

# Volumetric Method for Following the Rate of Intercalation of Liquid Molecular Guests into Layered Hosts

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**Abstract.** A new experimental method is suggested for the kinetic measurements of intercalation reactions in systems formed by a polycrystalline layered host and a liquid molecular guest. The method is based on the fact that the molecular guest decreases its molar volume on entering the space between the host layers. Hence the volume of the system in which an intercalation process takes place is measurably decreased. The time course of the intercalation process can thus be monitored by measuring the volume change of the system. The method has been used to obtain kinetic data about heterogeneous intercalations of some liquid aliphatic compounds into layered structures of anhydrous vanadyl phosphate and sulfate.

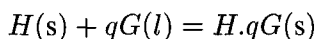
**Key words:** Intercalation, rate of intercalation, observing intercalation processes, change of volumes of intercalating systems, vanadyl phosphate, vanadyl sulfate.

## 1. Introduction

A number of studies of the kinetics and mechanism of intercalation processes have been published in which the guest species are atoms (see review [1]). Interesting phenomena have been observed and described, such as the existence of stages [2], superstructures [3], the Daumas–Hérold zones [4], etc.

On the other hand, little attention has been paid to studies 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 distribution of concentration of the molecules intercalated in the host crystal because it rapidly changes after an interruption of the intercalation process. Another complication consists in the fact that the intercalation of a crystal with molecules results in its disintegration with formation of a polycrystalline product. Hence the selection of methods applicable to obtaining data about such systems is rather limited.

When analyzing the lattice parameters of molecular intercalates published to date we have noticed that in all cases these layered complexes have a smaller volume than the sum of the molar volumes of the host and guest themselves. For a complex of the general formula  $H.qG$  formed by the heterogeneous chemical reaction



we can write

$$V_m(H.qG) < V_m(H) + q.V_m(G) \quad (1)$$

where  $V_m(H.qG)$ ,  $V_m(H)$ , and  $V_m(G)$  are the molar volumes of the complex  $H.qG$ , the host  $H$ , and the guest  $G$ , respectively, at the same temperature. From the published data [5–12] on the diffraction measurements of layered complexes it follows that the structure of host layers (and, hence, the molar volume of the host) is changed only negligibly upon intercalation. The lattice constants characterizing the periodicity along the host layers are almost always increased during intercalation but the increase does not exceed 1%. Therefore the condition

$${}^1V_m(H) = V_m(H) \quad (2)$$

( ${}^1V_m(H)$  is the effective molar volume of the host in the intercalate) is approximately valid. Accepting this presumption Equation (3) can be used to estimate the effective molar volume of the guest in the complex ( ${}^1V_m(G)$ ) formed

$${}^1V_m(G) = \frac{B(H.qG) - B(H)}{q.Z} . N_A \quad (3)$$

where  $B(H.qG)$  is the experimentally determined volume of the unit cell of the complex,  $B(H)$  is the volume of the unit cell of the host,  $q$  is the quotient in the formula of the complex,  $Z$  denotes the number of formula units per unit cell, and  $N_A$  stands for the Avogadro number. Relation (3) is valid if the unit cells of both the complex and the host are defined so that they contain an identical number of formula units.

The comparison of the molar volumes of guests calculated in this way with those in the liquid phase shows that intercalation is accompanied by a considerable volume decrease. Thus, e.g., the intercalation [5] of aliphatic alcohols ( $C_1$  to  $C_8$ ) into  $VOSO_4$  is accompanied by a 10% decrease in their molar volume. A similar change is also found during the intercalation of primary aliphatic amines into  $NiPS_3$  [6] and  $VOPO_4$  [7]. Large volume contractions are observed during intercalation of pyridine into  $TaS_2$ ,  $TiS_2$  (15%) [8],  $FeOCl$  (20%) [9],  $VOPO_4$  and  $VOAsO_4$  (18%) [10]. The intercalation [11] of pyridine into  $Zr(HPO_4)_2$  is accompanied by a 7% decrease in the molar volume of the liquid guest. For ethylenediamine entering  $TiS_2$ ,  $NbS_2$ , or  $TaS_2$  a 6% volume change of the guest is observed [12].

The changes in molar volumes of guests 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.

## 2. The Principle of the Method

A closed heterogeneous system formed from a polycrystalline host  $H$  and liquid molecular guest  $G$  decreases its volume during the intercalation process. The infinitesimal change,  $dV$ , of the overall volume of the system caused by the intercalation of the amount  $d[n(H)]$  of the host with the amount  $d[n(G)] = q \cdot d[n(H)]$  of the guest is expressed by the equation

$$dV = d[n(H)] \cdot \{q[V_m(G) - {}^1V_m(G)] + [V_m(H) - {}^1V_m(H)]\} . \quad (4)$$

Denoting the initial overall volume of the system as  $V_0$ , and the starting amount of the host present in the system as  $n_0(H)$ , the overall volume  $V_\tau$  of the system after a time  $\tau$  can be expressed by the equation

$$V_\tau = V_0 - \alpha \cdot n_0(H) \cdot \{q \cdot [V_m(G) - {}^1V_m(G)] + [V_m(H) - {}^1V_m(H)]\} . \quad (5)$$

In this equation,  $\alpha$  denotes the actual degree of the transformation at time  $\tau$ , and the other symbols have the meanings given above. The  $\alpha$  value can be simply obtained by the ratio  $\Delta V_\tau / \Delta V_\infty$ , where  $\Delta V_\tau$  is  $V_\tau - V_0$  and  $\Delta V_\infty$  is the change of the total volume at complete intercalation. Equation (5) is valid if the system contains a stoichiometric excess of the liquid guest. In such a case, the degree of the transformation process is determined by the consumption of the host  $H$ . No other reaction except intercalation can take place in the system, and the host must not dissolve in the liquid  $G$ . It is desirable that the intercalation process is spontaneous with its equilibrium shifted in favour of the formation of the layered complex. Most intercalating systems composed of a solid host and a liquid guest fulfil both these conditions.

Obviously, a precise measurement of the time changes of volume of the system within the interval of  $\alpha = 0$  to 1 will provide the dependence  $\alpha = f(\tau)$ , i.e. the kinetic curve.

## 3. Experimental

The measurements can be carried out in any apparatus allowing:

- (1) Thermostating of the host powder and removal of superficially sorbed gases and moisture from it by evacuation.
- (2) Thermostating of the liquid guest and removal of the dissolved gases by evacuation.

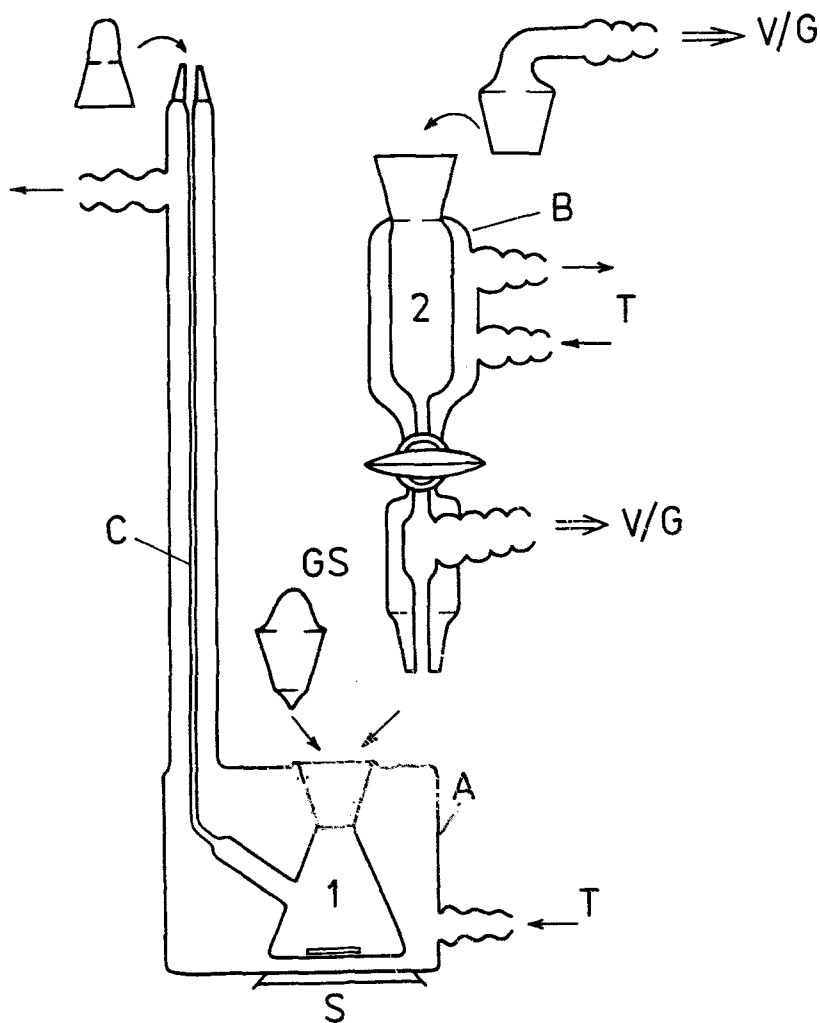


Fig. 1. The apparatus for measuring the volume changes in the heterogeneous intercalating systems.

- (3) Mixing of host and guest without interruption of thermostating, stirring of the suspension obtained, further precise thermostating, and measurement of volume changes of the system from the beginning till the end of the process.

The apparatus designed by us is represented in Figure 1. Section A is formed by the measuring area (ca. 5 mL) with a capillary and thermostating jacket. The extension B serves for the thermostating of the guest and evaporation of the gases dissolved therein. The apparatus was made of a chemically resistant glass with a dilatation coefficient of  $3.2 \times 10^{-6} \text{ K}^{-1}$ .

The measurement procedure consists of the following operations:

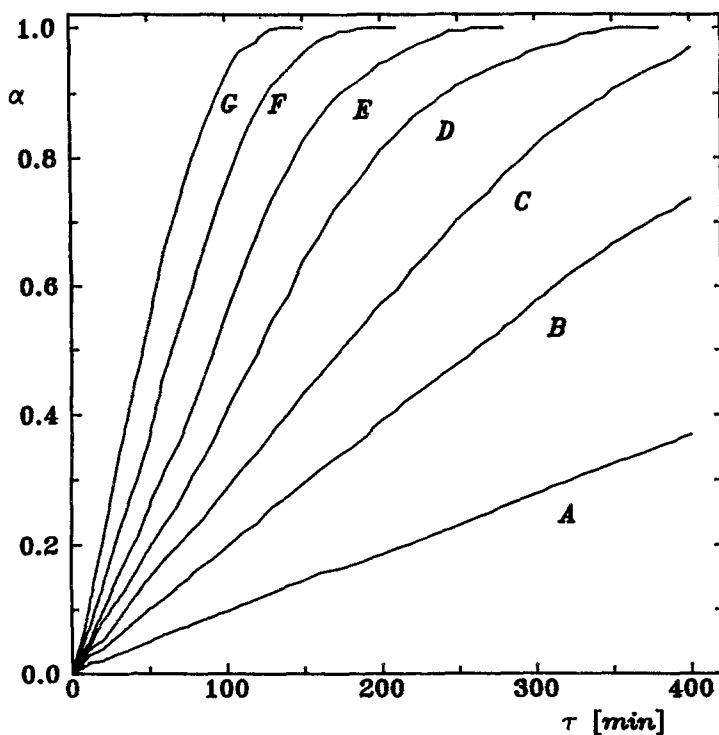


Fig. 2. Kinetic curves of intercalation of liquid 1-butanol into solid  $\text{VOSO}_4$  (dependence of degree of reaction conversion  $\alpha$  on the time  $\tau$ ) measured at the following temperatures: (A) 25°C, (B) 35°C, (C) 40°C, (D) 45°C, (E) 50°C, (F) 55°C, (G) 60°C.

- (1) Introduction of the weighed amount (ca. 0.1 g) of host powder having a definite grain size ( $0.1 \pm 0.01$  mm) into section 1 of part A and pouring the liquid G into section 2 of part B. Connecting the extension B to part A.
- (2) Thermostating of the whole apparatus (T), evacuation of sections 1 and 2 and manifold switching between vacuum and inert gas (V/G).
- (3) Transfer of the liquid guest to the host in section 1 so that the ground connexion is also filled with the liquid. Removal of the extension B, closing of section A with a stopper (GS). Start of magnetic stirrer (S). Adjusting the meniscus in the capillary (C) using a syringe. (All the operations described in (3) should be practised so as to be carried out within 15 seconds.)
- (4) Recording the position of the meniscus in the capillary at definite time intervals.

The position of the meniscus in the capillary was read by means of a cathetometer. The thermostating of the apparatus was accomplished with a thermostat filled with water; the temperature (20–60°C) was maintained with a maximum deviation of  $\pm 0.02^\circ\text{C}$ .

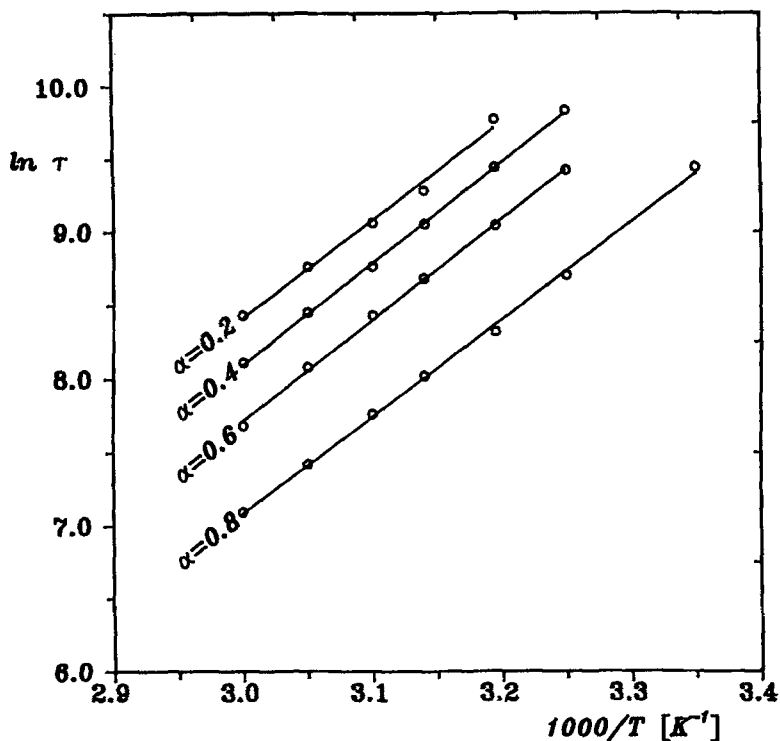


Fig. 3. Graphical determination of activation energy. Dependence of  $\ln \tau$  (s) on the reciprocal value of temperature for reaction conversion degrees  $\alpha = 0.2, 0.4, 0.6$  and  $0.8$ .

A typical value of  $\Delta V_{\infty}$  in the experimentally studied systems (5 mL of liquid and 0.1 g of host) was about 20–30  $\mu\text{L}$ . The values of volume changes were estimated with an error  $\pm 1\%$ .

The anhydrous salts  $\text{VOSO}_4$  and  $\text{VOPO}_4$  were prepared from the corresponding dihydrates by heating at  $300^\circ\text{C}$  *in vacuo* for 4 hours.

The dihydrate  $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$  was obtained by the reaction of  $\text{V}_2\text{O}_5$  with dilute sulfuric acid and  $\text{SO}_2$  [13].  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  was obtained similarly from  $\text{V}_2\text{O}_5$  and dilute phosphoric acid at boiling temperature [14].

The organic compounds used as the guests were dried to a moisture content of 0.1% and distilled under dry inert gas before use for intercalation.

#### 4. Experimental Verification of the Method

The suggested method was used to estimate the time course of intercalations in the systems studied earlier in detail [5,7,15,16]. The hosts were anhydrous vanadyl sulfate and vanadyl phosphate. The two compounds are isostructural, forming a tetragonal layered lattice of  $P4/n$  symmetry group. Aliphatic alcohols, amines,

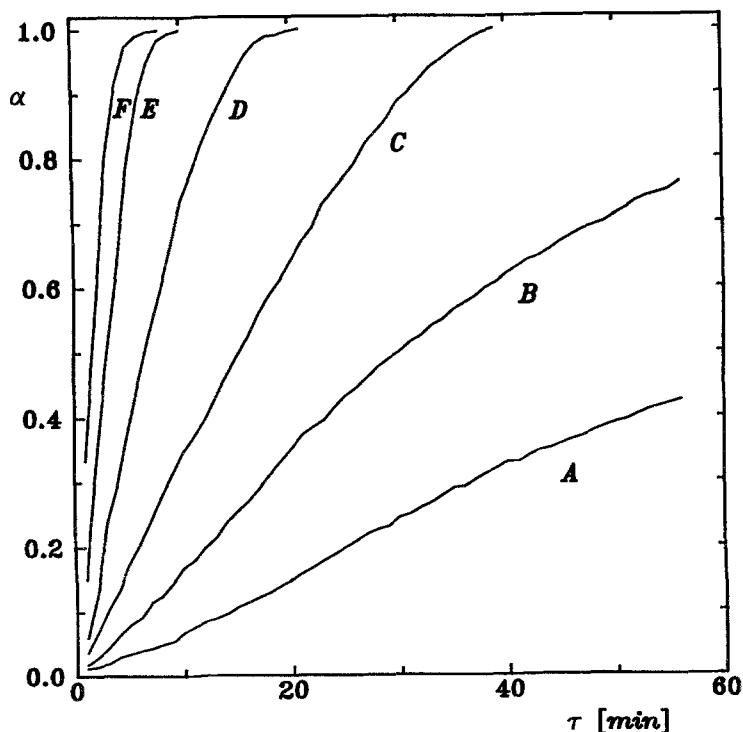
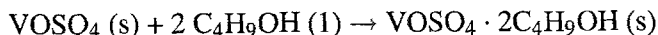


Fig. 4. The acceleration of the intercalation reaction in the system  $\text{VOPO}_4 - \text{C}_2\text{H}_5\text{OH}$  with the water content in the liquid guest (A = 0.8 wt%, B = 1.3%, C = 1.7%, D = 2.7%, E = 3.6% and F = 4.5%  $\text{H}_2\text{O}$ ).

and carboxylic acids were used as guests. The layered intercalation complexes are formed in these systems usually on contact of the polycrystalline anhydrous host with the liquid molecular guest, i.e. in the way for which this method was designed.

Examples of results of applications of the method are given in Figures 2–4. Figure 2 presents the kinetic curves of intercalation of liquid 1-butanol into anhydrous vanadyl sulfate. The reaction is described by the equation:



The measurements were carried out at seven different temperatures. The reproducibility of measurements with a host of constant distribution of grain sizes was excellent.

Figure 3 presents a graphical treatment of the curves from the previous figure. The  $\ln \tau$  values are plotted against the reciprocal values of temperature for the reaction conversion degrees  $\alpha = 0.2, 0.4, 0.6,$  and  $0.8$ . In the whole interval of these  $\alpha$  values the slope of the straight lines obtained is the same. Hence the activation energy has a constant value within the range  $0.2 \leq \alpha \leq 0.8$  and the

temperature range 25–60°C. The value of  $E_a = 0.57$  eV (54.6 kJ mol<sup>-1</sup>) has been determined from the slope of the straight lines in Figure 3.

The rate of the intercalation process could be influenced by moisture in the liquid guests. The most distinct effect of this kind was observed with the system VOPO<sub>4</sub> – C<sub>2</sub>H<sub>5</sub>OH – (H<sub>2</sub>O) in which the intercalation process produces the intercalate VOPO<sub>4</sub> · 2C<sub>2</sub>H<sub>5</sub>OH. The kinetic curves for  $\alpha = f(\tau)$  in Figure 4 show a strong acceleration of the reaction which is caused by the presence of water in the system in amounts as little as 0.1% weight.

The kinetic measurements were also carried out with other similar systems. The respective results will be presented in a future communication.

Obviously, the volumetric method suggested is suitable for kinetic studies of molecular heterogeneous intercalation processes of the type described fulfilling the above-mentioned conditions. The efficiency and correctness of the method suggested could not be verified by comparison with results of any other experimental procedure, because these measurements have not been performed in any other way.

The method suggested can be improved by adopting a more suitable experimental technique, particularly by means of continuous reading of the volume changes of the system and automated handling of the reactants before and at the beginning of the measurements.

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