488. *The Alums. Part II.* A Theory of Hydrate Dissociation and Aqueous Dissociation Pressure, with Particular Reference to the Alums.*

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The aqueous dissociation pressure results reported in Part I * have been critically examined to see if they throw light on the mechanism of dehydration. It has been shown that the constant (k) of the equation $p = k e^{-\Delta H/\mathbf{R}T}$, represents, at least in part, the contribution of the crystal structure as a whole and it is suggested that it manifests itself in the formation of a partially dehydrated crystalline zone which separates the reaction interface from the partially (or completely) dehydrated amorphous product of the reaction.

THE earlier measurements of hydrate aqueous dissociation pressures focused attention on the slightly different values obtained by static methods (*e.g.*, the Frowein tensimeter) and dynamic methods (*e.g.*, the transpiration method). Partington (*J.*, 1911, **99**, 466) suggested as a possible explanation the formation during dehydration of an unstable,

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* Part I, preceding paper.

probably amorphous, lower hydrate or anhydrous salt, which slowly passes into a stable crystalline modification. Other explanations have been offered by Tammann (*Ann. Physik*, 1888, **33**, 322), Nernst (*Z. physikal. Chem.*, 1908, **64**, 425), Baker (*Ann. Reports*, 1911, **8**, 34), and Campbell (*Trans. Faraday Soc.*, 1914, **10**, 195). Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 1951), taking very careful precautions, showed that the differences were less significant than hitherto supposed and that the discrepancy was within the limits of experimental error. Partington's suggestion of a phase change during dehydration represents, however, a significant advance on earlier views regarding the mechanism of dehydration.

Langmuir (*ibid.*, 1916, **38**, 2263) showed that dehydration occurs only at the boundary of the two phases. He suggested that the rate of the dissociation reaction is proportional to the number of uneffloresced molecules adjacent to effloresced molecules in the reaction zone, whilst the reverse reaction is proportional to the pressure and to the number of effloresced molecules (*i.e.*, adsorption sites) in the same boundary zone. Crowther and Coutts (*Proc. Roy. Soc.*, 1924, *A*, **106**, 215) distinguish between different types of behaviour in dehydration reactions and note the possible impedance effect of a layer of lower hydrate on a hydrate crystal. Damerell, Hovorka, and White (*J. Phys. Chem.*, 1932, **36**, 1255) assume that rearrangement of the lattice structure occurs during dehydration with formation of the lower hydrate or anhydrous salt; the case of aluminium oxide trihydrate which they investigated appeared, however, to be exceptional in this respect since *X*-ray diffraction evidence indicated no such lattice change. Taylor and Taylor (*Ind. Eng. Chem.*, 1935, **27**, 672) investigated the rates of dehydration for hydrates having different rates of formation of nuclei; they found the rate to be proportional to the area of interface and noted that the resultant anhydrous salt is so porous in comparatively thin layers as to offer very little resistance (impedance) to the escape of water molecules. The presence of gases, other than water vapour, absorbed in the amorphous phase may however impede such escape. Damerell and Tower (*Colloid Symp. Monograph*, 1935, **12**, 143) found that the equilibrium vapour pressure results of many investigators agreed with the theory that, as water of crystallisation leaves the surface, the residual skeleton lattice structure remains as a film, held to the unchanged lattice by valency forces. As water continues to evaporate, this film becomes thicker and the outer portions (in most cases) become metastable. The instability finally causes rearrangement to the lattice of the other solid phase. The (average) constant thickness of this skeleton lattice is, they say, the cause of the constancy of vapour pressure during dehydration.

More recently attention has been focused on measurement of rates of dehydration with single crystals, and of especial importance in this connection have been the contributions by Topley (*Proc. Roy. Soc.*, 1931, *A*, **134**, 224; 1932, *A*, **136**, 413; 1933, *A*, **139**, 588; *J.*, 1929, 124, 2633; *Trans. Faraday Soc.*, 1931, **27**, 94) and by Garner (*Proc. Roy. Soc.*, 1940, *A*, **174**, 487; 1947, *A*, **189**, 508; *Sci. Progr.*, 1938, 33). These investigators attacked the problem of the equilibrium vapour pressure by analysing the rate processes involved in dehydration of single crystals under non-equilibrium conditions. Factors which play a part in these processes, excluding the still imperfectly understood induction period, include hindrance to escape of water molecules (impedance), the difficulty of initiating efflorescence on a perfect crystal owing to the higher vapour pressure of small nuclei (Bradley, *Quart. Reviews*, 1951, **5**, 315), and the acceleration of dehydration by impurites (cf. observations reported in Part I on pure and impure NaAl alums). The results show that the primary process may originate at lattice defects within the crystal structure (Garner, 1938, 1947) related to the Frenkel and/or Schottky disorder, or to surface nucleation (in its true sense of an initial process). Garner has investigated the rate processes from microscopical examination of "nuclei," where the lower limit of size is of the order of 10^{-3} cm., and has shown how dehydration tends in general to follow preferred directions within the crystal lattice. Such evidence has a direct bearing on the influence of the nature of the crystal lattice on dehydration processes.

Analysis of the Aqueous Vapour Pressure of the Alums.—Lipson and Beevers (*Proc. Roy. Soc.*, 1935, *A*, **148**, 664) have shown that the water of crystallisation contained in the alum structure belongs to one or other of two types, depending on whether the related metal ion is M^+ or M^{3+}. The former is regarded as structural water and is more mobile than the latter; the results recorded in Part I of this series showed that the former are the molecules of water concerned in the dissociation equilibrium first established; some of these results are reproduced in Table 1. Clearly, in this series of alums, reduction in ΔH, the heat of hydration, leads in each of the three types of structure (α, β, or γ) to an increase in the equilibrium aqueous pressure. For alums of α-structure (KAl and NH_4Al), it may be supposed that the structural environment of the escaping water molecules is essentially the same in the two cases (see Part I), leading to rather similar values of k in the equation $p = ke^{-\Delta H/RT}$. The heats of hydration for the two cases are distinctly different, however, and it is tempting to conclude that the factor $e^{-\Delta H/RT}$ is in this case the dominating factor and leads, as actually found, to a decrease in vapour pressure (p) with increase in ΔH.

TABLE 1.

Alum	Structure	p (mm. Hg; 25°)	ΔH (cals.)	Alum	Structure	p (mm. Hg; 25°)	ΔH (cals.)
NaAl	γ	20·48	10,763	KCr	α	10·90	12,944
$NH_3 \cdot OHAl$ ...	γ?	12·20	11,982	NH_4Cr	α	7·11	14,290
KAl	α	2·21	13,083	NH_2MeAl ...	β	4·31	24,615
NH_4Al	α	1·62	14,725				

That the k factor may sometimes prove more significant than the exponential factor is suggested by the equilibrium aqueous pressure results for alums having the same M^+ but different M^{3+} (cf. Table 2). Here again a decrease in ΔH parallels an increase in p, with the difference that a very small change in the heat of dehydration produces a remarkably large change in p, remarkable because large changes in ΔH produce only small changes in p for the results described in Table 1. If the factor k in the equation $p = ke^{-\Delta H/RT}$ is assumed to play a minor role in the case of the results of Table 1, it is logical to infer that k must be the significant factor in the case of those in Table 2.

TABLE 2.

Alum	Structure	p (mm. Hg; 25°)	ΔH (cals.)	Alum	Structure	p (mm. Hg; 25°)	ΔH (cals.)
KAl	α	2·21	13,083	NH_4Al	α	1·62	14,725
KCr	α	10·96	12,944	NH_4Cr	α	7·07	14,290
				NH_4Fe	α	14·45	14,200

Further consideration of the results shows that the sizes of the M^+ and M^{3+} ions appear to have opposite influences on p and ΔH. Thus both a decrease in p and an increase in ΔH results (in Table 2) from an increase in radius of the M^+ cation (r_{M^+}), whereas the same changes (in Table 2) require a decrease in $r_{M^{3+}}$. This dependence of an equilibrium, involving only the rather mobile M^+-type water molecules, on the sizes of both the univalent and tervalent cation shows that the values of p and ΔH are determined by the structure of the alum as a whole, and not merely by the immediate environment of the M^+-type water molecules.

The Theory of the Partially Dehydrated Crystalline Zone.—No direct evidence is available on the structure (*i.e.*, whether crystalline or amorphous) of the dehydrated product formed at the reaction interface, although it is generally held that the product has at first a zeolitic structure which then collapses and finally crystallises (Garner, *loc. cit.*, 1938). The present author however, believes that Damarell and Tower's suggestions (*loc. cit.*) are significant and can be developed, as described below, to account qualitatively for the variations in vapour pressure reported in Tables 1 and 2.

When a given hydrate system is in equilibrium, it may be supposed that no very drastic change in crystal structure occurs at the reaction interface, but that the removal of water results in a metastable partially dehydrated structure which still retains the same crystal structure as the original hydrate. Such a partially dehydrated crystalline zone might, in general, have a zeolitic character, although the arguments developed below would suggest that it does not differ from that of the parent crystal. The zone may be supposed to have a finite thickness and to separate the fully hydrated part of the crystal from the amorphous part; the latter may be considered to result rather sharply from a collapse of the intermediate zone at the outermost boundary.

Further consideration of this hypothetical partially dehydrated crystalline zone suggests that the number of vacant sites (due to removal of water molecules) at any point in it will increase the further that point is from the dehydration interface. The water molecules may be regarded as moving from one site to the next, in a manner analogous to the so-called Frenkel disorder. Clearly a stage will eventually be reached at which the number of vacant sites has increased to such an extent that the crystalline structure collapses, producing an amorphous zone. The precise point at which this occurs will depend on the forces existing between the ionic species present in the crystal. It might be expected, for example, that of two isomorphous crystals, that having the stronger structural forces will survive the loss of water in the crystalline dehydration zone more easily than will the other; it should, in fact, produce a wider partially dehydrated crystalline zone. In general, for those alums which have the same crystal structure one might expect this width to vary inversely with the nth power of the radii of the cations, with n probably of the order of 2.

TABLE 3. *Constant B* $\times \log_e 10$.

	M^{3+}	Al	Cr	Fe
M^+	Radius (Å)	0·57	0·64	0·67
Na	0·98	9·20	—	—
NH_3OH	1·2 ?	9·87	?	—
K	1·33	9·94	10·53	—
NH_4	1·43	11·01	11·33	11·57
CH_3NH_3	2·2 ?	18·68	—	—

The intermediate zone is to be regarded as a hazard which reduces the rate of loss of water and hence reduces the equilibrium vapour pressure. It is perhaps worth noting that the heat of hydration ΔH is determined by $d(\ln p)/dT$ and so is, of course, not determined by the actual values of p at a given temperature, or by the kinetics which determine the magnitude of p. The function of this intermediate zone is thus seen to be concerned only with the constant of the integrated equation $\ln p = -\Delta H/\boldsymbol{R}T +$ constant (B) (or k in the equation $p = ke^{-\Delta H/\boldsymbol{R}T}$).

Table 3 gives the values of the constant B for the alums reported in Part I. It is seen that dB/dr is positive, *i.e.*, that B increases with increase in radius of both the M^+ and the M^{3+} ion; but increase in the radii of the M^+ or the M^{3+} ion will produce a more expanded unit cell and so tend to weaken the crystal structure; this might consequently be expected to reduce the thickness of the partially dehydrated crystalline zone and so facilitate the escape of water molecules from the innermost reaction face. For isomorphous hydrates having almost the same heat of hydration, this will increase the vapour pressure and thus the constant B. The suggestion of an intermediate crystalline zone recalls the work of Damerell, Hovorka, and White on $Al_2O_3,3H_2O$, where no amorphous phase could be detected by X-ray diffraction methods.

Explanation of the Aqueous Vapour Pressure Results.—The equation $p = ke^{-\Delta H/\boldsymbol{R}T}$ may now be expressed in the form $p = \text{const.} \times (1 - \text{structure factor}) \times e^{-\Delta H/\boldsymbol{R}T}$ where the "structure factor" is a quantity which increases with increase in the electrostatic forces present in the crystal structure. In the case of the alums, the variables are the M^+ and M^{3+} ions and these will operate in the sense that any increase in their radii (with a resultant decrease in their electrostatic field effect as measured by $1/r^2$) will reduce the structure factor. This factor may also be related to the melting point. Thus in the series KAl, KCr, and KFe, the melting points (or in the case of the alums, the transition temperatures) decrease, whilst the structure factors increase. The vapour pressure results noted in Table 2 for alums of the type M^+M^{3+} (*e.g.*, NH_4Al, NH_4Cr, and NH_4Fe, for which ΔH is sensibly constant) are in agreement with these views.

When, however, the alums are of the type in which M^{3+} is unchanged (Table 1), large changes in ΔH are found (showing that the M^+-type water molecules are not merely structural), and the variations in the equilibrium vapour pressures must be almost entirely determined by the exponential term of the vapour-pressure equation. Since ΔH decreases with decrease in r_{M^+}, this term might be expected to decrease with increase in the radius, thus accounting qualitatively for the results reported in Table 1.

Other processes may occur during dehydration which also control the facility or otherwise of escape of the water molecules, and mention might be made of the impedance effects noted by Crowther and Coutts, Taylor and Taylor, and Topley (*locc. cit.*), which should be non-constitutional since they occur in the amorphous zone and so would not be revealed in the present analysis of the alum hydrate pressures.

The theory postulating the partially dehydrated crystalline zone also suggests possible explanations for some of the phenomena encountered in hydrate vapour pressure work. Thus the induction period may be determined, after the formation of the dehydration nuclei (Melville, *Ann. Reports*, 1948, **45**, 35), by the time required for this zone to reach its maximum value. The smaller the tendency of the crystal to effloresce, the longer will this period be. Since efflorescence begins initially at points of disorder on the surface of the crystal, the reaction zone will initially have zero area but, as the centres grow, they will merge into a common front and the area of the reaction zone will become sensibly constant. During this period the vapour pressure will increase from zero to a value usually in excess of the true equilibrium value (*e.g.*, Menzies and Hitchcock, *J. Phys. Chem.*, 1931, **35**, 1660; Collins and Menzies, *ibid.*, 1936, **40**, 379; Partington *J.*, 1923, 160). As efflorescence proceeds further, the partially dehydrated crystalline zone increases in width, thereby producing a gradual fall in the vapour pressure. Eventually it reaches its maximum thickness, and the vapour pressure reaches the equilibrium value. Further efflorescence leads to collapse of the partially dehydrated zone at its outermost boundary, and formation of the opaque amorphous zone shows that the crystal has started to effloresce. This point will not necessarily coincide in the dynamic transpiration method with the equilibrium vapour pressure since the latter will depend on the quantity of hydrate present and also on the volume of the containing vessel and free air space.

Anomalous Vapour Pressure Results.—The difficulties sometimes encountered in determinations of hydrate vapour pressure, wherein, for example, a variable lower vapour pressure sometimes results, may be due to impedance becoming significant (Taylor and Taylor, *loc. cit.*; Topley, *loc. cit.*). More usually values in excess of the true equilibrium value are encountered and these have been discussed by Collins and Menzies (*loc. cit.*). In Part I, examples occur of double (and triple) series of equilibrium vapour pressure results which, however, appear to be real. These and the derived heats of dissociation for the KAl and NH_4Al alums are assembled in Table 4. They were obtained on the same material (for each series) with the bulk of the crystals present in the uneffloresced (or only slightly effloresced) form and it is therefore suggested that the equilibria involved are respectively: lowest series, $M^+Al(SO_4)_2,12 \longrightarrow 6H_2O$; middle series, $12 \longrightarrow 3H_2O$, and upper series $12 \longrightarrow 0H_2O$.

TABLE 4. *Equilibrium aqueous vapour pressures* (*mm.* Hg).

	Lowest series		Middle series		Upper series	
Temp.	NH_4Al	KAl	NH_4Al	KAl	NH_4Al	KAl
20°	1·07	1·53	1·41	1·81	—	—
25	1·62	2·18	2·20	2·74	—	3·28
30	2·46	3·19	3·37	4·38	—	6·82
35	(4·65)	—	5·04	6·42	(6·03)	14·95
ΔH (cals.)	14,725	13,083	15,267	15,294	—	—

Zawadski and Breitsnajder (*Trans. Faraday Soc.*, 1938, **34**, 951; *Z. physikal. Chem.*, 1938, *B*, **22**, 60) showed that vapour pressure values in excess of the normal equilibrium values can be produced in the calcium carbonate system, the effect being attributed to nuclei growing to a critical size corresponding to a stabilisation of the vapour pressure at a value in excess of that expected over a plane surface. Some such effect may be responsible for the middle and upper series of results of Table 4, although the facts pertaining to them would appear to rule out such an explanation. In particular it is noted that the ΔH values for the middle series of results are almost identical (the slight difference being explained by the smaller field effect of the larger NH_4^+ ion compared with that of the K^+ ion). This suggests that the Al-type water molecules are involved in the dissociation equilibrium.

Furthermore, with reference to the equation $p = ke^{-\Delta H/RT}$, this slight difference in ΔH should (if k were constant) produce somewhat lower values of p for KAl than for NH_4Al alum. The opposite is in fact the case, and k must be regarded as the significant factor. The evidence of the previous section suggests that k will have a larger value for KAl than for NH_4Al alum owing to the smaller radius of the K^+ ion, and this variation in k appears to explain the relative magnitudes of the two middle series of vapour pressures.

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