746. *Zeolite Studies. Part V.*[1] *Dehydration Behaviour of* Na–*P Zeolites and Some Ion-exchanged Derivatives*

By A. M. Taylor and Rustum Roy

This Paper reports the experimental determination of a variety of types of reaction that occur during the dehydration of zeolites, which do not conform to the classical view of zeolitic dehydration. Another remarkable finding is the absence of continuous solubility or "zeolitic exchange" of cations when the zeolite contains two different cations; remarkably rapid and complex exsolution and solution phenomena are found.

The dehydration behaviour of synthetic cubic and tetragonal Na–*P* zeolites and some mono- and di-cationic ion-exchanged derivatives has been studied by static, stepwise dehydration in conjunction with *X*-ray powder diffractometry at elevated temperatures, both under controlled conditions of water-vapour pressure. First-order collapse, or stepwise dehydration-type reactions are common, and in most cases two, but sometimes three such reactions occur during the dehydration of a *P* zeolite. These reactions result in the formation of new contracted zeolite structures having less water than the original. The reaction-point temperatures are strongly dependent on the water-vapour pressure and on solid solution of other exchangeable cations. Dehydration of the zeolite K–P_t provides an excellent example of a second-order type collapse reaction characterised by a rapid, but continuous contraction of the anionic framework with accompanying water loss, over a short temperature range, and resulting in the formation of a "collapsed" structure without an intervening two-phase region. The cubic $\leftrightarrow$ tetragonal Na–*P* transition is considered to be a rare example of a true enantiotropic phase transition in a zeolite. Conversions of *P* zeolites into low-symmetry *H* zeolites are explained as monotropic reactions towards the more stable phase under the selected conditions.

Low-temperature exsolution phenomena were studied in the dehydration of Na,K–P_t and Na,Ca–P_t zeolites. On heating, the expanded zeolite structure transforms into two new structures each having a different exchangeable cation content. This takes place by a first-order reaction to a completely collapsed structure and by a second-order reaction to a partially collapsed structure. The reaction is reversible on cooling and rehydration. Heating the Na,K–P_t zeolites to above 500° results in the formation of a continuous solid solution again in the nearly anhydrous zeolite structure. Exsolution occurs on cooling and rehydration, until the final single-phase expanded structure stable at room temperature is formed. The phenomenon of low-temperature exsolution and resultant perthitic intergrowths may have been overlooked in natural polycationic zeolites.

The nomenclature used has been explained in Part IV. The "*P* zeolite group" is that group of zeolites having an aluminosilicate framework linked in a manner identical to that of the cubic Na–*P* zeolite. The *P* group includes tetragonal Na–*P*, which is related to the cubic form by a reversible, displacive-type transition, and also any derivatives of these zeolites formed by aqueous ion-exchange treatment at low temperatures (<100°). The subscripts, *e.g.*, P_c and P_t refer to the symmetry of the phase, *i.e.*, cubic *P*, tetragonal *P* zeolites.

The different structural forms of a zeolite encountered on dehydration have been designated *S*0, *S*1, *S*2, etc., *S* signifying structure; *S*0 is always the structure stable at room temperature, and *S*1, *S*2, etc., are successive structures stable as the temperature is raised. The phase relationships existing in the *P* zeolite group at room temperature, and also the synthesis and ion-exchange preparation of the phases studied here, have been described previously.[1] Under study is a quinary system Na_2O–K_2O–CaO–*X*–H_2O (where

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[1] Part IV, A. M. Taylor and R. Roy, *Amer. Mineralogist*, 1964, **49**, 656.

$X = SiO_2 : Al_2O_3$) with temperature and water-vapour pressure as the variables. The effect of temperature and P_{H_2O} on the phase relationships in this system is here presented for *P* zeolites having a $SiO_2 : Al_2O_3$ ratio in the narrow range 3·49 to 3·63 (abbreviated to 349 to 363, see Part IV [1]). A variation of *X* from 2 to 6 is considered likely and the effect of this component variable on the phase relations is unpredictable.

The first systematic study of the effect of temperature on zeolites that undergo structural collapse reactions was that by Hey [2] and Hey and Bannister.[3] An isohydric method was used whereby the vapour pressure of the zeolite, having constant composition, was measured with a manometer for a series of temperatures. Phase boundaries determined by Hey for the reactions natrolite $\longrightarrow$ metanatrolite, scolecite $\longrightarrow$ metascolecite, and thomsonite $\longrightarrow$ metathomsonite, are reproduced in Figure 10. A study of the dehydration and stability of zeolites and hydrous oxides was undertaken by Milligan and Weiser [4] using thermogravimetry and *X*-ray powder photography at high temperatures. They found that discontinuities in the dehydration curves of some zeolites were related to structural transformations. In general, in most of the previous work, very little explicit attention has been paid to the importance of controlling the partial pressure of water in equilibrium and structural studies of this type.

An indication of the interesting dehydration behaviours of the *P* group of zeolites was first afforded by Barrer *et al.*,[5] who reported a discontinuity in the equilibrium dehydration curve of the cubic Na–*P* zeolite. Later work by Barrer and Denny [6] on the synthesis and dehydration properties of some Ca-zeolites presented new data for Ca-harmotome (Ca–P_t). A d.t.a. thermogram of Ca-harmotome shows three well-defined endothermic peaks at *ca.* 100, 190, and 370°, and is compared with a similar thermogram of a Ca-harmotome prepared by ion-exchange from Na-harmotome (Na–P_t); continuous-heating thermogravimetric curves are also given. A dehydration curve obtained by continuous heating is complimentary to a d.t.a. chart of the same material when the heating rates are equal. These dynamic methods of study are not particularly suitable for use with *P* zeolites as the slow rates of the collapse reactions result in non-equilibrium conditions throughout the dehydration; data obtained by these methods are of limited usefulness.

EXPERIMENTAL

The weight-loss studies were made using a Mauer magnetic recording analytical balance, which consists of a type "BB" Ainsworth chain-type balance, coupled through an appropriate amplifier measuring a restoring force signal, to a Minneapolis–Honeywell "Electronik" strip chart which records the weight changes. 400—800 mg. of the hydrated zeolite powder was contained in a double-decker platinum crucible, and suspended by a fine platinum wire from the left-hand balance pan. An adjustable, Kanthal-wound furnace could be raised and fixed so that the crucible was situated in the hot-spot of the furnace. Above the furnace, the wire suspending the crucible was protected from convection currents by an enclosing silica-glass tube of 1½ inches diameter. Two chromel–alumel thermocouples, insulated from each other by ceramic tubing, were fixed in the furnace so that the ends were within ¼ inch of the platinum crucible. One thermocouple was attached to the temperature controller for the furnace, and the other was used to measure directly the furnace temperature by means of a potentiometer. Two West model temperature controllers of different ranges were used, one for temperatures up to 400°, and the other for up to 1000°. The partial pressure of water in the furnace atmosphere was controlled by having a slowly circulating air column. Air was bubbled through a Fisher–Milligan gas washer filled with a saturated solution of $CaCl_2$, and fed into the base of the furnace. At a normal room temperature of 24°, saturated $CaCl_2$ solution has a water-vapour pressure of 7·0 mm. Hg. A chart scale of either 50 or 100 mg. for a full scale deflection of 10 inches was used, and weight changes were read to 0·1 mg. The chart speed was 4 inches/hr.

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[2] M. H. Hey, *Mineralog. Mag.*, 1931, **22**, 422; 1932*a*, **23**, 243; 1932*b*, **23**, 243; 1933, **23**, 421; 1934, **23**, 483; 1936, **24**, 257.

[3] M. H. Hey and F. A. Bannister, *Mineralog. Mag.*, 1933, **23**, 305; 1934, **23**, 556.

[4] W. O. Milligan and H. B. Weiser, *J. Phys. Chem.*, 1937, **41**, 1029.

[5] R. M. Barrer, F. W. Bultitude, and I. S. Kerr, *J.*, 1959, 1521.

[6] R. M. Barrer and P. J. Denny, *J.*, 1961, 983.

The method consisted of stepwise heating in 10—30° increments, the temperature being kept constant at each step until a constant weight loss was attained. The time required to attain a constant weight loss for each temperature increment is shown graphically on some of the dehydration curves. In some cases, the rehydration curve obtained by cooling the sample in stages, is given. The numbers next to each point on a hydration curve represent the number of hours the sample was held at that constant temperature, unless otherwise stated.

In the *X*-ray investigation of the zeolite reactions at high temperatures, up to 800°, a Tem–Pres model HX-2A diffractometer furnace fitted to a Norelco diffractometer was used. The humidity of the furnace atmosphere was controlled as explained above. The sample holder was aligned by the recommended instruction procedures, and a number of strong diffraction peaks of the zeolite were scanned at $\frac{1}{2}$° or $\frac{1}{4}$°/min., in the range of 2θ from 10 to 60° at room temperature. As the *X*-ray pattern of each zeolite had previously been accurately recorded using an internal standard, correction factors were thus obtained for the peak positions recorded for that particular alignment of the sample in the diffractometer furnace. These room-temperature correction factors were used at high temperatures when *X*-ray charts were taken at the same scanning speed, *i.e.*, either $\frac{1}{2}$° or $\frac{1}{4}$°/min. Obviously the ideal procedure is to use an internal standard at high temperatures, but this has disadvantages for initial investigations such as this. Many problems were encountered in indexing unknown *X*-ray powder patterns taken at high temperatures, without having interferences from additional peaks due to an internal standard. A change in unit-cell dimensions of 0·05% [*i.e.*, about 0·005 Å or 0·02° shift in 2θ in (310) or (103) peak positions] may be significant within a 25° temperature range, hence fairly accurate percentage changes in cell dimensions can be calculated for a collapse reaction even though the experimental values may both be off in the same direction, by 0·02 Å or more.

At each temperature halt, *X*-ray charts were taken over the range of 2θ of 27—32° at $\frac{1}{4}$°/min. and for each structural form encountered, complete charts were obtained at $\frac{1}{2}$°/min. and 2°/min Chart scales used for each scanning speed were $\frac{1}{4}$°/min. 4 inches to 1° 2θ; $\frac{1}{2}$°/min., 2 inches to 1° 2θ; 2°/min., $\frac{1}{2}$ inches to 1° 2θ.

Some zeolites were investigated at a water-vapour pressure of 1 atm. A flask of boiling water adjacent to the diffractometer furnace produced steam which was fed into the furnace *via* a heated pipe. Transformation temperatures for a zeolite were often obtained by oscillating the diffractometer over certain strong diffraction peaks, usually (301), (103), while the sample was heated very slowly, *e.g.*, 1° per 5 min. The initial formation of a new zeolite phase has an immediate effect of reducing the intensity of the (301), (103) peaks of the previously stable phase, and additional peaks due to the new phase will appear within the same scanning region. By this method, the temperature of the first appearance of a new phase could often be determined to within ±2°, and the values were reproducible. To determine unequivocally an equilibrium point, it is necessary to study the reaction proceeding in both the forward and reverse directions; this was attempted only in a few cases as the reverse reaction rates were usually fairly slow.

The *P* zeolites are readily prepared by reaction of solutions of NaOH, $NaAlO_2$, and Ludox (ammonia-stabilised colloidal SiO_2) at 100° for 1—4 days. Details of the synthesis, ion-exchange treatment, and characterisation by *X*-ray powder data of the samples reported here are in Part IV.[1]

RESULTS AND DISCUSSION

(A) *Dehydration of Monocationic Zeolities.*—Na–P_c (352). The dehydration behaviour of Na–P_c was found to be almost identical to that reported by Barrer *et al.*[5] for this phase. The dehydration curve has a marked step at 83° ± 4°; above and below the step the curve is continuous without irregularities (Figure 1). A constant weight loss could be attained within 30 min., except for the temperature increment spanning the reaction point for which several hours were required.

At room temperature, Na–P_c has a unit-cell edge of $a = 10{\cdot}03$ Å; heating to 75° causes the loss of 3 molecules of water, and a slight contraction of the cubic cell to 10·00 Å. *X*-Ray patterns of the collapsed * phase *S*1, taken between 85° and 300, are very similar

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* The terms " collapsed phase," " collapse reaction," etc., are used for want of any better terms to describe the phase with the smaller unit cell volume, and either a continuous or discontinuous reaction which leads to such a smaller volume cell.

to the *X*-ray pattern of the Na–P_t, *S*4 collapsed phase, which has a tetragonal unit cell with $a = 9{\cdot}58$ Å, $c = 9{\cdot}10$ Å at 360°. The weight-loss discontinuity at 83° may thus be considered to mark the simple dehydration reaction of the expanded structure *S*0, with $a = 10{\cdot}0$ Å, to the collapsed structure *S*1, which probably has a tetragonal unit cell approximating $a = 9{\cdot}6$ Å, $c = 9{\cdot}1$ Å (volume decrease ~ 16%). The water loss recorded was 3 molecules below the step and 3 molecules at the step, of a total 14 water per unit cell in the room temperature, $P_{H_2O} = 7$ mm. Hg, state.

K^{ex}Na–P_c (352). This zeolite has a contracted pseudocubic unit cell ($a = 9{\cdot}83$ Å) at room temperature. The dehydration curve is continuous up to 500°, which indicates that no stepwise collapse reactions occur (Figure 1). On cooling, hydration is quite rapid, but quickly approaches zero when the temperature stops falling and becomes constant. *X*-Ray results were not obtained at high temperatures.

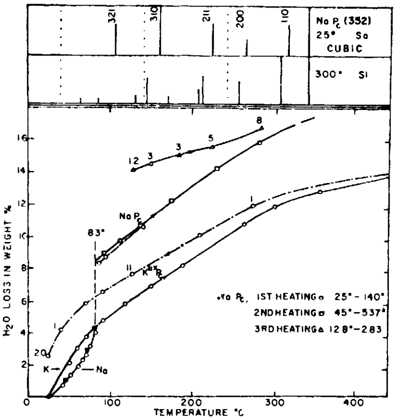

FIGURE 1. Dehydration and rehydration curves for zeolites Na–P_c (352) and K^{ex}Na–P_c. Upper: *X*-Ray powder patterns of Na–P_c,*S*O at 25°, and *S*1 at 300°

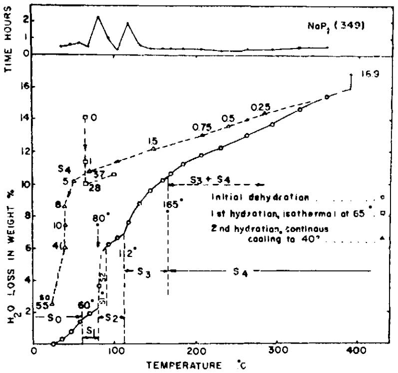

FIGURE 2. Dehydration and rehydration curves for zeolites Na–*P* (349), showing the temperature intervals over which the five structural forms *S*0, 1, 2, 3, 4 are found

Dehydration of Na–P_t (349) *and* (363). The tetragonal Na–*P* zeolite was studied in greatest detail because it constituted the starting material for all the (363) ion-exchanged forms. The weight-loss measurements were made on (349) material, but the *X*-ray data are for the (363) material, a larger batch of slightly different composition. The dehydration curve (Figure 2) shows a large step beginning at 80°, a small step at 112°, and weak inflections at 60 and 165° (all ±5°). This indicated an unexpectedly complex dehydration behaviour. The dehydration was repeated on fresh material with identical results. The data indicated that at least two different collapsed structures existed, and also delineated their probable range of stability, information that proved very helpful in the subsequent *X*-ray investigation at elevated temperature.

After a comparison of the *X*-ray diffractometer charts for various temperature intervals we concluded that five distinct structural phases of zeolite Na–P_t exist, which were named conventionally *S*0, 1, 2, 3, 4 (Figure 3).

The temperature at which the tetragonal *S*0 $\longrightarrow$ cubic *S*1 phase change commences was determined at 60° ± 3°, in three experiments, and was found to be rapidly reversible at a few degrees below the transition point. The two structures *S*0, *S*1 have the same unit-cell volume (Table 1), hence the transition should take place without loss of water. This is confirmed by the dehydration curve, which has a change in slope, but no discontinuity, at the transition point. The ready reversibility of the transition indicates that it is the result of a small displacive movement of the anionic framework of the zeolite. This reaction must therefore be considered as a rare example of a true first-order displacive phase transition [7,8] in a zeolite.

TABLE 1

Estimated values of unit-cell dimensions for different structural forms of Na–*P* (363), that coexist at specific reaction points

*S*0 ⟶ *S*1		*S*0	*S*1	*S*2 ⟶ *S*3		*S*2	*S*3
60°	*a* (Å)	10·08	10·00	120°	*a* (Å)	10·03	9·88
	c (Å)	9·84	—		*c* (Å)	9·27	9·03
	v (Å^3)	1000	1000		*v* (Å^3)	933	881
		$\Delta v = 0$				$\Delta v = 52$ Å^3 (5·6%)	
*S*1 ⟶ *S*2		*S*1	*S*2	*S*3 ⟶ *S*4		*S*3	*S*4
85°	*a* (Å)	9·99	10·02	165°	*a* (Å)	9·84	9·61
	c (Å)	—	9·31		*c* (Å)	8·97	9·02
	v (Å^3)	997	935		*v* (Å^3)	869	833
		$\Delta v = 62$ Å^3 (6·2%)				$\Delta v = 36$ Å^3 (4·1%)	

The *S*1 ⟶ *S*2 reaction beginning at 85° is the first of three collapse reactions. A contraction of 7% occurs along one axis of the cubic *S*1 structure, resulting in the formation of the tetragonal *S*2 structure, having a unit cell with $a > c$. Only a slight expansion (0·3%) occurs perpendicular to the *c*-direction. The water loss accompanying the reaction is estimated at 2·5 H_2O molecules per unit cell.

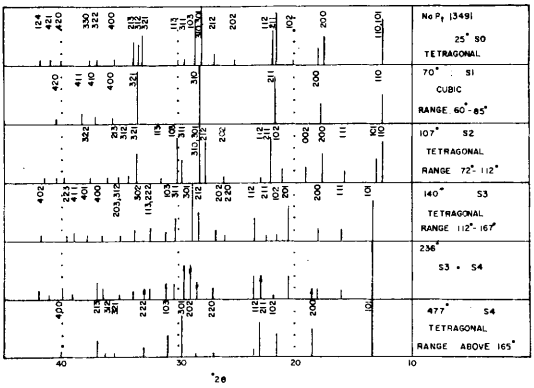

FIGURE 3. *X*-Ray powder patterns of zeolite Na–P_t (349) taken at various temperatures, and illustrating the five structural forms encountered on dehydration

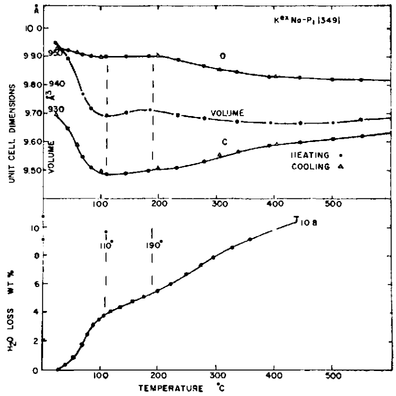

FIGURE 4. Lower: Dehydration curve for zeolite K^{ex}Na–P_t (349). Upper: Unit-cell dimensions and volume of same zeolite as a function of temperature

The second collapse reaction, *S*2 ⟶ *S*3, results in a substantial reduction in both the *a*- and *c*-dimensions of the tetragonal unit cell (*viz.*, *a*, 1·5%; *c*, 2·6%). Although the volume reduction of 52 Å^3 at this step is not greatly different from that of the preceding reaction, the water loss is considerably lower, probably less than 1 water molecule per unit cell. There is therefore, considerably less free volume in this phase.

The final collapse reaction *S*3 ⟶ *S*4, differs from the preceding two in that the structural movement occurs predominantly at right angles to the *c*-direction of the tetragonal unit cell (2·3% contraction). No values of the c_4-dimension near the reaction point are available on the heating cycle. However, if the value of *c* for *S*4 estimated for 165° on cooling is a good approximation (9·02 Å, this may be too low), then the reaction results

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[7] M. J. Buerger, " Phase Transformations in Solids," John Wiley, New York, 1951.
[8] R. Roy, *Abst., Bull. Amer. Ceram. Soc.*, 1962, **41**, 225.

in an expansion of 0·6% in the *c*-direction. The reaction is extremely sluggish, which seems a likely result of the unique structural movements that must occur. Although the *S*4 phase first appears near 170°, the reacting *S*3 phase will persist for many hours well above this temperature, hence the dehydration curve drawn in this region does not represent equilibrium weight loss conditions.

A sample (349) heated to 360° on the thermogravimetric balance and then placed in a saturator at room temperature for 14 hours, was found to have a net weight loss of 2·5%, and to be completely converted into the expanded *S*0 phase.

$K^{ex}Na$–P_t (349) *and* (363). The dehydration curve for $K^{ex}Na$–*P* (349) differs notably from that of other ion-exchanged P_t zeolites, in that it is continuous throughout its complete length (Figure 4). Although no first-order discontinuities are present, the curve does show certain distinctive features. The steepest section is between room temperature and 100°, and in this region a constant weight loss could be attained within 20 to 30 min. Above 100°, this time decreased to 10 min. or less and remained at this low value up to 365°. On cooling to room temperature, the zeolite returned almost to its original hydration state within one day.

A preliminary *X*-ray investigation of the zeolite revealed that a tetragonal structure, similar to the one present at room temperature, existed at temperatures up to 700°, but at 800° it was partly destroyed. A detailed investigation was undertaken and the unit-cell dimensions were determined at various temperature intervals, up to 600°. From the variation of cell dimensions with temperature (Figure 4), it is apparent that the zeolite undergoes certain unique structural movements during dehydration. These movements are continuous rather than discontinuous, as the same structural phase is present at every temperature during the entire dehydration.

From room temperature to 110°, the tetragonal unit cell undergoes a substantial contraction in the *c*-direction (9·69 to 9·49 Å), and a less contraction perpendicular to this direction (9·93 to 9·90 Å). The contraction in the *c*-direction ceases at 110°. Further heating causes an expansion which is at first rapid, but gradually decreases above 400°, and at 600° the *c*-dimension (9·63 Å) is nearing the original expanded value.

The thermal behaviour is somewhat different perpendicular to the *c*-direction. From 110 to 190°, the *a*-dimension changes very little from 9·90 Å, but at 190° a gradual contraction begins and continues up to at least 600°, reaching 9·82 Å. Thus, when the zeolite is heated above 190°, the tetragonal unit cell expands in the direction parallel to the *c*-axis and contracts perpendicular to this direction. The latter type of thermal behaviour should not be too uncommon with the fibrous and lamellar zeolites. It is known to occur with some anhydrous tectosilicates, *e.g.*, high quartz,[9] α-eucryptite.[10]

The zeolite was heated to a maximum temperature of 600°, and then cooled in stages to room temperature. The unit-cell dimensions calculated for specific temperature halts on cooling, all lie within 0·01% of the values determined for equivalent temperatures on heating, thus indicating near perfect structural reversibility.

$Ca^{ex}Na$–P_t (349, 363). The dehydration curve was determined up to 600° (Figure 5). It has two marked steps at 120 and 290°, which correspond to the reactions $S0 \longrightarrow S1$ and $S1 \longrightarrow S2$, respectively.

The first collapse reaction of the $Ca^{ex}Na$–P_t zeolite, at 120°, may be represented by the following equation:

$$\text{Ca–}P_t,S0,3{\cdot}9H_2O \longrightarrow \text{Ca–}P_t,S1,2{\cdot}9H_2O + H_2O$$

The collapse reaction occurs when the water content of the *S*0 phase has been reduced from 4·6 to 3·9 water molecules per Ca^{2+} ion. The cell dimensions of the *S*0, *S*1 phases at temperatures close to the collapse point are given in Table 2. The *S*0 and *S*1 phases both have tetragonal unit cells, the former with $c > a$, the latter with $a > c$. The $S0 \longrightarrow S1$ reaction

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[9] H. le Chatelier, *Compt. rend.*, 1889, **108**, 1046; see Eitel, " Physical Chemistry of the Silicates," Chicago Univ. Press, 1954, 605.

[10] F. H. Gillery and E. A. Bush, *J. Amer. Ceram. Soc.*, 1959, **42**, 175.

results in a unit-cell contraction of 0·1% in the *a*,*b*-directions and 11·0% in the *c*-direction, assuming that these directions do not change in the process. The volume reduction per unit cell is 111 Å^3 (11·3%) or 39·0 Å^3 per water molecule lost. The large contraction of the *c*-dimension is slightly greater than that determined by Fang[11] for the natrolite ⟶ metanatrolite collapse reaction (10·8% contraction in "*a*"). The volume reduction per molecule of water lost is the same for both zeolites.

TABLE 2

Unit-cell dimensions of the zeolites Ca^{ex}Na–P_t,*S*0,*S*1 and Na–P_t,*S*3 at specific temperatures

Unit-cell dimensions	Ca,*S*0 23°	Ca,*S*0 110°	Ca,*S*1 157°	Na,*S*3 127°
a (Å)	9·88	$9{\cdot}8_2$	$9{\cdot}8_1$	$9{\cdot}8_7$
c (Å)	10·30	$10{\cdot}2_1$	$9{\cdot}0_9$	$9{\cdot}0_2$
v (Å^3)	1005	985	874	879

The Ca,*S*1 phase has unit-cell dimensions nearly equal to that of the Na,*S*3 phase (Table 2) and the *X*-ray powder patterns of the two phases are directly comparable. The stability range of the *S*1 phase extends from 120 to 285° and corresponds to the loss of one molecule of water per Ca^{2+} ion. The final collapse begins at 285°, when the water content has been reduced to slightly less than two molecules of water per Ca^{2+} or *ca.* 5 water per unit cell.

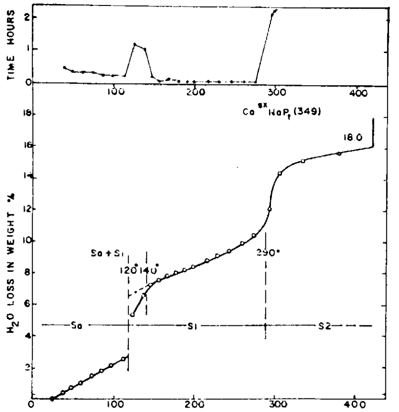

FIGURE 5. Dehydration curve for zeolite Ca^{ex}Na–P_t (349)

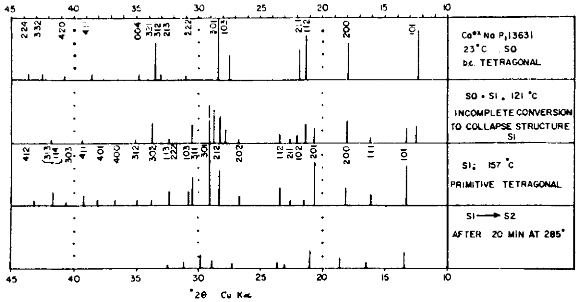

FIGURE 6. *X*-Ray powder patterns of zeolite Ca^{ex}Na–*P* (363) taken at various temperatures

The *X*-ray pattern of *S*2 is comparable with that of *S*1 (Figure 6) except for the large reduction in intensity and a peak displacement of 0·5—1·0° of 2θ, towards higher angles. As no two-phase region is encountered in the reaction zone, the observations indicate that *S*1 structure gradually breaks to a highly disordered, short-range-order phase, over a narrow temperature interval. Heating above 285° causes further compaction and disorder of the *S*2 phase until at 350°, the zeolite is quite amorphous to *X*-rays and nearly anhydrous.

The Ca-exchanged zeolite and other bivalent ion forms are considerably less stable to dehydration than are the univalent ion forms, which is understandable for a zeolite that readily undergoes large lattice contractions. It seems that the water molecules act as a stablising "filler" for the expanded zeolite structure at room temperature. As the water molecules are driven off by heat, the structure collapses to a more compact arrangement, and it is as expected that six permanent stabilising entities per unit cell, *e.g.*, Na$^+$, K$^+$

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[11] J. Fang, Ph.D. Thesis, Pennsylvania State Univ., 1961.

ions, would be more effective than three, more polarising, bivalent ions, in preventing a complete structural collapse to a compacted and disordered array of (Si,Al)O_4 tetrahedra.

The first-order reaction temperatures determined for all the monocationic *P* zeolites studied are summarised in Table 3.

TABLE 3

Temperatures at which first-order reactions begin for ion-exchanged forms of zeolite Na–P_t at P_{H_2O} = 7 mm. Hg

Li	42°, 132°	Ag	50°	Cd	150°
Na	85°, 120°, 165°	Mg	140°, 190°	Pb	60°, 95°
K	none	Ca	120°, 285°	Ni	149°, 220°
Rb	225°	Sr	85° (230°)	Cu	105°, 200°
Cs	135°	Ba	55°, 290°	Co	135° (200°)

(B) *Dehydration of Dicationic Zeolites.*—Na,K–P_t *System.* The dehydration properties of the Na–P_t and K–P_t zeolites have been fully investigated. The Na–P_t zeolite is an excellent example of a zeolite that undergoes a series of discontinuous structural changes on heating and dehydration. On the other hand, the K–P_t zeolite is unique in that the structure collapses in a continuous manner during dehydration, a process that was shown to be reversible on cooling. In view of these contrasting collapse phenomena, it was decided to investigate the dehydration behaviour of a *P* zeolite containing both Na and K as exchangeable cations. A study of the structural changes at high temperatures of Na,K–P_t zeolites having different cation compositions, has established a new collapse process that is potentially possible for all polycationic zeolites.

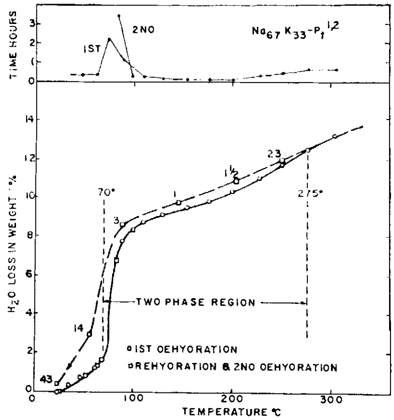


FIGURE 7. Dehydration and rehydration curves for zeolite $Na_{67}K_{33}$–$P_t^{1,2}$ (363)

Detailed *X*-ray data were obtained at high temperatures for seven different Na,K–P_t zeolites and the dehydration curve determined for one ($Na_{67}K_{33}$–$P_t^{1,2}$ see Figure 7). The X-ray data will be discussed in detail for only the latter zeolite as the remaining zeolites exhibited essentially the same behaviour.

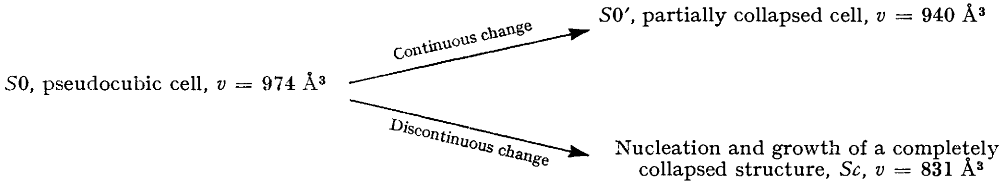
$Na_{67}K_{33}$–P_t (363). At room temperature this zeolite consists of a mixture of two phases, Na,K–P_t^1 and K,Na–P_t^2. On heating to 76°, two new phases formed in approximately equal amounts. Both appeared to have body-centered tetragonal unit cells, one being a collapsed cell. Gradual heating in stages caused the collapsed phase to increase in amount until at 302° it was the only phase present. On cooling, runs made at 248 and 204° showed the *S*0 phase to be re-forming, and at 204°, to be present in amount approaching that observed on heating. The sample was then allowed to cool to room temperature overnight. Next morning, the zeolite (at 23°) consisted of a single body-centered pseudo-cubic phase having an expanded unit cell.

The zeolite was reheated in stages to the point where the collapse reaction began.

The furnace temperature was set for 71°, and when it reached this temperature the diffractometer was set oscillating between 26 and 32° of 20 at 2° per min., in order to scan the (301), (103) peak positions. At zero time, two phases were present; these having a pseudocubic expanded cell and a collapsed cell *Sc* (ratio ~ 3 : 1). After 50 min., *Sc* had increased so that the two phases were present in about equal proportions. More important, however, the repeated pattern showed a continuous decrease in the *c*-dimension of the expanded phase, as the collapsed phase was forming. Thus an expanded structure, having a pseudocubic unit cell with $a = 9{\cdot}92$ Å, changed in a continuous manner and at constant temperature, to a structure having a tetragonal unit cell with $a = 9{\cdot}90$ Å, $c = 9{\cdot}60$ Å, while a new structure having a collapsed unit cell with $a = 9{\cdot}62$ Å, $c = 8{\cdot}94$ Å was forming. The reaction is represented in the scheme below. On cooling from 71 to 34° (15 min.), both of these phases disappeared and only a single phase having a pseudocubic expanded cell was present, hence the reaction is quite rapid.

The dehydration curve for this zeolite has a large step beginning at 70°, and between 70 and 100° about 45% of the total water is lost (Figure 7). After heating to 300°, the zeolite was cooled in stages to room temperature whereupon it returned almost to its original state of hydration.

$Na_{80}K_{20}$–$P_t^{1,2}$ (363). This zeolite consisted of a mixture of P_t^1 and P_t^2 structures at room temperature. Heating to 40° produced a single pseudocubic phase, which on cooling was reconverted into the original two tetragonal phases. The collapse reaction began at 77° and exhibited similar features to those described above. The extent of the two-phase regions determined for Na,K–P_t zeolites of other compositions can be seen in Figure 8 which represents an isobaric ($P_{H_2O} = 7$ mm. Hg) projection on the anhydrous base for the system. It is noteworthy that the tetragonal $\longleftrightarrow$ cubic transition point, which is at 60° for the Na–P_t zeolite, is gradually lowered by K-ion substitution to 34° ± 3° for $Na_{83}K_{17}$–P_t.



Discussion. The collapse reaction described above is clearly quite different from the reactions that occur on dehydration of monocationic zeolites. A typical collapse reaction for which there are two components (anhydrous zeolite *Z*, and H_2O) may be represented by the following equation:

$$Z^1,nH_2O \longrightarrow Z^2,mH_2O + (n-m)H_2O_v$$

When the three phases are in equilibrium at constant P_{H_2O}, there are no degrees of freedom remaining, hence the collapse point will be unique for any P_{H_2O}.

In the *X*-ray investigation of the zeolite $Na_{67}K_{33}$–P_t, it was found that two zeolite phases, of necessarily changing composition, were in equilibrium with water vapour of constant pressure, over the temperature range 70—275°, and the same two zeolite phases readily re-formed on cooling through this range (hence the two zeolite phases are at, or tend to approach, a certain equilibrium condition with one another, for any temperature within this range.) Thus there are three phases in equilibrium with each other and yet there remains one degree of freedom, *viz.*, temperature. For such a phenomenon to satisfy the Phase Rule, the number of components within the system must increase from two to three. The only three components possible are Na–*Z*, K–*Z*, and H_2O. The two zeolite phases *S*0, *Sc* are thus required to have different compositions, *i.e.*, different proportions of exchangeable cations.

The experimental results are easily reconciled with the above conclusion on considering the ready mobility of alkali cations within the zeolite, a state which is exemplified by the ion-exchange processes that occur at room temperature. A problem remaining is that of determining which of the *S*0, *Sc* phases is Na- or K-rich; obviously this can be determined only by indirect means. The clues presented by this one experiment are now to be considered.

At 71°, the phases *S*0, *Sc*, and K–P_t, Na–P_t, *S*4 have unit-cell dimensions as follows:

	*S*0	*K–*P_t	*Sc*	Na–P_t, *S*4
a (Å)	9·90	9·91	9·62	9·59
c (Å)	9·60	9·55	8·94	8·98
v (Å³)........................	940	937	831	826

It is reasonable to deduce from the above similarities in unit-cell dimensions (all phases have close to body-centered symmetry), that *S*0 is a K-rich and *Sc* a Na-rich phase. This conclusion is further substantiated by evidence derived from the study of collapse reactions of other Na,K–P_t zeolites.

The compositional changes of the zeolite phases are clearly shown in the anhydrous projection of the system (Figure 8). The unit-cell volume of the zeolite solid solutions are plotted on this diagram for a series of compositions at 304, 500°, and other temperatures. At 500°, where there is complete solid solution, the unit-cell volume of the anhydrous zeolite increases, with increase in K⁺ ion content, an effect opposite to that observed at 60° where there is complete solid solution between the hydrated and expanded Na,*S*1 and K,*S*0 phases.

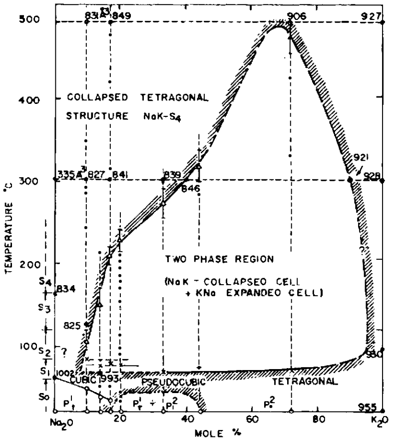


FIGURE 8. Isobaric (P_{H_2O} = 7 mm. Hg), anhydrous projection for the zeolite system Na–P_t, K–P_t (363)

The two-phase region extending from 70 to 500° is comparable to the closed solubility curves found to occur in certain liquid binary systems, *e.g.*, water and nicotine.[12] Attention must be drawn to the method of presentation of the data, *viz.*, the temperature–composition (*T–X*) diagrams drawn for both the Na,K–P_t zeolite system and the water–nicotine system are, in fact, projections down the *X* and *P* axis, respectively. The *T–X* diagram for the zeolite system is isobaric, but there is another compositional variable (water). On the other hand, water–nicotine phase relations were determined by the sealed-tube method, hence the vapour pressure is not constant.

The conclusive proof of the existance of the two-phase region in the Na,K–P_t zeolites is based on the exsolution phenomenon, which readily occurs over a range of temperature when the high-temperature collapsed phase is cooled below the upper solvus.

The configuration of the lower solvus on the Na-rich side requires some explanation.

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[12] Hudson, *Z. physikal. Chem.*, 1904, **43**, 113; see Findlay, "The Phase Rule," reprinted by Dover Publ., New York, 1951, 99.

On heating a zeolite to the collapse point, it was in all cases the *S*4 (Na-rich) structure that nucleated and grew. The expanded phase originally present changed in a continuous manner to a partially collapsed K-rich phase. This being the case, it is necessary for the lower solvus to have a positive slope towards the K end-member. The dicationic zeolites having 10 to 20% K^+ and Na–P_t have collapse-point temperatures between 75 and 85°. These temperatures are 8—18° higher than the 67° recorded for $Na_{67}K_{33}$–P_t. The temperature of collapse can readily be determined to within ±3° and the values recorded are reproducible. When a two-phase mixture is cooled towards the lower solvus, it is necessary to supercool the samples 25° or so below it, in order that a single phase will appear in any reasonable time. Thus the collapse-point temperatures could not be accurately confirmed by observing the reverse reaction taking place on cooling.

The possibility arises that the slightly higher collapse-point temperatures recorded for the Na-rich zeolites may be due to a metastable persistence of the expanded phase. In support of this explanation, one may consider the contrasting dehydration behaviours of the end-member zeolites. The K–P_t zeolite exhibits nearly ideal structural reversibility. The Na–P_t zeolite, however, undergoes a very sluggish collapse reaction above 165°, to form the *S*4 structure. When the *S*4 phase is cooled, the intermediate structures *S*2, *S*3 fail to appear within their temperature ranges. These results indicate that the probability of the existence of metastable phases is greatest in the Na-rich zeolites. A further possibility arises in that the Na–P_t, *S*2, *S*3 structures may, at all times, be metastable with respect to the completely collapsed *S*4 structure, and the effect of the presence of a very minor proportion of K^+ ions may be to destroy this metastability, thus preventing the formation of any *S*2, *S*3 phases in the dicationic system. Remember that Na–P_c,*S*0 collapses directly to a structure practically identical to *S*4 (Figure 1).

It is probable that this type of collapse process will be found to occur, to a greater or lesser extent, during the dehydration of certain natural zeolites since many of them are dicationic. Hoss and Roy [13] have investigated the dehydration behaviour of the polycationic zeolites phillipsite, harmotome, gismondine, gmelenite, and their ion-exchanged forms. In several cases they report the co-existence, over limited temperature ranges, of two zeolite phases having expanded and collapsed structures. Whether the phases differ in cation content is not known. The lower degree of symmetry (orthorhombic, monoclinic) of these natural zeolites presents many difficulties for any detailed interpretation of the structural changes that occur during dehydration.

Na,Ca–P_t *System.* The pseudocubic zeolite $Ca_{63}(2Na)_{37}$–P_t^3 was the only one investigated. The dehydration curve (not given) resembles that of Ca–P_t by having three zeolitic stages, steps beginning at 75 and 275°. On cooling from 365° the zeolite absorbed little water until the temperature dropped below 60°; after 11 days at room temperature the weight loss remained constant at 8·5%.

TABLE 4

Unit-cell dimensions of $Ca_{63}(2Na)_{37}$–P_t^3*S*0,*S*0′,*S*4′ and Ca–P_t,*S*0,Na–P_t,*S*4 at specific temperatures

	*S*0, 24°	*S*0′, 92°	Ca–Pt_t, *S*0, 90°
a (Å)	9·94	$9\cdot7_5$	9·83
c (Å)	10·16	$10\cdot2_8$	10·23
v (Å^3)	1004	977	988

	*S*4′, 92°	Na–P_t, *S*4, 91°	*S*4′, 300°	Na–P_t, *S*4, 300°
a (Å)	$9\cdot6_8$	9·59	$9\cdot5_3$	$9\cdot5_8$
c (Å)	$8\cdot9_5$	8·99	$9\cdot1_3$	$9\cdot0_7$
v (Å^3)	838	826	830	834

The *X*-ray investigation at high temperatures revealed the existence of an extensive two-phase region above 75°. Heating of the expanded *S*0 form to 75° causes a continuous decrease in the *a*-dimension. Immediately above 75°, the *a*-dimension decreases and the

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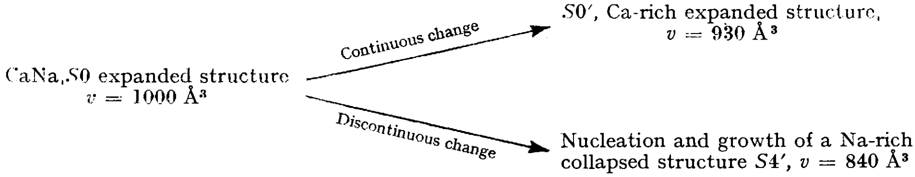
[13] H. Hoss and R. Roy, *Beitr. Mineral. u. Petrogr.*, 1960, **7**, 389.

c-dimension increases, both very rapidly, and a second phase appears having a collapsed unit cell. At 92°, the two phases (*S*0′ and *S*4′) were each present in major proportions. The unit-cell dimensions of these phases, as calculated from the (301), (103) peak positions, are in Table 4.

At 92° the cell dimensions of *S*0′ and *S*4′ closely approach the values for Ca–P_t,*S*0 and Na–P_t,*S*4, respectively, at the same temperature. *X*-Ray evidence indicates that a collapse process occurs similar to that discovered for the Na,K–P_t zeolites. The expanded structure CaNa,*S*0 splits into two contrasting fractions, a Na-rich collapsed structure *S*4′ and a Ca-rich expanded structure *S*0′, as shown in the annexed scheme.



On further heating, it was evident that at 128° the Ca,*S*0′ phase is replaced by a new one having an *X*-ray pattern identical to Ca–P_t,*S*1. At a slightly lower temperature (109°), three zeolite phases could be identified (*viz.*, Na,*S*4′, Ca,*S*0′, and Ca,*S*1′). These observations further confirm the supposition that the *S*4′ and *S*0′,*S*1′ structural forms differ in exchangeable cation content. The two-phase mixture formed by heating the zeolite to 200° readily converted into a single expanded phase, structurally analogous to the original *S*0 form, on cooling to room temperature. Reheating to higher temperatures revealed that the Ca,*S*1′ phase disappears at 275° ± 20° but the *S*4′ phase remained seemingly unaffected, except that further heating to 400° caused a 50% reduction in intensity. After cooling to room temperature the zeolite gave a low-intensity *X*-ray pattern of the *S*4′ phase.

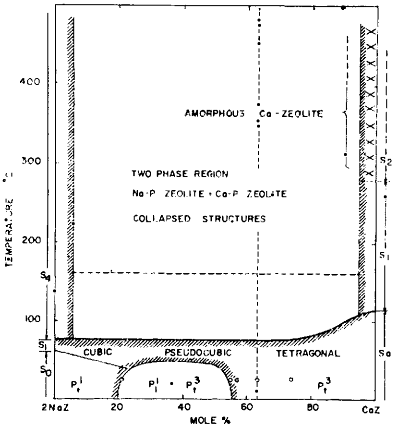


FIGURE 9. Suggested isobaric (P_{H_2O} = 7 mm. Hg), anhydrous projection for the zeolite system Na–P_t, Ca–P_t (363)

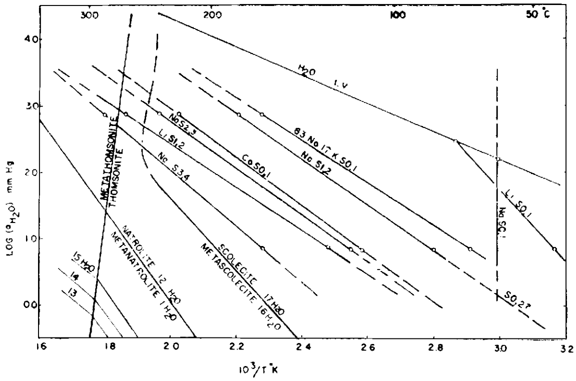


FIGURE 10. Zeolite reaction points as a function of temperature and water-vapour pressure

It seems that above 92° there is only very limited solid solution of the exchangeable cations in the $Ca_{63}(2Na)_{37}$–P_t^3 zeolite. The disappearance of the Ca,*S*1′ phase at about 275° appears to be due to its collapse to an amorphous state, analogous in behaviour to Ca–P_t,*S*1. Above 275°, the Na,*S*4′ phase coexists with this amorphous Ca-zeolite, hence return to the original expanded phase on cooling is not possible. The suggested isobaric, anhydrous projection for the Na,Ca–*P* system is in Figure 9.

K,Ca–P_t *System.* Weight-loss and X-ray data were obtained for the zeolite $(2K)_{49}Ca_{51}$–P_t^2 ($a = 9{\cdot}88$ Å, $v = 965$ Å^3). It remains cubic up to 120°, and a two-phase region is encountered between 120 and 225° which corresponds to the steepest part of the dehydration curve. Above 225° there exists a single phase having a very contracted tetragonal unit cell ($a = 9{\cdot}6_3$ Å, $c = 8{\cdot}4_4$ Å, $v = 873$ Å^3 at 328°). At 500° the zeolite becomes amorphous.

(C) *Effect of Water-vapour Pressure on Zeolite Transformations.*—The transformation temperature of a number of P zeolites were determined as a function of pressure up to a maximum of $P_{H_2O} = 1$ atm. ($\sim$735 mm. Hg.) by oscillating the diffractometer over the (301) and (103) peak positions and slowly heating while steam was blown into the heating chamber. The variation of transformation temperature with water vapour pressure was assumed to be linear when the data are plotted as log p against $1/T°$(K) as shown in Figure 10. The slopes of the phase boundaries for the collapse reactions correspond to heats of hydration in the range 15—17 kcal./mole H_2O. Results for the natrolite, scolecite, and thomsonite reactions [2] are shown for comparison.

Figure 10 shows that the Na–P zeolite that grows from solution at 100° is the body-centred cubic phase $S1$, and that on cooling to room temperature it transforms into the primitive tetragonal polymorph Na–P_t,$S0$.

The phase boundaries between the expanded and collapsed forms of the other P zeolites do not intersect the LV curve for water, so this precludes any direct synthesis of the collapsed phases. As a consequence of the Na–P tetragonal $\longleftrightarrow$ cubic transition at 60°, it appears that a complete series of body-centered, cubic, or tetragonal, expanded zeolite structures, containing Na,K,Ca,Ba-ions could theoretically be synthesised (or formed by ion-exchange) at 60° or higher and at the appropriate water-vapour pressure. When such a polycationic zeolite is cooled to room temperature in contact with liquid water, each crystallite, depending on its composition, may divide into two or more structural domains (P^1, P^2, P^3) containing a particular distribution of cations such that the crystallite as a whole attains the lowest possible free energy. This would be an exsolution process similar to that known to occur in the feldspars, but since the exchangeable cations of a zeolite are so weakly bonded, the process can occur at room temperature. No doubt the final product of such a process would be perthitic intergrowth of two or more zeolite structures in each crystallite. Fudali [14] has reported the exsolution of a Na-rich leucite, synthesised at 800° and 1000 bars, to an analcite + leucite "perthite" on cooling.

A single-phase polycationic P zeolite may exsolve more effectively at 100°, simply as a result of a drop of water-vapour pressure (*e.g.*, Morey bomb leaks). Two collapsed or partially collapsed structures, segregating the like cations, would form immediately the water-vapour pressure dropped below a certain critical value; cooling to room temperature may cause further changes in symmetry and composition of each phase

The existence of cationic immiscibility gaps between related zeolite structures (*e.g.*, in the analcime, natrolite, and phillipsite groups) is an important factor to consider in connection with the synthesis and natural formation of these zeolites. An investigation of these immiscibility gaps over a wide range of temperature and vapour pressure may increase our understanding of the great variety of zeolite species found in nature.

(D) *Zeolite Phase Changes; Conclusions.*—It is evident from the preceding X-ray investigations of zeolitic phase changes, and on the dependence of their reaction points on water-vapour pressure, that several types of phase change can be distinguished and their characteristic features delineated. Any classification of zeolitic phase changes should be based on the structural changes that take place; however, the latter in most cases can only be implied from the behaviours observed, as the structures of the P zeolites are not known in any detail. Some features of the structural classification of transformations established by Buerger [7] may usefully be applied to zeolite phase changes, which, it must be remembered, involve two or sometimes three components. Thus with zeolites, we are only rarely

[14] R. F. Fudali, Ph.D. Thesis, Pennsylvania State Univ., 1961.

dealing with "transitions" in the strict sense. This implies the existence of a one-component system. Most of the dehydrations involve dissociation reactions of the type $A \longrightarrow B + H_2O$, in which case the term "reaction" is to be preferred.

Considering the zeolite family as a whole, one consequence of the large range in size of the cations present and the necessary differences in co-ordination with oxygen anions is that the energies of the bonds within the structure may differ from one another by several orders of magnitude. The weakest bonds are those between the water dipoles and the exchangeable cations, and the oxygens of the anionic framework. Intermediate in value are the exchangeable cation–network oxygen ionic bonds, whereas the strongest are the (Si,Al)–O bonds, which are tetrahedrally directed and partly covalent.

The transformation of an expanded zeolite structure into a collapsed one, will result in a change of the secondary co-ordination of the Si^{4+} and Al^{3+} ions enclosed within the anionic framework. For nearly all collapse reactions this will occur *via* a purely displacive change, but in special cases a small proportion of the (Si,Al)–O bonds may be broken and re-formed. If the transformation is reconstructive to any degree with respect to (Si,Al)–O bonding, it would certainly be irreversible on cooling. The collapse to an amorphous state of many *P* zeolites containing bivalent cations (*e.g.*, Ca, Co, Ni, Cu) most probably results in a few reconstructive changes of the anionic framework; at least this would explain the irreversible nature of such transformations.

The effect of a collapse reaction on the co-ordination of exchangeable cations with the network oxygens and water molecules would be considerable; changes in primary co-ordination may occur owing to a sudden loss of water and to displacive shifts of the anionic framework. The maximum effect, however, is on the most weakly bonded entities, the water molecules. Even if no substantial loss of water occurs during a transformation, complete changes in lattice position and bonding of water molecules is likely to take place.

Zeolitic phase changes that take place over a range of temperatures may be due to certain ordering or disordering processes. The gradual formation of an amorphous zeolite on heating is due to increasing disorder of the $(Si,Al)\text{–}O_4$ tetrahedra such that there is no longer any representative unit cell for the zeolite. Examples of an ordering process causing a collapse reaction to take place over a temperature range are afforded by many dicationic *P* zeolites. The ordering process consists of segregation of like cations into two different collapsed or partially collapsed structures, which coexist in equilibrium over a range of temperatures.

The non-reversible transformation of the high-symmetry *P* zeolites to the orthorhombic or monoclinic *H* zeolites on hydrothermal treatment[1] must obviously involve reconstructive changes of the oxygen framework. As a specific example, the conversion of zeolite 2K,Ca–P_c into 2K,Ca–*H* is considered. The dry, hydrated zeolite 2K,Ca–P_c was sealed in a gold capsule and subjected to an outside pressure of 1000 bars and temperatures 245—325° for 10 days. The product 2K,Ca–*H* was also dry, hence it is reasonable to assume that the water contents of the two phases are equal. The unit-cell dimensions of the reactant and product, and also of natural phillipsite are presented in Table 5.

TABLE 5

Orthohombic cells of 2K,Ca–*H*, phillipsite, and the cubic and calculated orthorhombic cell of 2K,Ca–P_c

	a (Å)	*b* (Å)	*c* (Å)	*v* (Å³)		*a* (Å)	*b* (Å)	*c* (Å)	*v* (Å³)
2K,Ca–P_c ...	9·88	—	—	965	2K,Ca–*H* ...	9·90	14·29	14·29	2021
2K,Ca–P_c ...	9·88	13·97	13·97	1929	Phillipsite[5]...	9·84	13·85	14·3	1949

The orthorhombic unit cell of 2K,Ca–*H* has about a 5% greater volume than the calculated orthorhombic cell of 2K,Ca–P_c, but this is probably not so under the pressure and temperature conditions of the reaction. The reconstructive transformation Na–*P* zeolite → analcime was found to occur at temperatures as low as 270° in dry runs at 1000 bars; the reaction however results in the formation of free water. The reaction

$P_t \longrightarrow H$ zeolite occurred in several cases at 150° and 1000 bars in dry runs. One might tentatively conclude that the $P_t \longrightarrow H$ reaction involves fewer reconstructive changes than the $P_t \longrightarrow$ analcime reaction.

In summary, the following types of zeolite phase changes can be distinguished.

(1) *True enantiotropic phase transitions.* A transformation resulting from a displacive rearrangement of the anionic framework, such that the volume change is sufficiently small not to effect a loss of water. The two zeolite structures are of different symmetry, and when in equilibrium with one another, have identical compositions. The transition is readily reversible. The transition temperature is changed by solid solution of other exchangeable cations, and it also must be a function of the extent of solid solution of water in the zeolite (which in turn depends on P_{H_2O}). The phase boundary on a pressure–temperature diagram may have a positive or negative slope but will be characteristically much steeper than for dehydration reactions, and will therefore intersect the *LV* curve for water, *e.g.*, Na–P_t tetragonal $\rightleftarrows$ cubic; thomsonite $\rightleftarrows$ metathomsonite.

(2) *Monotropic reactions.* When one zeolite structure is stable and another metastable over the entire range of its existence, conversion of the latter into the former is an irreversible or monotropic reaction. The two phases involved would have the same composition, except for the water content but this is not necessarily different. The anionic framework of each zeolite is differently linked and the reconstructive reaction normally proceeds from the more open framework to a more densely packed one, consequently the water content decreases. The hydrothermal reaction series for synthetic sodium zeolites, $X,Y \longrightarrow A \longrightarrow P \longrightarrow$ analcime is an excellent example of monotropic reactions involving a continuous decrease in anionic framework density and water content. The *X,Y* synthetic zeolites are structurally similar to the natural zeolite faujasite; they have the most open anionic framework known.[15] The conversion of mono- and di-cationic *P* zeolites into the corresponding *H* zeolites having lower symmetry are examples of monotropic reactions that can involve negligible changes in packing density and water content.

(3) *Collapse (= dehydration) reactions (first order).* The zeolite structure undergoes a sudden collapse in one or several directions of the unit cell, concurrent with discharge of water. The structural collapse involves a displacive movement of the anionic framework, with or without a slight reconstructive change. The number of water molecules lost is related to the volume reduction of the unit cell. The volume reductions so far recorded range from 2 to 18% of the expanded cell volume.

The data obtained by Hey [2] indicate that these reactions occur generally when the water content of the zeolite is reduced to a certain fixed number of water molecules per unit cell, so that on the pressure–temperature diagram, the phase boundary will parallel the isohydric lines. The reaction point temperature is thus a function of P_{H_2O}, but it is also changed by solid solution of other exchangeable cations, in some cases to the extent that certain low-temperature collapse reactions may be made to occur at room temperature by the ion-exchange process, *e.g.*, notably in the system K,Ba–P_t. The majority of these collapse reactions are reversible; the exceptions always involve a poorly crystalline or amorphous, final collapsed phase, which is the normal product of the dehydration of *P* zeolites containing bivalent cations. The latter type of reaction although irreversible, cannot be considered monotropic with respect to the original partially collapsed structure, *e.g.*, Ca–P_t,$S0 \longrightarrow S1 + H_2O$; natrolite $\longrightarrow$ metanatrolite + H_2O. In principle these reactions do not differ from the dehydration of a hydrated salt such as gypsum $CaSO_4,2H_2O$ or $Na_2SO_4,10H_2O$. In practice the mechanism of the structural change is much simpler and therefore the kinetics much faster.

(4) *Collapse (= dehydration) reactions (second order).* A zeolite structure loses water and collapses in a continuous manner, over a short temperature range, to form a contracted structure, without an intervening two-phase region. Anomalous coefficients of expansion are frequently characteristic, *e.g.*, K–P_t; Ca–P_t,$S1 \longrightarrow S2$. Indeed it is this

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[15] W. H. Baur, *Amer. Mineralogist.*, 1964, **49**, 697.

phenomenon of continuous dehydration which has been held to be characteristic and definitive property of a zeolite. It is noteworthy that it is not by any means either the typical or the commonest dehydration reaction of zeolites in general. The Na,K–P_t zeolites undergo both types of collapse reaction (= continuous and discontinuous dehydration) at the same time, as a consequence of the collapse process involving two zeolite structures of differing composition.

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