandite. The large values found for the heats of hydration (about 20,000 cal. per gram-mol. H_2O) show that the water is very unlikely to be held by mere adsorption, but must be more firmly attached, and it is difficult to imagine water irregularly filling all the lattice cavities as held by other than weak van der Waals forces. For heulandite, Tiselius found that the diffusion coefficient showed a marked variation with temperature, indicative of an activation energy of the order of 5000 cal. per gram-mol. H_2O at some stage of the diffusion

¹ F. Simon, *Zeits. Elektrochem.*, 1928, vol. 34, p. 528 [M.A. 5-82].

² W. Hartwig, *Zeits. Krist.*, 1931, vol. 78, p. 173 [M.A. 5-29] (analcime); B. Lengyel, *Zeits. Physik*, 1932, vol. 77, p. 133 [M.A. 5-355] (chabazite).

³ W. H. Taylor, *Zeits. Krist.*, 1930, vol. 74, p. 1 [M.A. 4-369]; W. H. Taylor, C. A. Meek, and W. W. Jackson, *ibid.*, 1933, vol. 84, p. 373 [M.A. 5-354]; W. H. Taylor and R. Jackson, *ibid.*, 1933, vol. 86, p. 53 [M.A. 5-354]; J. Wyart, *loc. cit.*

process. This is most readily understood if it is assumed that a definite integral number of equilibrium lattice positions per unit cell are available for water molecules, and that the molecules spend most of their time in these positions. But since their activation energy of migration is relatively small, they will change their positions with some frequency, and will show that mobility which is so characteristic of zeolitic hydrates.

*The rate of diffusion of water in a zeolite crystal.*¹

When a dehydrated crystal of a zeolite is allowed to reabsorb water, the rehydration process consists of two parts, the absorption of water by the surface layer, and its diffusion into the body of the crystal. The former process is governed by the equation

$$\begin{aligned} (dx/dt)_{\text{surface}} &= [axNp \cdot e^{-N\eta/RT}] / \sqrt{2\pi MRT} - \\ &\quad - [2(1-x)\sqrt{2N(\epsilon-\eta)} \cdot e^{-N\epsilon/RT}] / \pi\chi D\sqrt{M} \\ &= 2(1-x)\sqrt{2N(\epsilon-\eta)} \cdot e^{-N\epsilon/RT} \cdot (p-p_x) / \pi\chi Dp_x\sqrt{M}, \end{aligned}$$

where p_x is the equilibrium vapour pressure corresponding to the momentary dehydration fraction x .

If the diffusion through the body of the crystal is slower than the absorption of water (which will not always be the case), this surface layer will be in a practically steady state, with a water content but little below that corresponding to equilibrium with the external pressure of water vapour. If this condition is not fulfilled, the rehydration phenomena will be much more complex, but, if it is fulfilled, the process can be treated on the assumption that the water content in the surface layer remains steady at approximately the equilibrium value.

The second process, the diffusion of water into the body of the crystal, is more difficult to treat. Using the same symbols as before, we may first consider a layer within the crystal, normal to the water channels, of area 1 sq. cm. and thickness D . Then the number of molecules in this layer having sufficient energy μ to migrate² will be $\nu(1-x)e^{-N\mu/RT}$, but only a fraction $(x+\delta x)$ of them will be opposite vacant positions in the next layer (which has a dehydration fraction $(x+\delta x)$) and so be able to migrate, and only half of these will

¹ It need hardly be mentioned that the results here obtained for the diffusion of water in a zeolitic hydrate will apply to the diffusion of the volatile component in any zeolitic compound.

² The activation energy, μ , for migration within the lattice is likely to be considerably less than the activation energy, ϵ , for escape from the lattice.

be moving in the right direction at any instant. The activation energy will vary with x , and may be written $\mu = \mu_0\{1 + \psi(x)\}$. Assuming as before that the motion of the molecules approximates to simple harmonic motion, and introducing a factor χ to correct for this assumption, their rate of migration from the first to the second layer will be :

$$v(1-x)(x+\delta x)\sqrt{2N\mu_0}\{1+\psi(x+\frac{1}{2}\delta x)\}.e^{-N\mu_0(1+\psi(x))/RT}/\pi\chi D\sqrt{M},$$

provided that $N\mu_0/RT$ is fairly large.

To find the rate of change of the water content of a layer of the zeolite, of dehydration fraction x , the rate of influx of molecules from and efflux to the neighbouring layers must be found and summed algebraically. Assuming the neighbouring layers have dehydration fraction $x + \delta_1x$ and $x + \delta_2x$, then :

$$\begin{aligned} \partial x/\partial t = & [(1-x)(x+\delta_1x)\sqrt{2N\mu_0}\{1+\psi(x+\frac{1}{2}\delta_1x)\}.e^{-N\mu_0(1+\psi(x))/RT}/\pi\chi D\sqrt{M} \\ & + [(1-x)(x+\delta_2x)\sqrt{2N\mu_0}\{1+\psi(x+\frac{1}{2}\delta_2x)\}.e^{-N\mu_0(1+\psi(x))/RT}/\pi\chi D\sqrt{M} \\ & - [x(1-x-\delta_1x)\sqrt{2N\mu_0}\{1+\psi(x+\frac{1}{2}\delta_1x)\} \times \\ & \quad e^{-N\mu_0(1+\psi(x+\delta_1x))/RT}/\pi\chi D\sqrt{M} \\ & - [x(1-x-\delta_2x)\sqrt{2N\mu_0}\{1+\psi(x+\frac{1}{2}\delta_2x)\} \times \\ & \quad e^{-N\mu_0(1+\psi(x+\delta_2x))/RT}/\pi\chi D\sqrt{M}. \end{aligned}$$

The dehydration fractions $x + \delta_1x$ and $x + \delta_2x$ can be expressed in terms of the position of the layer in the crystal. If z be the co-ordinate measuring the distance of the layers from the surface, let the first considered layer, of dehydration fraction x , have position z , while $x + \delta_1x$ corresponds to a position $z + D$ and $x + \delta_2x$ to a position $z - D$. Then

$$\delta_1x = D\partial x/\partial z + \frac{1}{2}D^2\partial^2x/\partial z^2 + \dots,$$

$$\text{and} \quad \delta_2x = -D\partial x/\partial z + \frac{1}{2}D^2\partial^2x/\partial z^2 - \dots$$

With this substitution, and neglecting higher powers of D (since D is a very small quantity), the above expression reduces to :

$$\partial x/\partial t = K\partial^2x/\partial z^2 + (\partial K/\partial x)(\partial x/\partial z)^2 = \partial(K\partial x/\partial z)/\partial z,$$

$$\text{where } K = [D\sqrt{2N\mu_0}\{1+\psi(x)\}/\pi\chi\sqrt{M}] \times e^{-N\mu_0(1+\psi(x))/RT}. [1+x(1-x)\psi'(x)N\mu_0/RT].$$

If μ does not vary with x , $\psi(x)$ and $\psi'(x) = 0$, and the equation reduces to

$$\partial x/\partial t = K_0\partial^2x/\partial z^2,$$

$$\text{where} \quad K_0 = [D\sqrt{2N\mu_0}/\pi\chi\sqrt{M}].e^{-N\mu_0/RT}.$$

The above equations were derived for one particular direction in the crystal only; they may be formally generalized for all directions by writing $\mu = \mu_{00}\{1 + \zeta(x, \theta)\}$ and $D = D_0\{1 + \xi(\theta)\}$, where θ defines direction in the crystal; D_0 and μ_{00} refer to the direction $\theta = 0$, which may conveniently be parallel to the water channels, in which direction μ_0 is likely to be a minimum. The generalized diffusion constant then becomes:

$$K = [D_0\{1 + \xi(\theta)\}\sqrt{2N\mu_{00}\{1 + \zeta(x, \theta)\}}/\pi\chi\sqrt{M}] \cdot e^{-N\mu_{00}\{1 + \zeta(x, \theta)\}/RT} \times [1 + x(1-x)N\mu_{00}\partial\zeta(x, \theta)/RT\partial x].$$

Even this equation is only applicable provided all the water molecules are structurally of the same kind, which is often not the case. A general treatment is not at present practicable, as the transfer of water molecules between positions belonging to different sets has to be considered. But two important special cases can be dealt with. If the activation energy differences for dehydration and rehydration, E , are approximately the same for the several sets of water molecules, then to a first approximation, the water can all be considered as belonging to one set for the calculation of the diffusion constant. And if the values of E differ markedly for the several sets, then the less volatile sets must be almost completely filled before any water can remain stably in the more volatile sets. Then if all the sets of positions are very nearly filled, except the most volatile one, the water in the less volatile positions can be neglected for the purpose of calculating the diffusion constant; but if some of the less volatile positions are vacant, it is probably permissible to calculate the diffusion as if all the empty positions belonged to one set. For example, in the case of heulandite, where there are $24\text{H}_2\text{O}$ per unit cell, occupying three (or possibly six) sets of lattice positions, if it can be assumed that the values of E for the several sets are markedly different, then a crystal having $20\text{H}_2\text{O}$ present per unit cell will have two sets of positions almost completely filled, and one half-filled; here the two full sets may probably be neglected, and the value of x , 0.5, for the most volatile set taken for diffusion purposes. But a crystal having only $14\text{H}_2\text{O}$ present per unit cell will have one set almost completely empty, one filled, and one containing $6\text{H}_2\text{O}$; here the figure to be taken for diffusion purposes is not $x = 0.25$, the figure for the partially filled set of positions, but $x' = (8 + 2)/(8 + 8) = 0.625$, derived by including the (almost) empty set of positions.

The above treatment of the case where there are lattice positions

of several kinds is only tentative; it is based on the assumption that where E is large, μ is likely to be large also, so that migration from a less volatile, completely filled set of positions to a more volatile, incompletely filled set is likely to be negligible; but migration from a less volatile, partially filled set of positions to a more volatile, empty set will probably occur, though the migrating molecules are not likely to remain long in their new positions.

The only quantitative work yet done on the diffusion of water in a zeolite is that of A. Tiselius,¹ on heulandite. The relative volatility of the three or six sets into which the water of heulandite must be divided is not known, so that the application of the new equation to this data is necessarily tentative; but if it is assumed that the water is divided into three groups of markedly different volatility, treatment on the lines suggested above becomes possible.

Unfortunately, the variation of the diffusion coefficient with temperature does not give the activation energy of migration directly, since

$$\partial \log_{10} K / \partial (1/T) = - [N\mu_0 \{1 + \psi(x)\} (\log_{10} e) / R] \times \\ [1 - x(1-x)\psi'(x) / \{1 + x(1-x)\psi'(x)N\mu_0 / RT\}].$$

This makes the derivation of the several constants more difficult, but the last factor of the above expression is fortunately usually nearly unity, so that the method of successive approximations is available.

The data for diffusion normal to the face $t(201)$ are the most complete and lead unambiguously to a value for the activation energy $(N\mu)_{201} = 4.79(1 + 0.13x) \times 10^3$ cal. per gram-mol. of water, and for the constant $\log D/\chi = 8.55$, or $D/\chi = 3.6 \text{ \AA.}$ approx., a quite reasonable value. The X-ray data is not sufficient to fix D with certainty, but it must be a simple sub-multiple of 6.7 \AA. The values of the diffusion constant K_{201} for several temperatures and water contents, calculated from these constants, are given in table V, and compared with Tiselius's measurements.

For diffusion normal to the face $c(001)$, the data are much less complete; the most probable value for the activation energy is approximately $(N\mu)_{001} = 7.3(1 + 0.08x) \times 10^3$ cal. per gram-mol. water, which leads to the rather high figure for $\log D/\chi$ of 7.28 , or $D/\chi = 19 \text{ \AA.}$ Values of K_{001} for several temperatures, and of the ratio

¹ A. Tiselius, *Nature*, 1934, vol. 133, p. 212; *Zeits. Physikal. Chem., Abt. A*, 1934, vol. 169, p. 425 [M.A. 6-126].

K_{201}/K_{001} for several water contents are compared with Tiselius' measurements¹ in table V.

TABLE V. Diffusion data for heulandite. Calculated values from the new equation, compared with the experimental values of A. Tiselius. Water percentages calculated on the anhydrous mineral.

H ₂ O %	19	18	17	16	15	14
x	0.10	0.255	0.41	0.56	0.71	0.865
$K_{201} \times 10^7$ (20° C.)	}	Obs.	3.3, 3.5	4.0, 4.1	4.0, 4.0	3.5, 3.6	2.6, 2.7	2.1,
			4.1	4.2	4.2		2.0	
		Calc.	4.47	4.27	3.80	3.32	2.70	2.14
Temp. °C.	20.0	33.8	46.1	60.0	75.0	
$K_{201} \times 10^7$, for $x = 0.71$	}	Obs.	2.7	4.1	4.8	7.6	11.1	
			2.70	4.10	5.60	7.90	11.0	
		Calc.						
H ₂ O %	18.5	17.5	16.5	15.5	14.5	13.5
x	0.18	0.33	0.48	0.64	0.79	0.94
K_{201} (46° C.)	}	Obs.	1.7	2.0	1.8	1.8	1.8	1.7
\bar{K}_{201} (20° C.)		Calc.	1.93	1.93	1.94	1.98	2.03	2.09
Temp. °C.	20.0	33.0	46.1	60.0	75.0	
$K_{001} \times 10^7$, for $x = 0.71$	}	Obs.	0.23	0.45	0.66	1.45	2.8	
			0.25	0.48	0.74	1.23	2.05	
		Calc.						
H ₂ O %	13.21	14.43	15.50	16.25	17.36	
x	0.96	0.80	0.64	0.52	0.35	
K_{201}/K_{001} (20° C.)	}	Obs.	13.0	11.6	12.2	10.2	11.6	
		Calc.	11.0	11.1	11.6	11.8	11.9	

The above constants only relate to the most volatile group of water molecules in heulandite, that is, to material containing more than 13.11 % of water, calculated on the anhydrous material. Tiselius found that at lower water contents the diffusion constant fell sharply, decreasing by a factor of about 10 between 13 and 11 % H₂O (anhydrous basis). This is doubtless due to a sharp increase in the activation energy, for there is no reason to expect any marked change in D , so that the experimental data tend to justify the above assumption as to the relative volatility and mobility of the groups of water molecules.

Thus the available data, while not adequate fully to test the proposed equation, are in good agreement with it. A better test of the equation would be obtained with data for zeolites having only one set of water lattice positions, such as chabazite, natrolite, or analcime,

¹ Tiselius found the diffusion to be faster normal to $t(201)$ and $s(\bar{2}01)$ than normal to $c(001)$; according to P. Gaubert (Bull. Soc. Franç. Min., 1929, vol. 52, p. 162 [M.A. 4-377]) the opposite is the case.

but the experimental difficulties would be much greater than with heulandite.

Summary.

A simple kinetic treatment leads to an equation for the dissociation pressure of a 'zeolitic' compound of a volatile and a non-volatile component:

$$\log_e p = \log_e 4\sqrt{NR(\epsilon - \eta)/aND\chi}\sqrt{\pi} + \frac{1}{2}\log_e T - \log_e x/(1-x) - N(\epsilon - \eta)/RT,$$

where p is the equilibrium pressure in dynes per sq. cm., N the Avogadro number, R the gas constant in ergs, T the absolute temperature, ϵ and η the activation energies in ergs per molecule of volatile component for dissociation and re-combination respectively, x the fraction of unoccupied lattice positions for the volatile component (assumed all of the same kind), D the distance between lattice positions for the volatile component, measured along the channels along which the latter migrates, a the difference between the effective cross-sections of a molecule of the volatile component and of a channel, and χ a constant not greatly different from unity.

The more usual case where the volatile component occupies several different sets of lattice positions is also considered, also the variation in $\epsilon - \eta$ and in a with x . It is emphasized that the equation can only be regarded as a first approximation, but it represents the available data reasonably well.

The approximate 'condensation areas', a , found for several 'zeolitic' systems are discussed and shown to be in reasonable agreement with what is known of the size of the water-bearing channels in zeolites and of the dimensions of the volatile molecules concerned.

The condition of the water in the zeolites is discussed in the light of the evidence now available.

Kinetic treatment of the rate of diffusion of the volatile component, on the assumption that it only occupies one set of lattice positions, leads to an expression for the diffusion constant:

$$K = [D_0 \{1 + \xi(\theta)\} \sqrt{2N\mu_{00} \{1 + \xi(x, \theta)\}} / \pi\chi\sqrt{M}] \times e^{-N\mu_{00}\{1 + \xi(x, \theta)\}/RT} \cdot [1 + x(1-x)N\mu_{00}\partial\xi(x, \theta)/RT\partial x],$$

where θ defines direction in the crystal, D_0 the distance between lattice positions for the volatile component in the direction $\theta = 0$, and $D_0 \{1 + \xi(\theta)\}$ the distance in the direction θ , μ_{00} the activation

energy of migration in ergs per molecule of the volatile component for $x = 0$ and $\theta = 0$, and $\mu_{00}\{1 + \zeta(x, \theta)\}$ the energy for x, θ ; M is the molecular weight of the volatile component. The other symbols have the meaning defined above.

The case where the volatile component occupies more than one set of lattice positions is considered, and it is shown that on certain assumptions the experimental data of A. Tiselius are reasonably well reproduced.
