



Review Article

Possible Mechanisms of Intercalation

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Abstract. Recent knowledge of the kinetics and intercalation mechanisms are summarized and accompanied by examples of intercalation reactions of water and ethanol into anhydrous vanadyl phosphate and redox intercalation of alkali metal cations into vanadyl phosphate dihydrate. Three possible mechanisms of intercalation are presented which are based on: (i) a concept of exfoliation of layers; (ii) the formation of stages and randomly stacked layers; (iii) co-existence of intercalated and non-intercalated parts of crystals of the host separated by an advancing phase boundary. The corresponding kinetic curves are ascribed to mechanisms (ii) and (iii).

Key words: intercalation, mechanism, kinetics, vanadyl phosphate.

1. Introduction

Intercalates are a special type of inclusion compound formed by the insertion of molecules or ions into vacancies between layers of a layered materials. All intercalation reactions are accompanied by a partial or total transfer of the charge to the lattice and cause a change of the interlayer distance (basal spacing). The molar ratio need not necessarily be an integer ratio.

The first intercalates were prepared more than 150 years ago, and the first host lattice was graphite. Graphite is the only material which permits the intercalation of molecules without a lone electron pair or with a deficiency of electrons.

Other host lattices have been used from the beginning of the sixties. The most frequently investigated lattices for these processes are the chalcogenides of tetravalent metals, hydrogenphosphates of tetravalent metals or their hydrates, lamellar oxide halides of trivalent metals, layered oxides, metal phosphorus chalcogenides, layered minerals (montmorillonite, bentonite etc.) and vanadyl and niobyl com-

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pounds of the type MOXO_4 . The intercalation chemistry of these compounds has been reviewed in several monographs [1, 2].

A number of studies of the kinetics and mechanism of intercalation processes have been published in which the guest species are atoms. Several possible phenomena that occur during these intercalations have been observed and described.

- In the crystal of the host, intercalated and nonintercalated parts of the crystal coexist. A two phase system is formed which is a transition area which has been designed as an advancing phase boundary [3, 4].
- Due to intercalation across the layers, a superstructure is generated in the crystal [5]. When these intercalations lead to a regular alternation of empty interlayer space (galleries) and galleries filled with guest, so-called staging is observed [6]. Staging means a situation in layer compounds in which certain galleries are filled, whereas others are empty. The intercalate thus forms sequences in which empty galleries regularly alternate with full galleries. The stages are numbered according to the number of galleries in one sequence (empty plus full ones). The filled galleries are not usually spread over the whole crystal; rather, the guest creates islands known as Daumas–Hérol zones [7]. A transition from one stage to another can be explained by using the idea of these zones. In cases where the empty and full galleries alternate randomly, the so-called Hendricks–Teller effect occurs [8].

During the last fifteen years, interest has been paid to a study of the dynamics of domain shifts, transformations of the stages and to the kinetics of the guests entering into the host structures. Experimental work of this type are scarce [9, 10]. Theoretical studies devoted to the modeling of these processes are not very common and are applied to the graphite intercalates [11–14].

On the other hand, little attention has been paid to the study of the kinetics of intercalation of polyatomic molecules, because the measurements of these systems often involve considerable experimental problems. An especially difficult one is the low stability of the complexes formed. For instance, in most cases it is impossible to determine the concentration distribution of the molecules intercalated in the host crystal, because it changes rapidly after an interruption of the intercalation process. Another complication consists in the fact that the intercalation of a crystal with molecules results in the disintegration of the host, with formation of a polycrystalline product. Hence the selection of methods applicable to obtaining data about such systems is rather limited.

An indirect proof of the formation of stages has been given by measurement of the crystal thickness in relation to time during the intercalation of sulfuric acid into graphite [15]. The same results gave measurements of graphite electrode potential during intercalation [16].

A comparison of the molar volumes of intercalated guests calculated from XRD data with those in the liquid phase shows that intercalation is accompanied by a considerable volume decrease. The changes in molar volumes of the guest during intercalation processes are probably caused by a more regular arrangement of the guest molecules between the host layers as compared with the arrangement in the liquid state. The molecular guest in the intercalates adopts the arrangement of the long-range type because its molecules are bound to the host layers. These phenomena suggest a new experimental method enabling determination of the time course of the intercalation process by means of precise measurements of volume changes of the heterogeneous reacting system of host and guest [17]. This volumetric method was experimentally verified in the VO_2SO_4 -1-butanol system.

Another method for the study of the kinetics consists in monitoring the intercalation by real-time, *in situ* X-ray diffraction. The intercalation of cobaltocene from dimethoxymethane solution into SnS_2 was studied by this method using a synchrotron as the source of radiation [18].

When trying to suggest mechanisms by which large particles such as organic molecules could enter between layers of a host during intercalation reactions, the presumption that the host layers are bent in the reaction zone cannot be avoided. A computational procedure has been suggested to enable estimates to be made of the flexibility of individual layers of layered materials from their crystallographic structure [19]. The calculated flexibility of the layers increases in the order: $\text{MPS}_3 < \text{TX}_2 < \text{FeOCl} = \text{Zr}(\text{HPO}_4)_3 < \text{VOPO}_4$ (where $\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cd}^{\text{II}}$; $\text{T} = \text{Nb}^{\text{IV}}, \text{Ta}^{\text{IV}}, \text{Mo}^{\text{IV}}$; $\text{X} = \text{S}^{-\text{II}}, \text{Se}^{-\text{II}}$). The same trend is observed for the ability of these compounds to form molecular intercalates. A distinct anisotropy of flexibility has been found by calculation for most of the structures studied.

The time course of the intercalation of vanadyl phosphate with water and ethanol, and the co-intercalation of vanadyl phosphate dihydrate with alkali metal ions has been studied and is summarized in this paper.

2. Intercalation of Water into VOPO_4

The time course of intercalation of water into VOPO_4 was followed by *in situ* X-ray diffraction and by measurement of the thickness across layers of the crystal using an apparatus for thermomechanical analysis (TMA) [20].

The changes of thickness of the crystal of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ during heating are shown on the left-hand part of Figure 1. The original thickness of the dihydrate decreases relatively rapidly to the thickness corresponding to monohydrate and then more slowly to the value corresponding to anhydrous α_1 - VOPO_4 . This two-step dehydration is in agreement with previous results [21]. The right-hand part of Figure 1 shows the behavior of the dehydrated crystal left at room temperature in a flow of wet air. The thickness of the crystal returns to the original value and the time dependence of the thickness has an exponential shape. No significant dwell corresponding to a monohydrate formation is observed in this part of the figure.

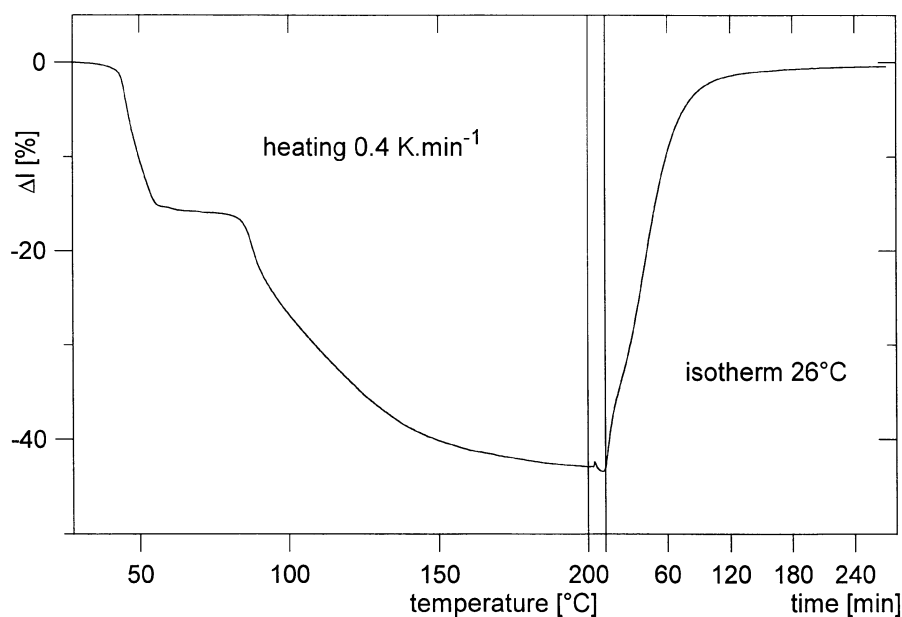


Figure 1. Relative changes of the thickness Δl of the crystal of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ during heating, cooling, and during intercalation of water.

Staging was not observed in this case. If the sample of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is heated to 70°C only, there is a very rapid, reversible hydration of the monohydrate formed to dihydrate.

Hydration of $\alpha_1\text{-VOPO}_4$ was studied by *in situ* X-ray diffraction where the reaction of polycrystalline VOPO_4 with water vapor was followed. The results of this study are summarized in Figure 2. The formation of $\text{VOPO}_4 \cdot \text{H}_2\text{O}$, which has a very intense (001) line ($d = 6.3 \text{ \AA}$), is not observed during hydration. Diffractograms do not show sets of (00*l*) lines corresponding to staging of the sample. The (00*l*) lines of the parent host and the intercalate formed are observed. The interplanar distance belonging to the (001) line of anhydrous vanadyl phosphate gradually decreases while the linewidth of this line increases (marked 'H' in Figure 2). Similarly, the (001) and (002) interplanar distances of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (marked 'I' in Figure 2), which appears during hydration, are at first significantly shifted and gradually become closer to values corresponding to pure $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. At first, these lines are remarkably broad. The broadening of the (00*l*) lines of both phases can be explained by fragmentation of the microcrystals during the intercalation of water, but the shifts of the line position remain unexplained. The behavior described above can be elucidated in terms of the formation of a Hendricks–Teller disordered layered lattice [22]. Molecules of water probably fill the interlayer space randomly, creating a disordered layer lattice, which is composed of $\alpha_1\text{-VOPO}_4$ and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ layers.

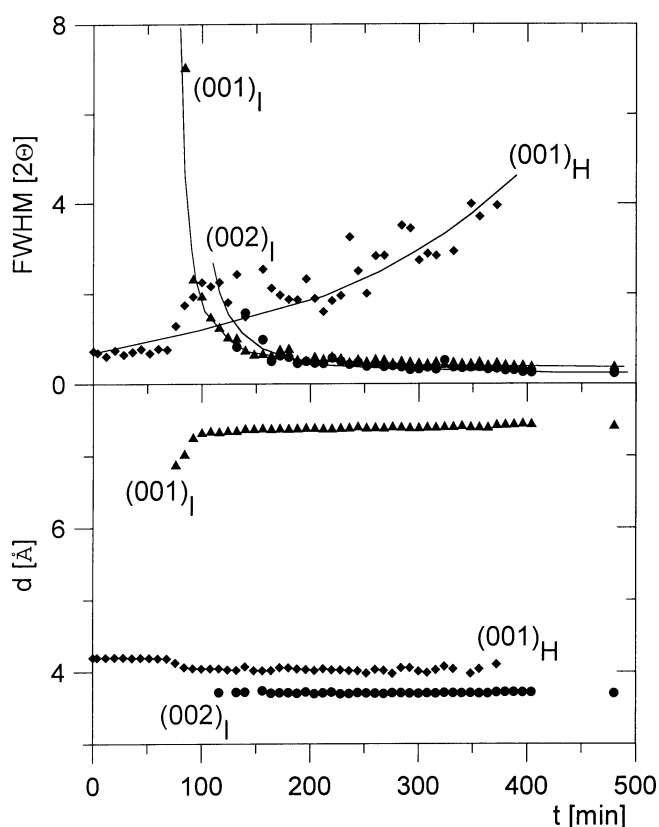


Figure 2. Dependence of the interplanar distances d and full-widths-at-half-maxima, FWHM, of the diffraction lines on time t of the intercalation of water into VOPO_4 .

3. Intercalation of Ethanol into VOPO_4

Intercalation of ethanol into VOPO_4 was studied by *in situ* X-ray diffraction, by measurement of the thickness across layers of the crystal (TMA), and by a volumetric method [23].

In situ X-ray diffraction was employed to follow the reaction of polycrystalline VOPO_4 with ethanol vapor. The lines observed in the diffractograms belong to either anhydrous VOPO_4 or intercalated vanadyl phosphate, which indicate that there is no intermediate product such as $\text{VOPO}_4 \cdot \text{C}_2\text{H}_5\text{OH}$. In the region investigated, three sharp $(00l)$ lines of the intercalate ($\text{VOPO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$) were observed giving the same value of the basal spacing. The interlayer distances of the $(00l)$ reflections of both phases remain constant as it is seen in the lower part of Figure 3. Changes of the linewidths during intercalation can be explained by a decrease of the size of diffracting crystallites of the host and increase of the size of crystallites of the intercalate formed (upper part of Figure 3). It can be assumed from the XRD results that the intercalate is formed directly in a greater part of the crystals, without

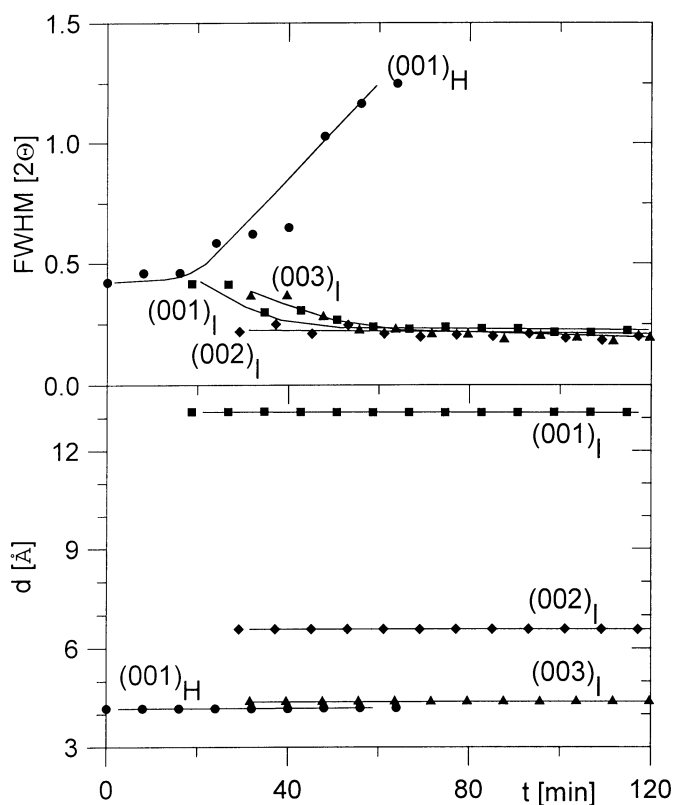


Figure 3. Dependence of the interplanar distances d and full-widths-at-half-maxima, FWHM, of the diffraction lines on time t of the intercalation of ethanol into VOPO_4 .

any occurrence of the random stacking of the layers (Hendrick–Teller effect). Formation of the regular alternation of the intercalated and nonintercalated galleries (staging) was also not found.

The dependence on reaction time of the extent of reaction (calculated from the intensities of the (001) lines) of anhydrous VOPO_4 and the ethanol intercalate is given in Figure 4. The curves were observed to have a sigmoidal shape corresponding to a decreasing content of VOPO_4 and an increasing content of $\text{VOPO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$, respectively. A delay in the formation of the product in comparison with the decrease of the pristine host was observed. This phenomenon can be explained by the existence of an advancing phase boundary [4]. The advancing phase boundary (APB) is an area of the crystal which is formed immediately at the beginning of the reaction, thus decreasing the amount of the pristine host present. From the point of view of X-ray diffraction, APB has a disordered structure and is shown as a slight increase of the baseline of the diffractogram only. During intercalation, the APB spreads and shifts in the crystals being replaced by the intercalate formed. The amount of this non-diffracted APB corresponds to a difference of

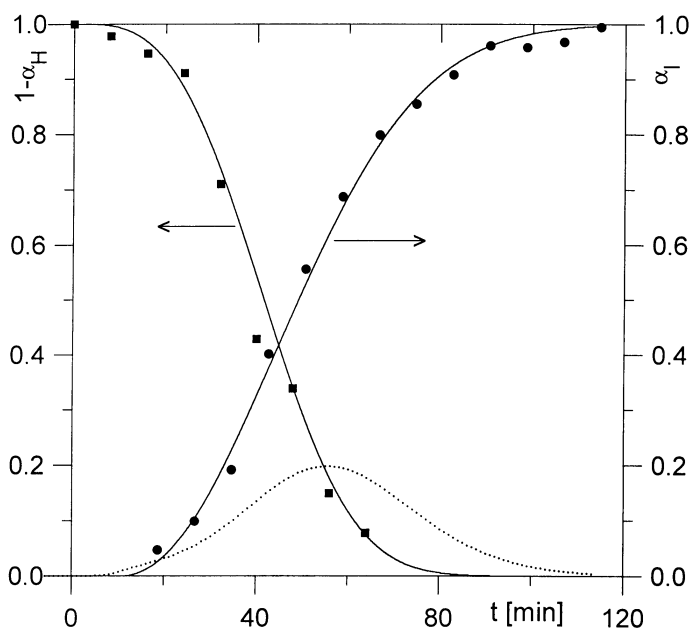


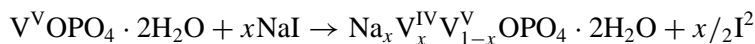
Figure 4. Dependence of the extent of reaction of the parent host α_H and the product α_1 , on time t during intercalation of ethanol into VOPO_4 . The difference $\alpha_H - \alpha_1$ (dotted line) corresponds to the amount of the advancing phase boundary in the reaction system. Reprinted from Ref. 23 with the kind permission of Kluwer Academic Publishers.

$\alpha_H - \alpha_1$, which is shown in Figure 4 as a dotted line. The reaction rate calculated for the decrease of the host is in agreement with the reaction rate found for formation of the intercalate.

The sigmoid shape of the kinetic curve was also found for intercalation of liquid ethanol into VOPO_4 monocrystal as was observed by the TMA method and for intercalation of liquid ethanol into VOPO_4 studied by a volumetric method [23].

4. Intercalation of Alkali Metal Cations into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$

Generally, cations can be intercalated into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in the presence of a proper reducing agent. It was shown that some good reducing agents like I^- , $\text{S}_2\text{O}_3^{2-}$, SO_2 , $\text{N}_2\text{H}_5\text{Cl}$, etc., present in the system enables cations such as Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} to intercalate into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ [24–27]. For instance, the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with an ethanolic solution of NaI according to the equation



is rapid and spontaneous at room temperature. Strictly speaking, these redox intercalates are in fact co-intercalates of water molecules and metal ions inserted in the interlayer space.

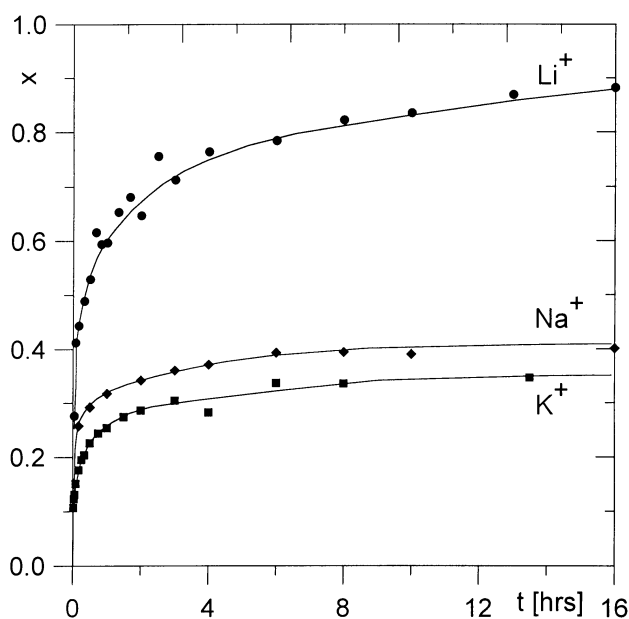


Figure 5. Dependence of the alkali metal ion content x in $\text{Me}_x\text{VOPO}_4 \cdot y\text{H}_2\text{O}$ on time t at 20 °C.

The time course of intercalation of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with acetone solutions of lithium, sodium, and potassium iodides has been studied [28–30]. The amount of the alkali metal cation intercalated was determined by iodometric titration of iodine released during redox intercalation. An attempt was made to identify the intermediate phases formed and to determine their ratio in the solid reaction products and their dependence on reaction time.

The dependence on reaction time of the total content x of the cation intercalated in $\text{Me}_x\text{VOPO}_4 \cdot y\text{H}_2\text{O}$ at 20 °C (Figure 5) shows an exponential character. The rate of intercalation decreases with increasing atomic number of the alkali metal cation used. Vanadyl phosphate fully intercalated with lithium ($x = 1$) was prepared by the reaction of the starting compounds for 3 days, while potassium needs 67 days at 40 °C to become fully intercalated.

Four phases with different basal spacings were found in the samples during intercalation of lithium into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and their relative contents w were calculated from X-ray diffraction data. These phases are formed consecutively (see Figure 6) with maximum relative ratio at lithium content in the samples $x = 0.33$, 0.5, 0.66, 1. The contents of lithium in each phase were calculated by multidimensional linear regression. The existence of four phases is probably caused by staging of the intercalation compound. From the definition of stages given above, we find a stage in which the stoichiometric coefficient $x = 0.66$. The most plausible structure of this stage is a sequence of two full galleries and one empty gallery. A stage number, therefore, must be newly defined as a ratio of the number of

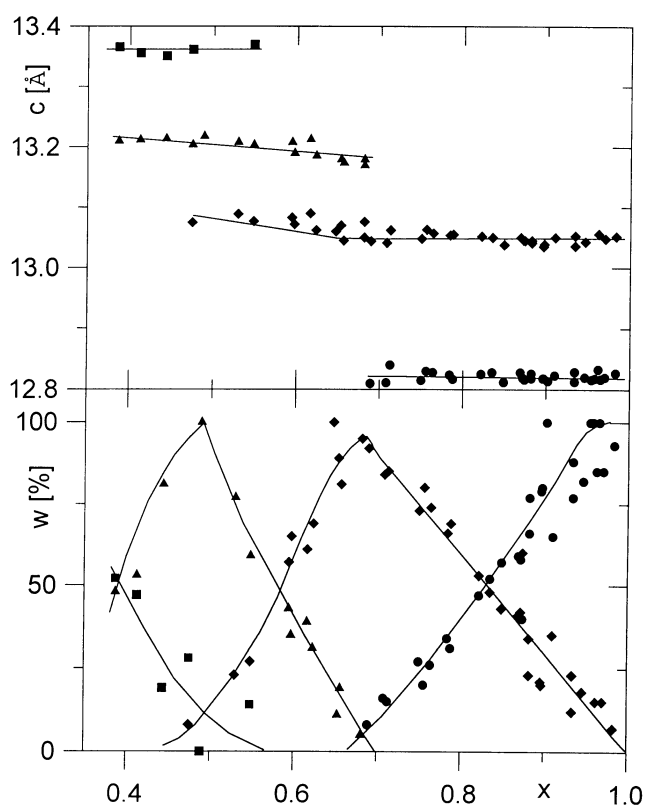


Figure 6. Dependence of the basal spacing c and relative content w of the stages 3 (squares), 2 (triangles), 3/2 (diamonds), and 1 (circles) on the lithium content x in $\text{Li}_x \text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

all the galleries (empty and full ones) to the number of the full galleries in each sequence. This stage was thus numbered as 3/2. The numbering of the other stages is not changed [29]. This means that the intercalates with $x = 0.33$, 0.5, and 1 correspond to stages 3, 2, and 1, respectively. A similar situation was observed during intercalation of sodium into $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, where stages 3, 2, and 1 were found [28]. The stage 3/2 was not observed in this case.

Staging was not observed during preparation of potassium-intercalated $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ [30]. The XRD data show several reflections which appear at the position of the (001) lines, but which do not correspond with sufficient precision to the (002) lines. This may probably be caused by formation of mixed stages or a partially disordered phase during intercalation. An exception is $\text{K}_{0.66} \text{VOPO}_4 \cdot \text{H}_2\text{O}$ with a basal spacing of 6.387 Å for all three (00 l) reflections. The interlayer separations calculated from the (001) lines for the series of samples are shown in Figure 7.

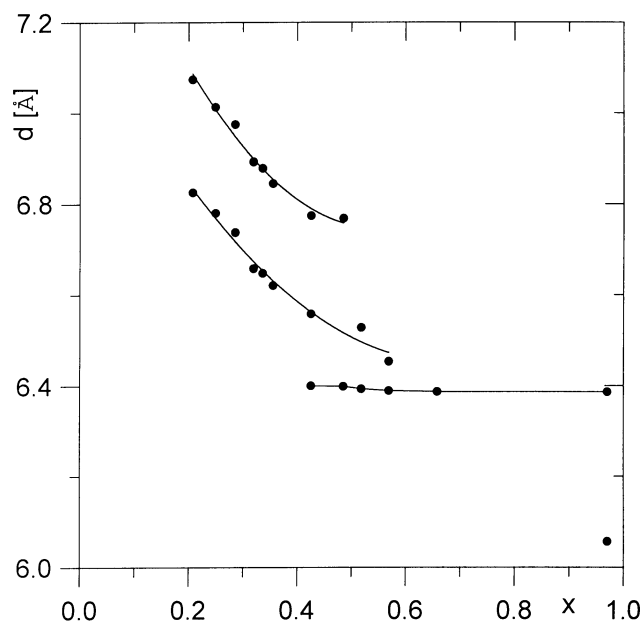


Figure 7. Dependence of the interlayer distances d on composition for $K_x \text{VOPO}_4 \cdot y\text{H}_2\text{O}$. Reprinted from Ref. 30 with the kind permission of Elsevier Science, NL.

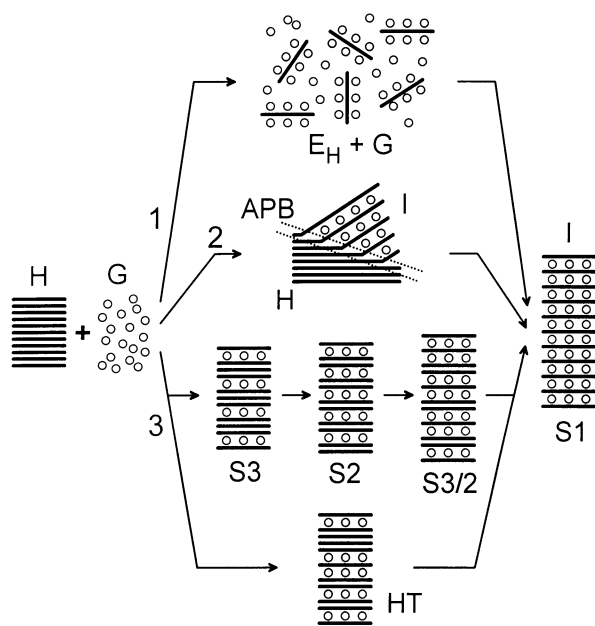


Figure 8. Schematic representation of the intercalation mechanisms. H – host, G – guest, I – intercalate, E_H – exfoliated host layers, APB – advancing phase boundary, S3, S2, S3/2, and S1 – stages, HT – Hendricks–Teller disordered layer structure.

5. A Survey of Mechanisms of Intercalation

Our up-to-date knowledge leads us to an idea of three possible mechanisms of intercalation given schematically in Figure 8.

1. Intercalation proceeds *via* exfoliation of the host layers in the environment, which contains guest molecules. The host layers are then reassociated, taking the molecules of guest between them and forming an intercalate. This mode of intercalate formation is rare and needs special conditions. This phenomenon has been observed during reintercalation of water molecules in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with alcohols and diols in a microwave field [31].
2. Particles of the guest start intercalation by nucleation of the first subsurface van der Waals zone. Growth of the intercalate in this layer causes nucleation of the adjacent van der Waals zone. This process continues, further causing intercalation of the whole crystal. This process is manifested by coexistence of the original host and the intercalate in one crystal. Both phases are separated by an advancing phase boundary. This nuclei-growth mechanism is characterized by a sigmoid shape of the kinetic curve and is expected during intercalation of larger molecules.
3. Particles of the guest start intercalation along the whole side of the layered crystal of the host. Stages, superlattices or randomly stacked intercalated and unintercalated layers (Hendricks–Teller disordered layer structure) are formed during intercalation. The transition between such structures proceeds *via* Daumas–Hérol zones. The kinetic curves of such intercalations, typical of smaller molecules or ions, have an exponential shape.

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References

1. M. S. Whittingham and A. J. Jacobson (Eds.): *Intercalation Chemistry*, Academic Press, New York (1982).
2. G. Alberti and T. Bein (Eds.): *Comprehensive Supramolecular Chemistry*, Vol. 7, Elsevier, Oxford (1996).
3. A. Clearfield: *Chem. Rev.* **88**, 125 (1988).
4. G. Alberti: *Acc. Chem. Res.* **11**, 163 (1978).
5. G. A. Scholz, R. F. Frindt, and A.E. Curcon: *Physica Stat. Solidi (a)* **72**, 483 (1982).
6. M. S. Whittingham and M. B. Dines: *Surv. Prog. Chem.* **9**, 55 (1980).
7. N. Daumas and A. Hérol: *C. R. Seances. Acad. Sci., Ser. C* **268**, 373 (1969).
8. D. C. Johnston and S. P. Flysinger: *Phys. Rev. B* **30**, 980 (1984).
9. M. Watanabe, D. C. Dahn, B. Blackford, and M. H. Jericho: *J. Microscopy* **152**, 175 (1988).
10. K. J. McKelvy and W. S. Glaunsinger: *Solid State Ionics* **25**, 287 (1985).
11. S. A. Safran and D. R. Hamann: *Phys. Rev. Lett.* **42**, 1410 (1979).

12. S. A. Safran: *Phys. Rev. Lett.* **44**, 937 (1980).
13. G. Kirczenow: *Phys. Rev. Lett.* **55**, 2810 (1985).
14. S. E. Ulloa and G. Kirczenow: *Phys. Rev. B* **33**, 1360 (1986).
15. W. Biberacher, A. Lerf, J. O. Besenhard, H. Möhwald, and T. Butz: *Mat. Res. Bull.* **17**, 1385 (1982).
16. N. Iwashita and M. Inagaki: *Tanso* **149**, 204 (1991); *CA* **116**, 257 239q (1992).
17. J. Votinský, J. Kalousová, L. Beneš, I. Baudyšová, and V. Zima: *J. Incl. Phenom.* **15**, 71 (1993).
18. S. M. Clark, J. S. O. Evans, D. O'Hare, C. J. Nuttall, and H. V. Wong: *J. Chem. Soc., Chem. Commun.* 809 (1994).
19. J. Votinský and L. Beneš: *Collect. Czech. Chem. Commun.* **56**, 2859 (1991).
20. L. Beneš and V. Zima: *J. Incl. Phenom.* **20**, 381 (1995).
21. V. Zima, L. Beneš, J. Málek, and M. Vlček: *Mat. Res. Bull.* **29**, 687 (1994).
22. S. Hendricks and E. Teller: *J. Chem. Phys.* **10**, 147 (1942).
23. L. Beneš, V. Zima, I. Baudyšová, and J. Votinský: *J. Incl. Phenom.* **26**, 311 (1996).
24. J. W. Johnson and A. J. Jacobson: *Angew. Chem., Int. Ed. Engl.* **22**, 412 (1983).
25. J. A. Jacobson, J. W. Johnson, J. F. Brody, J. C. Scanlon, and J. T. Lewandowski: *Inorg. Chem.* **24**, 1782 (1985).
26. V. A. Zazhigalov, A. J. Pyatnitskaya, I. V. Bachevikova, G. A. Komashko, G. Ladwig, and V. M. Belousov: *React. Kinet. Catal. Lett.* **23**, 119 (1983).
27. N. Casan-Pastor, D. Beltran-Porter, and E. Martinez-Tamayo: *Neuv. J. Etude Equil. Phases.* 77 (1983).
28. R. Šišková, L. Beneš, V. Zima, M. Vlček, J. Votinský, and J. Kalousová: *Polyhedron* **12**, 181 (1993).
29. V. Zima, L. Beneš, R. Šišková, P. Fatěna, and J. Votinský: *Solid State Ionics* **67**, 277 (1994).
30. V. Zima, L. Beneš, J. Votinský, and J. Kalousová: *Solid State Ionics* **82**, 33 (1995).
31. L. Beneš, K. Melánová, V. Zima, J. Kalousová, and J. Votinský: *Inorg. Chem.* **36**, 2850 (1997).