

A POLYCENTRIC GROWTH MODEL OF GALLIUM ARSENIDE EPITAXIAL LAYERS FROM THE GAS PHASE WITH SIMULTANEOUS DIFFUSION, ADSORPTION AND CHEMICAL REACTION

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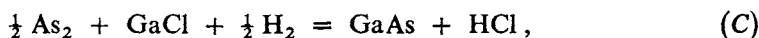
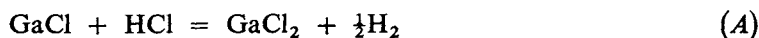
For a quantitative description of the epitaxial growth rate of gallium arsenide, two models are proposed including two rate controlling steps, namely the diffusion of components in the gas phase and the surface reaction. In the models considered, the surface reaction involves a reaction triple — or quadruple centre. In both models three mechanisms are considered which differ one from the other by different adsorption — and impact interaction of reacting particles. In every of the six cases, the pertinent rate equations were derived, and the models have been confronted with the experimentally found dependences of the growth rate on partial pressures of components in the feed. The results are discussed with regard to the plausibility of individual mechanisms and of both models, and also with respect to their applicability and the direction of further investigations.

This paper represents a continuation of the theoretical study¹⁻⁶ of kinetics of the epitaxial layer growth of gallium arsenide from the gas phase. In the latest papers^{5,6}, a single centre and a dual centre model has been formulated including two rate controlling steps, i.e. the diffusion and one of the steps of chemical nature, such as the surface reaction or the adsorption of some of the gaseous components. In the present paper, the polycentric models are investigated, i.e. the cases where the number of active centres involved in the activated complex formation is greater than two. In detail, the cases were studied, where the number of reaction centers is equal to three or four, i.e. triple centre models and the quadruple centre ones.

THEORETICAL

All the ideas concerning the metastable equilibrium in the gas phase and the presence of two rate controlling steps are kept from the previous models^{5,6}. The quantitative

description is based on an analysis carried out previously³ which resulted in respecting three chemical reactions



from which the first two reactions take place at equilibrium in the gas phase. In addition to the corresponding equilibrium relations, all equations remain valid concerning the diffusion of individual components and all equations expressing the steady state conditions. However, the rate equations of the second rate controlling step are different concerning the surface reaction which takes place by a triple centre or a quadruple centre mechanism. Here, the surface reaction is preferred, since, in the previous study⁶, it was shown to be the most probable one from all the steps of chemical nature. In the following, therefore, the pertinent rate equations are derived under the assumption, that the end product is formed in the reaction (C) and that the resulting growth rate is controlled by both the surface reaction and the diffusion. In agreement with the requirement of the activated complex theory, it has been supposed in all cases that in the forward and the backward direction, the same number of reaction centres take part in the formation of the activated complex, i.e. three or four.

Mechanism 3I

In this case, the surface reaction will be considered as the joint-rate controlling step (in addition to the diffusion) which takes place by a three-centre mechanism in such a way that one centre of the triple centre is occupied by an adsorbed atom of arsenic, the second centre is occupied by an adsorbed molecule of the gallium monochloride, and the third centre is occupied by an atom of hydrogen. Then, the stoichiometric equation of the rate controlling step may be written in the following form



so that, in addition to the solid product, an adsorbed molecule of hydrogen chloride is formed and simultaneously, two unoccupied centres are set free, denoted in the above equation as $2n$. Thus, it is a pure adsorption mechanism, where all the reactants and products are present in the adsorbed state. The rate of this rate controlling reaction in both directions will be proportional to the concentration of corresponding

triple centres according to the relation^{1,2}

$$r = k_+ c_{\text{AsGaClH}} - k_- c_{\text{HCl}_2\text{n}}, \quad (3I.1)$$

where c_{AsGaClH} denotes the surface concentration of triple centres occupied by the particles As, GaCl and H, whereas, the $c_{\text{HCl}_2\text{n}}$ represents the surface concentration of triple centres, in which one centre is occupied by a HCl molecule and the remaining two centres are unoccupied. The concentrations of the mentioned triple centres can be expressed in terms of single centre concentrations under assumption that the arrangement of centres on the surface of the substrate is regular, namely, that each centre has the same number of adjacent centres denoted as s , without making an additional assumption concerning its numerical value.

Thus, let us consider one centre occupied by an arsenic atom, which possesses s neighbour centres, some of which being occupied by additional As atoms or by GaCl or HCl molecules and some being unoccupied. Let us determine first the number of dual centres which may be formed by the considered central centre (occupied by an As atom) with the vicinal centres occupied by GaCl molecules. Denoting the fraction of surface centres occupied by GaCl molecules as Θ_{GaCl} , we can write

$$\Theta_{\text{GaCl}} = c_{\text{GaCl}}/L, \quad (3I.2)$$

where L denotes the total concentration of Langmuir adsorption centres, whether occupied or not. If the considered centre, occupied by an As atom, possesses s neighbours, only $s\Theta_{\text{GaCl}}$ from this number will be occupied by the GaCl molecules. Therefore, the considered central As atom form with adjacent centres $s\Theta_{\text{GaCl}}$ dual centres of As–GaCl. Further on, these dual centres can form triple centres in the sense of the equation (3I.1) with additional centres adjoining to the considered central centre which are occupied by hydrogen atoms. If the fraction of surface centres occupied by H atoms is denoted as Θ_{H} , it can be written

$$\Theta_{\text{H}} = c_{\text{H}}/L, \quad (3I.3)$$

and, therefore, one dual As–GaCl centre possesses in the vicinity of the central centre only $(s - 1)$ additional neighbours (since one vicinal centre is already occupied by a GaCl molecule), and from this number, the $(s - 1)\Theta_{\text{H}}$ centres will be occupied by H atoms in average. Accordingly, the considered As–GaCl dual centre can form $(s - 1)\Theta_{\text{H}}$ triple centres in the sense of the equation (3I.1). According to the above consideration, however, the number of such dual centres in the vicinity of the central centre equals to $s\Theta_{\text{GaCl}}$, so that one centre occupied by an As atom can form with its neighbours $s\Theta_{\text{GaCl}}(s - 1)\Theta_{\text{H}}$ triple As–GaCl–H centres in total. Since the number of such As atoms adsorbed on the unit surface of the substrate is

equal to c_{As} , the total concentration of triple As–GaCl–H centres will be given by the expression

$$c_{AsGaClH} = c_{As}s\Theta_{GaCl}(s-1)\Theta_H, \quad (3I.4)$$

or on substituting the definition equations (3I.2) and (3I.3)

$$c_{AsGaClH} = s(s-1)c_{As}c_{GaCl}c_H/L^2. \quad (3I.5)$$

In an analogous way, we arrive at an expression for the concentration of the other type of triple centres appearing in the equation (3I.1), i.e. of the HCl–2n centres. Accordingly, we obtain the relation

$$c_{HCl2n} = s(s-1)c_{HCl}c_n^2/2L^2, \quad (3I.6)$$

where, in contrast to the equation (3I.5), an additional factor of one half appears on the right hand side, since, in the mentioned procedure, each of the unoccupied centres is counted twice, firstly as a part of the dual HCl–n centre, and secondly as the third centre of the reaction triple centre. Substituting the expressions (3I.5) and (3I.6) into the rate equation (3I.1), we obtain on rearrangement

$$r = k_+s(s-1)[c_{As}c_{GaCl}c_H - c_{HCl}c_n^2/2K']/L^2, \quad (3I.7)$$

where the quantity $K' = k_+/k_-$, and has the meaning of the equilibrium constant of the surface reaction (3I.A).

If the surface reaction is the rate controlling step, the adsorption of all particles will take place at equilibrium, and we can write for the surface concentration^{1,2} of GaCl and HCl molecules from the equilibrium condition in adsorption

$$c_{GaCl} = c_n K_{GaCl} p_{GaCl}^* \quad (3I.8)$$

and

$$c_{HCl} = c_n K_{HCl} p_{HCl}^*, \quad (3I.9)$$

where c_n is the surface concentration of unoccupied active centres, and K_{GaCl} and K_{HCl} are equilibrium adsorption constants of corresponding components.

In the adsorption of arsenic, the situation is somewhat different. According to the equation (3I.A), the arsenic reacts in the form of adsorbed atoms, whereas in the gas phase, according to previous analyses³, the arsenic prevails in the form of diatomic molecules As_2 . Therefore, the adsorption of arsenic will be considered to take place in two steps so, that first an As_2 molecule is adsorbed on a dual centre, and in the second step a dissociation involving two single centres takes place. In the case of

such a dissociative adsorption, an expression has been previously⁶ derived for the concentration of adsorbed As atoms

$$c_{\text{As}} = c_n K_{\text{As}_2}^{1/2} (p_{\text{As}_2}^*)^{1/2}, \quad (3I.10)$$

where K_{As_2} represents the equilibrium adsorption constant of arsenic with dissociation. In an analogous way we arrive at a relation for the surface concentration of hydrogen atoms, c_{H}

$$c_{\text{H}} = c_n K_{\text{H}_2}^{1/2} (p_{\text{H}_2}^*)^{1/2}. \quad (3I.11)$$

Substituting the expressions from (3I.8) up to (3I.11) into the equation (3I.7), we obtain after rearranging

$$r = k_+ s(s-1) K_{\text{As}_2}^{1/2} K_{\text{GaCl}} K_{\text{H}_2}^{1/2} c_n^3 \left[(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2} - \frac{p_{\text{HCl}}^*}{2K' K_{\text{As}_2}^{1/2} K_{\text{GaCl}} K_{\text{H}_2}^{1/2} / K_{\text{HCl}}} \right] / L^2, \quad (3I.12)$$

where the concentration of unoccupied centres c_n , can be eliminated by means of the balance of active centres, according to which the total concentration of active centres, L , is equal to the sum of surface concentration of centres both unoccupied and occupied by particles of As, GaCl, H and HCl. Thus we can write

$$c_n + c_{\text{As}} + c_{\text{GaCl}} + c_{\text{H}} + c_{\text{HCl}} = L. \quad (3I.13)$$

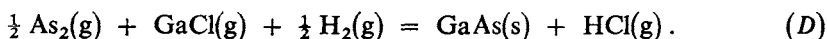
Substituting the expressions from (3I.8) up to (3I.11) into the balance (3I.13), the concentration of unoccupied centres can be expressed as

$$c_n = L / [1 + K_{\text{As}_2}^{1/2} (p_{\text{As}_2}^*)^{1/2} + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{H}_2}^{1/2} (p_{\text{H}_2}^*)^{1/2} + K_{\text{HCl}} p_{\text{HCl}}^*]. \quad (3I.14)$$

After substitution into the relation (3I.12) and after rearranging, the rate equation of the chemical rate controlling step is obtained in the form

$$r = \frac{k_+ s(s-1) L K_{\text{As}_2}^{1/2} K_{\text{GaCl}} K_{\text{H}_2}^{1/2} [(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2} - p_{\text{HCl}}^* / K_{\text{D}}]}{[1 + K_{\text{As}_2}^{1/2} (p_{\text{As}_2}^*)^{1/2} + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{H}_2}^{1/2} (p_{\text{H}_2}^*)^{1/2} + K_{\text{HCl}} p_{\text{HCl}}^*]^3}, \quad (3I.15)$$

where K_{D} is the equilibrium constant of the reaction

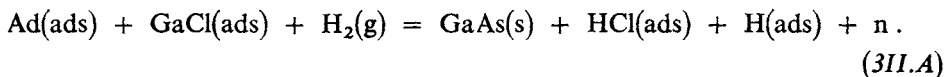


The equilibrium constant can be determined on the basis of purely thermodynamic data of substances appearing in the reaction (D). Its relationship to other equilibrium constants is given by the expression

$$K_D = 2 K' K_{As_2}^{1/2} K_{GaCl} K_{H_2}^{1/2} / K_{HCl} \quad (3I.16)$$

Mechanism 3II

In this mechanism, we will assume that the joint rate controlling step is again the surface reaction taking place by the triple centre mechanism, however, that one molecule of the gallium monochloride is adsorbed on two centres of the reaction triple centre and the remaining centre is occupied by an atom of arsenic. The activated complex will be completed by an impact of the hydrogen molecule so, that the stoichiometric equation of the rate controlling step can be written in the form



After decomposition of the activated complex, a molecule of the hydrogen chloride is formed, adsorbed on the second centre, whereas, the third centre remains unoccupied. Thus, the rate controlling reaction takes place by an impact mechanism and its rate will be given by the equation

$$r = k_+ [c_{AsGaCl} p_{H_2}^* - c_{HClHn} / K'] \quad (3II.1)$$

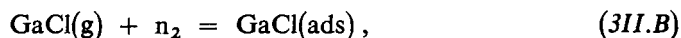
where K' denotes again the equilibrium constant of the surface reaction. To express the concentrations of triple centres, c_{AsGaCl} and c_{HClHn} , in terms of concentrations of simple centres, we will start again with the assumption of their regular arrangement. Let us consider one centre, denoted as the central one, on which the gallium atom of the adsorbed GaCl molecule is adsorbed. Since, according to this model, a GaCl molecule is adsorbed on a dual centre, one of the vicinal centres (vicinal with regard to the central one) will be occupied by a chlorine atom of the GaCl molecule, and the triple centre activated complex can be formed with the participation of an arsenic atom, adsorbed on some of the remaining $(s - 1)$ centres. If we denote the fraction of centres occupied by an arsenic atom as $\theta_{As} = c_{As} / L$, the number of activated complexes which can be formed by one gallium atom adsorbed on the central centre will be equal to $(s - 1) \theta_{As}$. And since the number of gallium atoms, adsorbed on the unit surface, is equal to the surface concentration of adsorbed GaCl molecules, i.e. to the quantity c_{GaCl} , the concentration of reaction triple centres will be equal to

$$c_{AsGaCl} = (s - 1) \theta_{As} c_{GaCl} = (s - 1) c_{As} c_{GaCl} / L \quad (3II.2)$$

(it equals to the surface concentration of triple centre activated complexes). For the surface concentration of arsenic atoms, c_{As} , the same expression is obtained in the case of the dissociative adsorption, as with the previous mechanism, i.e.

$$c_{As} = c_n K_{As_2}^{1/2} (p_{As_2}^*)^{1/2}. \quad (3II.3)$$

With the GaCl molecules, however, it is necessary to consider, that the gallium monochloride molecules are adsorbed on a dual centre according to the equation



where the symbol n_2 denotes an unoccupied dual centre. According to the Eq. (3II.B), the equilibrium of such an adsorption process will be given by the relation

$$c_{GaCl} = c_{n_2} K_{GaCl} p_{GaCl}^*, \quad (3II.4)$$

where c_{n_2} denotes the concentration of free (i.e. unoccupied) dual centres. This concentration may be expressed in terms of simple centres (using a procedure described previously⁶) by the relation

$$c_{n_2} = s c_n^2 / 2L. \quad (3II.5)$$

Combining the equations from (3II.2) up to (3II.5), an expression is obtained for the concentration of triple centres

$$c_{AsGaCl} = s(s-1) K_{As_2}^{1/2} K_{GaCl} c_n^3 (p_{As_2}^*)^{1/2} p_{GaCl}^* / 2L^2. \quad (3II.6)$$

To obtain an expression for the concentration of triple centres in the backward reaction, i.e. for the quantity c_{HClHn} , let us start with the idea of a central centre, which is occupied by a HCl molecule. This central centre can form a dual HCl-H centre with the next centre occupied by a hydrogen atom. If the fraction of centres, occupied by an atom of hydrogen, is denoted as Θ_H , then the central centre can form $s\Theta_H$ such dual centres. These dual centres can then form the reaction triple centres with additional centres, which are adjacent to the considered central centre and which are unoccupied in agreement with the above model. Denoting the fraction of unoccupied centres as $\Theta = c_n/L$, then the number of free centres in the vicinity of the central centre will equal on average to $(s-1)\Theta$, since one of the s vicinal centres is occupied by a hydrogen atom. Consequently, one central centre, occupied by a HCl molecule, can form $s\Theta_H(s-1)\Theta$ triple centres of the HCl-H-n type. Since the number of centres occupied by a HCl molecule on the unit surface is equal to c_{HCl} ,

the concentration of reaction triple HCl-H-n centres will be equal to

$$c_{\text{HClHn}} = c_{\text{HCl}} s \Theta_{\text{H}} (s - 1) \Theta, \quad (3II.7)$$

and on using the definitions of $\Theta_{\text{H}} = c_{\text{H}}/L$ and $\Theta = c_{\text{n}}/L$, the following expression is obtained

$$c_{\text{HClHn}} = s(s - 1) c_{\text{HCl}} c_{\text{H}} c_{\text{n}} / L^2. \quad (3II.8)$$

Since the adsorptions take place at equilibrium, the following relation is valid for the concentration of c_{HCl}

$$c_{\text{HCl}} = c_{\text{n}} K_{\text{HCl}} p_{\text{HCl}}^* \quad (3II.9)$$

and for the equilibrium dissociative adsorption of hydrogen, we obtain (as it was shown above)

$$c_{\text{H}} = c_{\text{n}} K_{\text{H}_2}^{1/2} (p_{\text{H}_2}^*)^{1/2}. \quad (3II.10)$$

By substituting the expressions (3II.9) and (3II.10) into the equation (3II.8), an expression is obtained for the concentration of HClHn triple centres

$$c_{\text{HClHn}} = s(s - 1) c_{\text{n}}^3 K_{\text{HCl}} K_{\text{H}_2}^{1/2} p_{\text{HCl}}^* (p_{\text{H}_2}^*)^{1/2} / L^2. \quad (3II.11)$$

Combining the relations (3II.6) and (3II.11) with the equation (3II.1), we obtain after rearrangement an expression for the reaction rate

$$r = k_+ s(s - 1) K_{\text{As}_2}^{1/2} K_{\text{GaCl}} c_{\text{n}}^3 \left[(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* p_{\text{H}_2}^* - \frac{p_{\text{HCl}}^* (p_{\text{H}_2}^*)^{1/2}}{K' K_{\text{As}_2}^{1/2} K_{\text{GaCl}} / 2 K_{\text{HCl}} K_{\text{H}_2}^{1/2}} \right] / 2L^2, \quad (3II.12)$$

where the concentration of unoccupied centres, c_{n} , will be expressed from the balance of active centres

$$c_{\text{n}} + c_{\text{As}} + c_{\text{GaCl}} + c_{\text{H}} + c_{\text{HCl}} = L. \quad (3II.13)$$

Into this balance, we will substitute for c_{As} from the relation (3II.3), for c_{H} from the equation (3II.10), for c_{HCl} from the expression (3II.9), and for c_{GaCl} from an equation, which will be obtained by combining the (3II.4) and (3II.5), that is

$$c_{\text{GaCl}} = s c_{\text{n}}^2 K_{\text{GaCl}} p_{\text{GaCl}}^* / 2L. \quad (3II.14)$$

By the indicated procedure, we arrive at an expression

$$c_{\text{n}} = 2L / [b + (b^2 + 2s K_{\text{GaCl}} p_{\text{GaCl}}^*)^{1/2}], \quad (3II.15)$$

where

$$b = 1 + K_{\text{H}_2}^{1/2}(p_{\text{H}_2}^*)^{1/2} + K_{\text{As}_2}^{1/2}(p_{\text{As}_2}^*)^{1/2} + K_{\text{HCl}} p_{\text{HCl}}^* . \quad (3II.16)$$

Substitution of this expression into the relation (3II.12) yields the rate equation of the chemical rate controlling step in the final form as

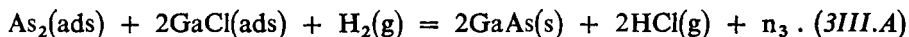
$$r = \frac{4k_+ s(s-1) L K_{\text{As}_2}^{1/2} K_{\text{GaCl}} [(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* p_{\text{H}_2}^* - p_{\text{HCl}}^* (p_{\text{H}_2}^*)^{1/2} / K_{\text{D}}]}{[b + (b^2 + 2s K_{\text{GaCl}} p_{\text{GaCl}}^*)^{1/2}]^3} . \quad (3II.17)$$

The quantity b in this equation is given by the expression (3II.16), and K_{D} denotes again the thermodynamic equilibrium constant of the reaction (D). Its relationship to other equilibrium constants appearing in this mechanism is given by the expression

$$K_{\text{D}} = K' K_{\text{As}_2}^{1/2} K_{\text{GaCl}} / 2 K_{\text{HCl}} K_{\text{H}_2}^{1/2} . \quad (3II.18)$$

Mechanism 3III

In this mechanism, we will assume that one centre of the reaction triple centre is occupied by an As_2 molecule and that each of the two remaining centres is occupied by one molecule of the gallium monochloride. The activated complex will be completed by an impact of the hydrogen molecule so, that the stoichiometric equation of the surface reaction (rate controlling step) assumes the form:



After decomposition of the activated complex, two molecules of the hydrogen chloride are formed which are leaving for the gas phase, and an unoccupied triple centre is regenerated. Thus, the rate of the surface reaction will be given by the equation

$$r = k_+ c(\text{As}_2 \text{ 2GaCl}) p_{\text{H}_2}^* - c(n_3) (p_{\text{HCl}}^*)^2 / K' , \quad (3III.1)$$

where K' denotes the equilibrium constant of the surface reaction. To express the surface concentration of triple centres, $c(\text{As}_2 \text{ 2GaCl})$, let us consider one centre occupied by an As_2 molecule which possesses s neighbour centres. On these s centres, a molecule of the gallium monochloride can be adsorbed, and on the remaining $(s-1)$ centres, the second GaCl molecule is adsorbed so, that, in the vicinity of the central centre, the number of couples occupied by two GaCl molecule is equal to $s \Theta_{\text{GaCl}}(s-1) \Theta_{\text{GaCl}}/2$.

Here, the factor of one half appears, because each couple is counted twice in this procedure. And since the concentration of centres, occupied by the As_2 molecules, is equal to c_{As_2} , the total concentrations of $c(\text{As}_2 \text{ 2GaCl})$ triple centres will be given

by the relation

$$c(\text{As}_2\text{GaCl}) = s(s-1) c_{\text{As}_2} c_{\text{GaCl}}^2 / 2L^2, \quad (3III.2)$$

if the definition relation $\Theta_{\text{GaCl}} = c_{\text{GaCl}}/L$ is used. In an analogous way, we can arrive at an expression for the concentration of unoccupied triple centres $c(n_3)$

$$c(n_3) = s(s-1) c_n^3 / 6L^2, \quad (3III.3)$$

where $6 = 3!$ represents the number of permutations of three unoccupied centres, forming a triple centre, which indicate how many times each centre is counted in this procedure. By substituting the relations (3III.2) and (3III.3), the rate equation is transformed to the form

$$r = k_+ s(s-1) [c_{\text{As}_2} c_{\text{GaCl}}^2 p_{\text{H}_2}^* - c_n^3 (p_{\text{HCl}}^*)^2 / 3K'] / 2L^2, \quad (3III.4)$$

where the surface concentrations c_{As_2} and c_{GaCl} are given by the conditions of adsorption equilibrium

$$c_{\text{As}_2} = c_n K_{\text{As}_2} p_{\text{As}_2}^* \quad (3III.5)$$

and

$$c_{\text{GaCl}} = c_n K_{\text{GaCl}} p_{\text{GaCl}}^*. \quad (3III.6)$$

Combining the equations from (3III.4) up to (3III.6), a relation is obtained

$$r = k_+ s(s-1) K_{\text{As}_2} K_{\text{GaCl}}^2 c_n^3 [p_{\text{As}_2}^* (p_{\text{GaCl}}^*)^2 p_{\text{H}_2}^* - (p_{\text{HCl}}^*)^2 / 3K' K_{\text{As}_2} K_{\text{GaCl}}^2] / 2L^2, \quad (3III.7)$$

where the concentration of unoccupied centres is to be determined from a balance over the active centres

$$c_n + c_{\text{As}_2} + c_{\text{GaCl}} = L. \quad (3III.8)$$

Substituting the relations (3III.5) and (3III.6) into the balance (3III.8), we obtain an expression for the concentration of unoccupied centres

$$c_n = L / (1 + K_{\text{As}_2} p_{\text{As}_2}^* + K_{\text{GaCl}} p_{\text{GaCl}}^*) \quad (3III.9)$$

and, after its substitution into the relation (3III.7) we arrive at a rate equation in its final form

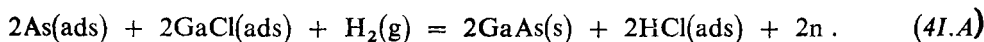
$$r = \frac{k_+ s(s-1) (L/2) K_{\text{As}_2} K_{\text{GaCl}}^2 [p_{\text{As}_2}^* (p_{\text{GaCl}}^*)^2 p_{\text{H}_2}^* - (p_{\text{HCl}}^*)^2 / K_D^2]}{[1 + K_{\text{As}_2} p_{\text{As}_2}^* + K_{\text{GaCl}} p_{\text{GaCl}}^*]^3}. \quad (3III.10)$$

In the above equation, the K_D denotes the thermodynamic equilibrium constant of the reaction (D) and its relation to other equilibrium constants is given by the equation

$$K_D^2 = 3K'K_{As_2}K_{GaCl}^2 \quad (3III.11)$$

Mechanism 4I

It will be considered in this case that the rate controlling step is the surface reaction taking place by a quadruple centre mechanism in such a way, that two centres are occupied by atoms of arsenic and that, on the next two centres, the molecules of gallium monochloride are adsorbed. The activated complex is completed by an impact of the hydrogen molecule from the gas phase onto the reaction quadruple centre so, that the stoichiometric equation of the rate controlling step can be written in the following form:



In addition to the solid product, two adsorbed molecules of the hydrogen chloride are formed in this reaction, and two unoccupied centres are set free simultaneously. Thus, we obtain an impact mechanism, which however, in contrast to the previous case, takes place with participation of a quadruple centre. In the given case, the rate of the surface reaction will be given by the following relation

$$r = k_+ [c_{2As_2GaCl} p_{H_2}^* - c_{2HCl_{2n}} / K'] \quad (4I.1.)$$

where K' denotes the equilibrium constant of the surface reaction which is equal to the ratio of rate constants in both directions, i.e. $K' = k_+ / k_-$. To express the concentration of quadruple centres, c_{2As_2GaCl} and $c_{2HCl_{2n}}$, in terms of simple centre concentrations, let us start with the assumption of their regular arrangement on the surface. Let us assume for instance, that an atom of arsenic is adsorbed on a selected central centre, and that a vicinal centre is occupied likewise by an arsenic atom. If the Θ_{As} denotes the fraction of centres occupied by arsenic atoms, then the number of As-As couples in the vicinity of the central centre will be equal to $s\Theta_{As}$. On the next $(s - 1)$ centres, a molecule of the gallium monochloride can be adsorbed, and on the next $(s - 2)$ centres, another GaCl molecule can be adsorbed. Thus one central centre, occupied by an arsenic atom, can form $s\Theta_{As}(s - 1)\Theta_{GaCl}(s - 2)\Theta_{GaCl}$ quadruple centres with its neighbours, if Θ_{GaCl} denotes the fraction of centres occupied by molecules of the gallium monochloride. And since the number of centres occupied by arsenic atoms on the unit surface is equal to c_{As} , the concentration of the reaction quadruple centres (As-As-GaCl-GaCl) will be equal to

$$c_{2As_2GaCl} = \frac{1}{2}c_{As}s\Theta_{As}(s - 1)\Theta_{GaCl}(s - 2)\Theta_{GaCl} \quad (4I.2)$$

since, in this procedure, each atom of arsenic is counted twice, once as a central centre and secondly as a vicinal one. If the definition equations $\Theta_{As} = c_{As}/L$ and $\Theta_{GaCl} = c_{GaCl}/L$ are substituted into the expression (4I.2), the relation (4I.2) is transformed to

$$c_{2As_2GaCl} = s(s-1)(s-2)c_{As}^2c_{GaCl}^2/2L^3. \quad (4I.3)$$

In the case of the dissociative adsorption, we obtain for the surface concentration of arsenic atoms, c_{As} , the same equation as above so that we can write

$$c_{As} = c_n K_{As_2}^{1/2} (p_{As_2}^*)^{1/2}. \quad (4I.4)$$

For the simple molecular adsorption of the gallium monochloride, the following will be valid¹

$$c_{GaCl} = c_n K_{GaCl} p_{GaCl}^*. \quad (4I.5)$$

On substitution of expression (4I.4) and (4I.5) into Eq. (4I.3), the relation follows

$$c_{2As_2GaCl} = s(s-1)(s-2) K_{As_2} K_{GaCl}^2 c_n^4 (p_{As_2}^*)^2 (p_{GaCl}^*)^2 / 2L^3. \quad (4I.6)$$

To obtain an expression for the concentration of quadruple centres in the backward reaction, i.e. for the quantity $c_{2HCl_{2n}}$, let us start from the idea of a central centre occupied by a HCl molecule, which consequently forms a dual HCl-HCl centre with the next centre occupied by another molecule of hydrogen chloride. This dual centre will form with an unoccupied centre a triple HCl-HCl-n centre, which forms a quadruple centre of HCl-HCl-n-n with the next free centre. In an analogous way, in which we have arrived at the equation (4I.3), an expression is obtained for the concentration of quadruple centres, $c_{2HCl_{2n}}$

$$c_{2HCl_{2n}} = s(s-1)(s-2)c_{HCl}^2c_n^2/2L^3. \quad (4I.7)$$

Since for the simple molecular adsorption of the hydrogen chloride the following is valid^{1,2}

$$c_{HCl} = c_n K_{HCl} p_{HCl}^*, \quad (4I.8)$$

a relation is obtained on combining the last two equations

$$c_{2HCl_{2n}} = s(s-1)(s-2) K_{HCl}^2 c_n^4 (p_{HCl}^*)^2 / 2L^3. \quad (4I.9)$$

The substitution of relations (4I.6) and (4I.9) into Eq. (4I.1) and a rearrangement yields an expression for the reaction rate

$$r = k_+ s(s-1)(s-2) K_{As_2} (K_{GaCl})^2 c_n^4 \left[p_{As_2}^* (p_{GaCl}^*)^2 p_{H_2}^* - \frac{(p_{HCl}^*)^2}{K' K_{As_2} K_{GaCl}^2 / K_{HCl}^2} \right] / 2L^3, \quad (4I.10)$$

where the concentration of unoccupied centres, c_n , will be expressed from a balance of active centres which, in the present case, is of the following form

$$c_n + c_{As} + c_{GaCl} + c_{HCl} = L. \quad (4I.11)$$

Into this balance, we will substitute for c_{As} from the relation (4I.4), for c_{GaCl} from the equation (4I.5), and for c_{HCl} from the expression (4I.8), so that we obtain

$$c_n = L / (1 + K_{As_2}^{1/2} (p_{As_2}^*)^{1/2} + K_{GaCl} p_{GaCl}^* + K_{HCl} p_{HCl}^*). \quad (4I.12)$$

Substituting this expression into the relation (4I.10) and rearranging, we arrive at a rate equation of the chemical rate controlling step in the form

$$r = \frac{k_+ s(s-1)(s-2)(L/2) K_{As_2} K_{GaCl}^2 [p_{As_2}^* (p_{GaCl}^*)^2 p_{H_2}^* - (p_{HCl}^*)^2 / K_D]}{[1 + K_{As_2}^{1/2} (p_{As_2}^*)^{1/2} + K_{GaCl} p_{GaCl}^* + K_{HCl} p_{HCl}^*]^4}. \quad (4I.13)$$

In this equation, K_D denotes again the thermodynamic equilibrium constant of the reaction (D) and its relation to other equilibrium constants appearing in this mechanism is given by the equation

$$K_D (K')^{1/2} K_{As_2}^{1/2} K_{GaCl} / K_{HCl}. \quad (4I.14)$$

Mechanism 4II

This quadruple centre mechanism will differ from the above one only in that the two molecules of hydrogen chloride, which are formed in the surface reaction, will not be present in an adsorbed state, but escape directly for the gas phase so, that an unoccupied quadruple centre is set free simultaneously. In this case, the stoichiometric equation will be of the form



where the symbol n_4 denotes an unoccupied quadruple centre, and the rate equation assumes the form

$$r = k_+ [c_{2As2GaCl} p_{H_2}^* - c(n_4) (p_{HCl}^*)^2 / K']. \quad (4II.1)$$

The surface concentration $c_{2As2GaCl}$ will be given by the same expression as in the previous mechanism, i.e. by the equation (4I.6). By extending the procedure given

above, we obtain a relation for the concentration of unoccupied quadruple centres $c(n_4)$

$$c(n_4) = s(s-1)(s-2)c_n^4/24L^3, \quad (4II.2)$$

where $24 = 4!$. Substituting both mentioned expressions into the rate equation (4II.1) we obtain after a rearrangement

$$r = k_+s(s-1)(s-2)K_{As_2}K_{GaCl}^2c_n^4 \left[p_{As}^*(p_{GaCl}^*)^2 p_{H_2}^* - \frac{(p_{HCl}^*)^2}{12K'K_{As_2}K_{GaCl}^2} \right] / 2L^3, \quad (4II.3)$$

where the concentration of unoccupied centres is to be determined from the balance

$$c_n + c_{As} + c_{GaCl} = L. \quad (4II.4)$$

Substituting the relations (4I.4) and (4I.5) into this balance, we obtain

$$c_n = L / (1 + K_{As_2}^{1/2}(p_{As_2}^*)^{1/2} + K_{GaCl}p_{GaCl}^*) \quad (4II.5)$$

and substituting the last expression into the relation (4II.3), we arrive at a rate equation of the surface reaction in its final form

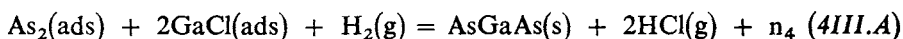
$$r = \frac{k_+s(s-1)(s-2)(L/2)K_{As_2}K_{GaCl}^2 [p_{As_2}^*(p_{GaCl}^*)^2 p_{H_2}^* - (p_{HCl}^*)^2/K_D']}{[1 + K_{As_2}^{1/2}(p_{As_2}^*)^{1/2} + K_{GaCl}p_{GaCl}^*]^4}. \quad (4II.6)$$

The thermodynamic equilibrium constant K_D , appearing in this equation, is related to other equilibrium constants by

$$K_D = (12K'K_{As_2})^{1/2} K_{GaCl}. \quad (4II.7)$$

Mechanism 4III

The difference between the present quadruple centre mechanism and the preceding one will consist in that the arsenic will not be adsorbed in an atomic form, but in the form of diatomic molecules As_2 which will be adsorbed on a free dual centre. In this case, the stoichiometric equation of the surface reaction assumes the form



and the corresponding rate equation can be written as

$$r = k_+[c(As_22GaCl)p_{H_2}^* - c(n_4)(p_{HCl}^*)^2/K']. \quad (4III.1)$$

To calculate the concentration of quadruple centres $c(\text{As}_2\text{GaCl})$, let us consider one centre occupied by an arsenic atom from the diatomic As_2 molecule, the other atom of which is adsorbed on one from the s adjacent centres. On the next $(s - 1)$ centres, a molecule of the gallium monochloride is adsorbed, and on the remaining $(s - 2)$ centres, the second GaCl is adsorbed. In the vicinity of the considered centre, the number of adsorbed GaCl - GaCl couples will thus be equal to $(s - 1) \Theta_{\text{GaCl}} \cdot (s - 2) \Theta_{\text{GaCl}}$, and the concentration of quadruple centres, $c(\text{As}_2\text{GaCl})$ will be given by the expression

$$c(\text{As}_2\text{GaCl}) = c_{\text{As}_2}(s - 1)(s - 2) \Theta_{\text{GaCl}}^2 = c_{\text{As}_2}(s - 1)(s - 2) c_{\text{GaCl}}^2 / L^2. \quad (4III.2)$$

The relations for surface concentrations of c_{GaCl} and of c_{As_2} follow from the conditions of equilibrium of adsorption of these components

$$c_{\text{GaCl}} = c_n K_{\text{GaCl}} p_{\text{GaCl}}^* \quad (4III.3)$$

and

$$c_{\text{As}_2} = c_{n_2} K_{\text{As}_2} p_{\text{As}_2}^* = s c_n^2 K_{\text{As}_2} p_{\text{As}_2}^* / 2L, \quad (4III.4)$$

since between the concentration of unoccupied dual centres $c(n_2)$ and the concentration of simple free centres, the following relation is valid

$$c_{n_2} = s c_n^2 / 2L. \quad (4III.5)$$

By substituting the expressions (4III.3) and (4III.4) into the relation (4III.2), the concentration of quadruple centres is obtained as

$$c(\text{As}_2\text{GaCl}) = s(s - 1)(s - 2) K_{\text{As}_2} K_{\text{GaCl}}^2 p_{\text{As}_2}^* (p_{\text{GaCl}}^*)^2 c_n^4 / 2L^3 \quad (4III.6)$$

and the expressions for the concentration of unoccupied quadruple centres $c(n_4)$ will be the same as in the preceding mechanism, i.e. it will be given by the relation (4II.2). By substituting the expressions (4III.6) and (4II.2) into the rate equation (4III.1), the following relation is obtained

$$r = k_+ s(s - 1)(s - 2) K_{\text{As}_2} K_{\text{GaCl}}^2 c_n^4 \left[p_{\text{As}_2}^* (p_{\text{GaCl}}^*)^2 p_{\text{H}_2}^* - \frac{(p_{\text{HCl}}^*)^2}{12 K' K_{\text{As}_2} K_{\text{GaCl}}^2} \right] / 2L^3, \quad (4III.7)$$

where the concentration of unoccupied centres will be determined from a balance, which is here of the form

$$c_n + c_{\text{As}_2} + c_{\text{GaCl}} = L. \quad (4III.8)$$

By substituting the relations (4III.3) and (4III.4) into the above balance, a quadratic equation results and, by its solution, an expression for the concentration of the unoccupied centres is obtained

$$c_n = 2L / \{1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + [(1 + K_{\text{GaCl}} p_{\text{GaCl}}^*)^2 + 2sK_{\text{As}_2} p_{\text{As}_2}^*]^{1/2}\}. \quad (4III.9)$$

The substitution of this expression into the relation (4III.7) leads to the rate equation of the surface reaction in its final form

$$r = \frac{8k_+s(s-1)(s-2)LK_{\text{As}_2}K_{\text{GaCl}}^2[p_{\text{As}_2}^*(p_{\text{GaCl}}^*)^2 p_{\text{H}_2}^* - (p_{\text{HCl}}^*)^2/K_D^2]}{\{1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + [(1 + K_{\text{GaCl}} p_{\text{GaCl}}^*)^2 + 2sK_{\text{As}_2} p_{\text{As}_2}^*]^{1/2}\}^4}, \quad (4III.10)$$

where the thermodynamic equilibrium constant K_D of the reaction (D) is related to other equilibrium constants of this mechanism by

$$K_D^2 = 12K'K_{\text{As}_2}K_{\text{GaCl}}^2. \quad (4III.11)$$

Comparison of Polycentric Models with Experiment

The resulting rate equations expressing three mechanisms of the triple centre model and three mechanisms of the quadruple centre model have been compared with the same experimental set as in the previous paper⁶. To evaluate the rate constants and the equilibrium adsorption constants, the same procedures has been applied. The results of this mathematical treatment are directly comparable with the results of the single centre model and for the dual site model⁶. The individual models and mechanisms are summarized in Table I and the final results of computations are contained in Table II.

TABLE I
Summary of models and mechanisms

Notation	Model	Occupation of reaction centre	
		in forward direction	in backward direction
3 I	triple centre	As-GaCl-H	HCl-n-n
3 II	triple centre	As-Ga-Cl	HCl-H-n
3 III	triple centre	As ₂ -GaCl-GaCl	n-n-n
4 I	quadruple centre	As-As-GaCl-GaCl	HCl-HCl-n-n
4 II	quadruple centre	As-As-GaCl-GaCl	n-n-n-n
4 III	quadruple centre	As ₂ -GaCl-GaCl	n-n-n-n

The constants denoted with an asterisk which are given in Table II with the mechanism 3I represent cumulative constants defined by the relations

$$k_+^* = k_+ / (1 + K_{H_2}^{1/2})^{1/3} \quad (3I.17)$$

$$K_{GaCl}^* = K_{GaCl} / (1 + K_{H_2}^{1/2})^{1/3} \quad (3I.18)$$

$$K_{As_2}^* = K_{As_2} / (1 + K_{H_2}^{1/2})^{1/3} \quad (3I.19)$$

$$K_{HCl}^* = K_{HCl} / (1 + K_{H_2}^{1/2})^{1/3} \quad (3I.20)$$

This situation arises from the fact that, in the given set of experimental data, the partial pressure of hydrogen has been kept at a constant value so that it was not feasible to evaluate the equilibrium adsorption constant of hydrogen K_{H_2} separately, but only in groupings with other constants according to the relations from (3I.17) up to (3I.20).

TABLE II

Computed results of triple centre and quadruple centre models

Mechanisms	Rate constant		Equilibrium adsorption constant		Standard deviation
	meaning ^a	value	meaning ^a	value	
3 I	$k_+^* s(s-1) L K_{H_2}^{1/2}$	$8.436 \cdot 10^{-6}$	$K^*(GaCl)$	41.1	4.0
			$K^*(As_2)$	0	
			$K^*(HCl)$	0	
3 II	$k_+ s(s-1) L$	$5.877 \cdot 10^{-6}$	$K(GaCl)$	135.7	4.0
			$K(H_2)$	0	
			$K(As_2)$	0	
			$K(HCl)$	0	
3 III	$k_+ s(s-1) L$	$1.843 \cdot 10^{-5}$	$K(GaCl)$	227.6	2.6
			$K(As_2)$	94.36	
4 I	$k_+ s(s-1)(s-2) L$	$1.593 \cdot 10^{-4}$	$K(GaCl)$	133.1	2.6
			$K(As_2)$	9.345	
			$K(HCl)$	0	
4 II	$k_+ s(s-1)(s-2) L$	$1.593 \cdot 10^{-4}$	$K(GaCl)$	133.1	2.6
			$K(As_2)$	9.345	
4 III	$k_+ (s-1)(s-2) L$	$8.682 \cdot 10^{-6}$	$K(GaCl)$	131.9	2.7
			$K(As_2)$	154.3	

^a Chemical formulae are given in parentheses.

RESULTS AND DISCUSSION

As it is evident from Table II, the most probable mechanism of the triple centre model seems to be, the one denoted as 3III. Here an adsorbed As_2 molecule reacts with two molecules of the gallium monochloride.

In the quadruple centre model, all considered mechanisms exhibit practically the same probability and the values of constants of the mechanism 4I and 4II are the same. This situation stems from that, in the mechanism 4I, the adsorption of the hydrogen chloride has been considered. In the backward direction, however, a zero value of the equilibrium adsorption constant of the hydrogen chloride results from the computations, and this means physically that the HCl adsorption is negligible. The mechanism 4I degenerates in this way to the mechanism 4II, in which the adsorption of the hydrogen chloride has been excluded a priori, and therefore, the same values of constants are resulting in both cases.

The most important result of the present study, however, is the following one. It follows namely from Table II quite clearly that, in passing from the triple centre model to the quadruple centre one, the standard deviation does not decrease, i.e. the accuracy of reproducing the experimental data increases no more. Comparing these results with the previous ones⁶, it is seen, that the standard deviation of the most probable dual centre model is the same as in the case of the most probable polycentric models. Besides, it is noteworthy, that the same level of reproduction has been achieved in the case of the dual centre model with two adjustable parameters, whereas, in the case of triple centre and quadruple centre models, with three parameters. The whole situation may be summarized concisely in the following way: the probability of the model increases only by passing from the single centre to the dual centre model, and does not change by continued increasing of the model complexity. Summarizing all the existing results, we arrive at a conclusion that the model of the reaction dual centre is shown to be the most suitable from the both gnoseological and practical points of view.

This result represents a termination of the phase, which consisted in increasing the complexity of the model by increasing the number of reaction centres. Simultaneously it represents a reliable starting point in the next phase, i.e. in the investigation of centres of different sorts, at least of two sorts in the first approximation.

Ending this phase of study, it is interesting to note that the equilibrium adsorption constant of the hydrogen chloride assumed a zero value in all the twenty three mechanisms (with only one exception), which have been up to now studied.

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