A DUAL SITE GROWTH MODEL OF GALLIUM ARSENIDE EPITAXIAL LAYERS FROM THE GAS PHASE

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‵ɔr a quantitative description of the epitaxial growth rate of gallium arsenide, a model is proposed ∶luding two rate controlling steps. One of these steps is the diffusion of gaseous components between the gas phase and the epitaxial layer surface, and the other step is of chemical nature, *i.e.* either the surface reaction or adsorption or desorption of one of the gaseous components. In the model considered, an active dual site is involved in the second rate controlling step, and twelve mechanisms are proposed for which the pertinent rate equations are derived. The individual mechanisms differ one from the other not only by the kind of the rate controlling step but also by the occupation of the dual site, *viz.* in the both direct and reversed direction. The proposed model is confronted with the dependences of the growth rate on partial pressures of components in the feed found by experiment. The results are discussed with regard to the phausibility of individual mechanisms and of the model as a whole, and also with respect to their applicability and to the direction of further investigations.

This paper represents a continuation of the theoretical study[1] of kinetics of the epitaxial layer growth of gallium arsenide from the gas phase, in which a single site 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 this paper, a model is proposed in which the joint rate controlling step of chemical nature takes place by a dual site mechanism, and which appears *a priori* as a more realistic one than the single site model considered previously. Since some of the ideas in the present model are identical with those in the previous one, we focus our attention first of all to changes as compared with the previous model.
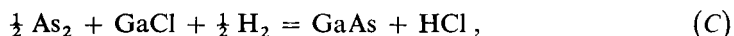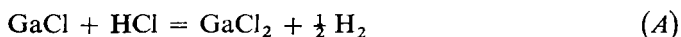
THEORETICAL

Basic Model Ideas

All ideas from the previous model[1] concerning the metastable equilibrium in the gas phase and the existence of two rate controlling steps remain here conserved. The essential difference consists in the number of active centres which are taking part in the formation of an active complex in the rate controlling step of chemical nature. While the model considered previously was based on a single centre mechanism, which appeared as the simplest model of this type, here an idea of an active dual centre is applied principially in all the variants, concerning the surface reaction particularly or in the adsorption of gaseous reactants or in the desorption of the gaseous product.

Quantitative Description of Dual Centre Model

The quantitative description stems from an analysis carried out previously[2,3] which resulted in respecting three chemical reactions

$$GaCl + HCl = GaCl_2 + \tfrac{1}{2} H_2 \tag{A}$$

$$2\, As_2 = As_4 \tag{B}$$

$$\tfrac{1}{2} As_2 + GaCl + \tfrac{1}{2} H_2 = GaAs + HCl, \tag{C}$$

from which the first two reactions take place at equilibrium in the homogeneous gas phase and closely at the surface of the substrate. In addition to the corresponding equilibrium relations, all equations remain valid concerning the diffusion of individual components and also all equations expressing the steady state conditions. However, the rate equations of the second rate controlling step are different, concerning either the surface reaction or of the adsorption of one of the components.

In the following, equations are derived describing the rate of the joint rate controlling step of chemical nature, which together with the diffusion controls the resulting growth rate of epitaxial layers of the gallium arsenide. From the steps of chemical nature, the following ones are considered; the surface reaction proper, the adsorption of reactants or the desorption of gaseous products. In every case it is assumed, that the rate controlling step takes place by a dual centre mechanism, *i.e.* that two adjacent centres take part in the formation of an activated complex in the rate controlling step, both in the direct and reversed direction, in agreement with the requirement of the activated complex theory[4,5]. On this basis, the rate equations have been derived for twelve feasible mechanisms, which differ one from the other not only by the rate controlling step but also by the occupation of the dual centre, both in the direct

and reversed direction. The summary of all considered mechanisms is contained in Table I, where in addition to the rate controlling step, the occupation of the dual centre in both directions is characterized more closely, together with the designation of individual mechanisms which is used in the following text.

Mechanism I

If the rate controlling step is the surface reaction, we consider first the case, where one molecule of the gallium chloride is adsorbed on each centre of the dual centre. Then, the rate controlling reaction will be of the following form

$$As_2(g) + 2 GaCl(ads) + H_2(g) = 2 GaAs(s) + 2 HCl(ads) \quad (I.A)$$
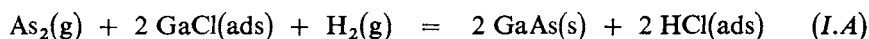
and its rate will be given by the relation[4,5]

$$r = k_+ p^*_{As_2} c_{2GaCl} p^*_{H_2} - k_- c_{2HCl}, \quad (I.1)$$

where c_{2GaCl} and c_{2HCl} denote the surface concentrations of dual centres occupied by two molecules of gallium chloride or of hydrogen chloride. Concentrations of these dual centres can be expressed in terms of concentrations of the simple centres under assumption of regular arrangement of centres on the surface of substrate.

TABLE I
Dual centre mechanisms

Designation	Rate controlling step of chemical nature	Occupation of dual centre	
		In forward direction	In backward direction
I	Surface reaction	2 GaCl	2 HCl
II	Surface reaction	GaCl	HCl
III	Surface reaction	As$_2$	2 HCl
IV	Surface reaction	As GaCl	HCl
V	Adsorption of GaCl	GaCl	HCl
VI	Adsorption of GaCl	2 GaCl	2 HCl
VII	Adsorption of GaCl	As GaCl	HCl
VIII	Adsorption of As$_2$	As$_2$	HCl
IX	Desorption of HCl	HCl	GaCl
X	Desorption of HCl	2 HCl	2 GaCl
XI	Desorption of HCl	HCl	As GaCl
XII	Desorption of HCl	2 HCl	As$_2$

This means, that each centre is surrounded by the same number of adjacent centres denoted as s, without making an additional assumption concerning its numerical value. Thus, one centre occupied by the GaCl molecule will possess s neighbours, some of which being occupied by additional molecules of GaCl or HCl and some being unoccupied. Denoting the fraction of surface centres occupied by GaCl molecules as Θ_{GaCl}, we can write

$$\Theta_{GaCl} = C_{GaCl}/L, \tag{I.2}$$

where L denotes the total concentration of Langmuir adosrption centres, whether uccupied or not. If the considered centre, occupied by a GaCl molecule, possesses s neighbours, only $s\Theta_{GaCl}$ from this number will be occupied by the GaCl molecules. Therefore, one molecule of GaCl can form with adjacent centres occupied by GaCl molecules $s\Theta_{GaCl}$ reaction dual centres in the sense of equation $(I.1)$. Since, however, the number of such molecules adsorbed on the unit surface of the substrate is equal to c_{GaCl}, the total concentration of dual centres occupied by two GaCl molecules will be given by the expression

$$c_{2GaCl} = (1/2)\, c_{GaCl} s \Theta_{GaCl}, \tag{I.3}$$

or on substituting from the relation $(I.2)$ by

$$c_{2GaCl} = (s/2L)\, c_{GaCl}^2. \tag{I.4}$$

In these equations, the factor of one half results from the fact, that in this way of summation each dual centre is counted twice; firstly when the given adsorbed GaCl molecule is taken as a central one, and the next time, when it is counted as adjacent to another centre.

In an analogous way, we arrive at an expression for the concentration of dual centres occupied by two HCl molecules, $i.e.$ for the quantity c_{2HCl}

$$c_{2HCl} = (s/2L)\, c_{HCl}^2. \tag{I.5}$$

Substituting the expressions $(I.4)$ and $(I.5)$ into the equation $(I.1)$, we obtain on rearrangement

$$r = k_+ s [p_{As_2}^* p_{H_2}^* c_{GaCl}^2 - (c_{HCl}^2/K')]/2L, \tag{I.6}$$

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

If the surface reaction is the rate controlling step, the adsorption of both GaCl and HCl molecules will take place at equilibrium, so that we can write for their

surface concentrations[4,5] from the equilibrium condition in adsorption

$$c_{\text{GaCl}} = c_n K_{\text{GaCl}} p_{\text{GaCl}}^* \tag{I.7}$$

and

$$c_{\text{HCl}} = c_n K_{\text{HCl}} p_{\text{HCl}}^*, \tag{I.8}$$

where c_n is the surface concentration of unoccupied active centres, and K_{GaCl} and K_{HCl} are equilibrium adsorption constants of pertinent components. Substituting the expressions $(I.7)$ and $(I.8)$ into the equation $(I.6)$, we obtain after rearrangement

$$r = (k_+ s/2L) K_{\text{GaCl}}^2 c_n^2 \left[p_{\text{As}_2}^* (p_{\text{GaCl}}^*)^2 \, p_{\text{H}_2}^* - \frac{(p_{\text{HCl}}^*)^2}{K'(K_{\text{GaCl}}/K_{\text{HCl}})^2} \right]. \tag{I.9}$$

The concentration of unoccupied centres, c_n, can be eliminated from the equation $(I.9)$ by means of a balance of active centres, according to which, the total number of active centres on the unit surface, L, is equal to the sum of surface concentrations of centres both unoccupied and occupied by molecules of GaCl and HCl. Thus we can write

$$c_n + c_{\text{GaCl}} + c_{\text{HCl}} = L. \tag{I.10}$$

Substituting the expressions $(I.7)$ and $(I.8)$ into the balance $(I.10)$, the concentration of unoccupied centres can be expressed as

$$c_n = L\big(1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{HCl}} p_{\text{HCl}}^*\big)^{-1}. \tag{I.11}$$

After substitution into the relation $(I.9)$ and after rearranging, the rate equation of the chemical rate controlling step is obtained in the form

$$r = \frac{k_+(s/2) \, L K_{\text{GaCl}} \big[p_{\text{As}_2}^* (p_{\text{GaCl}}^*)^2 \, p_{\text{H}_2}^* - (p_{\text{HCl}}^*/K_D)^2 \big]}{\big[1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{HCl}} p_{\text{HCl}}^* \big]^2}, \tag{I.12}$$

where K_D is the equilibrium constant of the reaction

$$\tfrac{1}{2}\text{As}_2(g) + \text{GaCl}(g) + \tfrac{1}{2}\text{H}_2(g) = \text{GaAs}(s) + \text{HCl}(g). \tag{D}$$
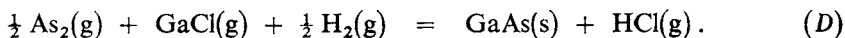
This equilibrium constant can be determined only on the basis of thermodyamic data of substances appearing in the reaction (D). Its relationship to other equilibrium constants is given by the expression

$$K_D^2 = K'(K_{\text{GaCl}}/K_{\text{HCl}})^2. \tag{I.13}$$

Mechanism II

This mechanism assumes that the rate controlling step is again the surface reaction and that only the gallium chloride is adsorbed from the reactants, but that, however, only one GaCl molecule is adsorbed on the dual centre. Thus, in the backward reaction, also one molecule of hydrogen chloride is adsorbed on the dual centre, so that the rate controlling reaction will take place according to the stoichiometric equation
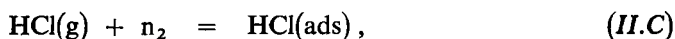
$$\tfrac{1}{2} As_2(g) + GaCl(ads) + \tfrac{1}{2} H_2(g) = GaAs(s) + HCl(ads) \qquad (II.A)$$
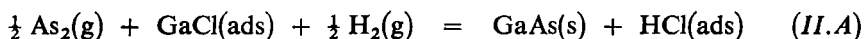
and its velocity may be written as

$$r = k_+ \left[(p_{As_2}^* p_{H_2}^*)^{1/2} c_{GaCl} - (c_{HCl}/K) \right], \qquad (II.1)$$

where K' denotes again the equilibrium constant of the surface reaction. Both adsorption steps will here take place according to the schemes

$$GaCl(g) + n_2 = GaCl(ads) \qquad (II.B)$$

and

$$HCl(g) + n_2 = HCl(ads), \qquad (II.C)$$
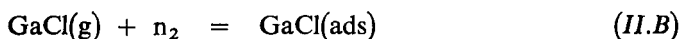
in which the symbol n_2 denotes an unoccupied centre. For equilibrium of both of these steps, we obtain according to Langmuir's ideas[4,5]

$$c_{GaCl} = c_{n_2} K_{GaCl} p_{GaCl}^* \qquad (II.2)$$

and

$$c_{HCl} = c_{n_2} K_{HCl} p_{HCl}^*, \qquad (II.3)$$

where c_{n_2} denotes the surface concentration of unoccupied dual sites. This concentration can be expressed by using an analogous procedure as in the case of the preceding mechanism. If the fraction of unoccupied centres will be denoted as Θ, the following relation will be valid

$$\Theta = c_n/L, \qquad (II.4)$$

where c_n denotes the concentration of unoccupied single centres. In the vicinity of one free centre, there will be s adjacent centres, from which only $s\Theta$ will be unoccupied, and this value gives the number of unoccupied dual centres which can be formed by the unoccupied centre considered. And since there are c_n unoccupied centres on the unit surface of the substrate, the total concentration of unoccupied dual centres will be given by the expression

$$c_{n_2} = (1/2) \, s\Theta C_n \tag{II.5}$$

and on substituting from the relation (II.4)

$$c_{n_2} = (sc_n^2)/2L. \tag{II.6}$$

The factor of one half appears here by the same reasons as in the preceding mechanism. After substituting the expression (II.6) into the relations (II.2) and (II.3) we obtain after combining with the equation (II.1)

$$r = k_+(s/2L) \, K_{GaCl}[(p_{As_2}^*)^{1/2} \, p_{GaCl}^*(p_{H_2}^*)^{1/2} - (K_{HCl}p_{HCl}/K'K_{GaCl})] \, . \tag{II.7}$$

To eliminate the concentration of unoccupied centres, c_n, from the equation (II.7), the balance of active centres is again used, which is in this case of the following form

$$c_n + 2c_{GaCl} + 2c_{HCl} = L. \tag{II.8}$$

Combining the balance (II.8) with the equations (II.2), (II.3), and (II.6), we obtain

$$c_n = 2L[1 + \sqrt{(4sK_{GaCl}p_{GaCl}^* + 4sK_{HCl}p_{HCl}^* + 1)}]^{-1} \, . \tag{II.9}$$

Substitution of this expression into the relation (II.7) yields the rate equation in the final form as

$$r = \frac{k_+L. \, 2sK_{GaCl}[(p_{As_2}^*)^{1/2} \, p_{GaCl}^*(p_{H_2}^*)^{1/2} - (p_{HCl}^*/K_D)]}{[1 + \sqrt{(1 + 4sK_{GaCl}p_{GaCl}^* + 4sK_{HCl}p_{HCl}^*)}]^2} \, , \tag{II.10}$$

where 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

$$K_D = K'(K_{GaCl}/K_{HCl}) \, . \tag{II.11}$$

Mechanism III

If the As_2 molecule is adsorbed from the reactants on a dual centre, the rate controlling reaction can be described by the equation

$$As_2(ads) \, + \, 2\,GaCl(g) \, + \, H_2(g) \quad = \quad 2\,GaAs(s) \, + \, 2\,HCl(ads) \tag{III.A}$$
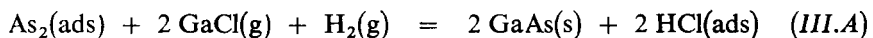
and its velocity may be expressed by the relation

$$r = k_+c_{As_2}(p_{GaCl}^*)^2 \, p_{H_2}^* - k_-c_{2HCl} \, , \tag{III.1}$$

where c_{As_2} and c_{2HCl} denote surface concentrations of dual centres occupied by a molecule of As_2 and by two molecules of HCl. If a diatomic molecule of arsenic is adsorbed on a dual centre n_2 according to the equation

$$As_2(g) + n_2 = As_2(ads), \qquad (III.B)$$
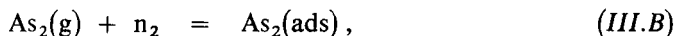
the equilibrium in this adsorption step can be described by the relation

$$c_{As_2} = c_{n_2} K_{As_2} p^*_{As_2} . \qquad (III.2)$$

The concentration of unoccupied dual centres, c_{n_2}, will be expressed in the same way as in the preceeding mechanism (see equation $(II.6)$)

$$c_{n_2} = (s/2L) c_n^2 . \qquad (III.3)$$

Substituting the expression $(III.3)$ into the relation $(III.2)$, we obtain for the concentration c_{As_2}

$$c_{As_2} = (s/2L) c_n^2 K_{As_2} p^*_{As_2} . \qquad (III.4)$$

Adsorption of the hydrogen chloride takes place in this mechanism in the same way as in the mechanism I, and, therefore, the surface concentration of c_{2HCl} will be described by the same relationships. Thus, on combining the relations $(I.5)$ and $(I.8)$, the following expression is obtained

$$c_{2HCl} = (s/2L) c_n^2 K_{HCl}^2 (p^*_{HCl})^2 . \qquad (III.5)$$

Substituting the relations $(III.4)$ and $(III.5)$ into $(III.1)$ an equation is obtained for the reaction rate after some rearrangement

$$r = (k^+ s/2L) K_{As_2} c_n^2 [p^*_{As_2}(p^*_{GaCl})^2 p^*_{H_2} - (K_{HCl}^2/K' K_{As_2}) (p^*_{HCl})^2] , \qquad (III.6)$$

where $K' = k_+/k_-$ denotes the equilibrium constant of the surface reaction $(III.A)$. To eliminate the concentration of unoccupied centres c_n from the equation $(III.6)$, a balance of active centres is used again, which is in this case of the following form

$$c_n + 2c_{As_2} + c_{HCl} = L, \qquad (III.7)$$

since one molecule of As_2 is adsorbed on the dual centre, so that it is blocking two single centres. Substituting the relations $(III.4)$ and $(I.8)$, the balance $(III.7)$ turns into the form

$$c_n + c_n^2(s/L) K^*_{As_2} p_{As_2} + c_n K_{HCl} p^*_{HCl} = L, \qquad (III.8)$$

from which an expression is obtained for the concentration of unoccupied centres

$$c_n = 2L\{1 + K_{HCl}p^*_{HCl} + \sqrt{[(1 + K_{HCl}p^*_{HCl})^2 + 4sK_{As_2}p^*_{As_2}]}\}^{-1} . \quad (III.9)$$

Substituting this expression into the relation $(III.6)$, a rate equation of the chemical rate controlling step is obtained in its final form as

$$r = \frac{(k_+L/2) \cdot 4sK_{As_2}[p^*_{As_2}(p^*_{GaCl})^2 \, p^*_{H_2} - (p^*_{HCl}/K_D)^2]}{\{1 + K_{HCl}p^*_{HCl} + \sqrt{[(1 + K_{HCl}p^*_{HCl})^2 + 4sK_{As_2}p^*_{As_2}]}\}^2} , \quad (III.10)$$

where K_D is again the thermodynamic equilibrium constant of the reaction (D). Its relationship to other equilibrium constants is given here by the expression

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

Mechanism IV

Here it is considered that the rate controlling dual centre is occupied by an atom of arsenic on the one side, and by a molecule of GaCl on the other side, so that the rate controlling surface reaction can be described by the stoichiometric equation

$$As(ads) + GaCl(ads) + \tfrac{1}{2} H_2(g) = GaAs(s) + HCl(ads) . \quad (IV.A)$$
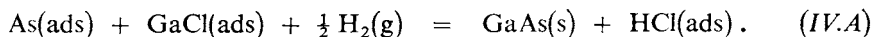
In the backward reaction, a molecule of the hydrogen chloride is adsorbed on the dual centre. In agreement with the ideas mentioned above, the rate of the reaction $(IV.A)$ can be expressed in the form,

$$r = k_+ c_{AsGaCl}(p^*_{H_2})^{1/2} - k_- c_{HCl} , \quad (IV.1)$$

where c_{AsGaCl} denotes the concentration of dual centres, where an atom of As is adsorbed on one centre, and a molecule of GaCl on the other, whereas c_{HCl} represents the concentration of dual centres, on which a molecule of HCl is adsorbed.

An expression for the concentration c_{AsGaCl} will be derived by an extension of the procedure given above in the following way. Let us consider one surface centre, on which an atom of As is adsorbed. With a regular arrangement of centres on the surface, each of such centres will possess s vicinal centres. If the fraction of centres occupied by GaCl molecules is denoted as $\Theta_{GaCl} = c_{GaCl}/L$ (see equation $(I.2)$), the considered centre will possess $s\Theta_{GaCl}$ vicinal centres on the average, on which the molecules of GaCl will be adsorbed. Consequently, the considered central site with an adsorbed atom of As can form on the average $s\Theta_{GaCl}$ dual centres, on the other centre of which a molecule of GaCl will be adsorbed. And since there are c_{As} centres

with an adsorbed As atom on the unit surface, the total concentration of dual centres c_{AsGaCl} will be given by the expression

$$c_{\text{AsGaCl}} = c_{\text{As}} s \Theta_{\text{GaCl}} = (s/L)\, c_{\text{As}} c_{\text{GaCl}} . \qquad (IV.2)$$

In contrast to the preceding mechanisms, the factor of one half does not appear here, since in this case each centre is counted only once. According to the equation $(IV.A)$, the arsenic reacts in the form of adsorbed atoms, whereas, in the gas phase, the arsenic prevails in the form of diatomic molecules of As_2, as follows from previous analyses[2]. Therefore, the adsorption of arsenic will be considered to take place in two steps so, that first a molecule of As_2 is adsorbed on a free centre n_2 according to the equation

$$As_2(g) \; + \; n_2 \quad = \quad As_2(ads) , \qquad (IV.B)$$
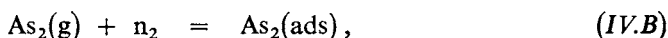
and in the second step, a dissociation takes place involving two single centres n according to the equation

$$As_2(ads) \; + \; 2n \quad = \quad 2\, As(ads) \; + \; n_2 . \qquad (IV.C)$$
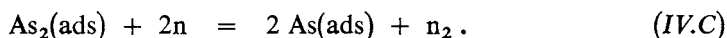
Hereby adsorbed atoms of arsenic are formed, and a free dual centre n_2 is regenerated. Since in this mechanism, the surface reaction $(IV.A)$ represents the rate controlling step, the remaining steps, including the dissociative adsorption of arsenic, will take place at equilibrium. Therefore, it is sufficient to consider the equilibrium of the summary process described by the equation

$$As_2(g) \; + \; 2n \quad = \quad 2\, As(ads) , \qquad (IV.D)$$
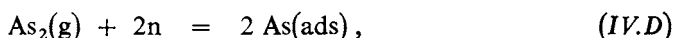
which is the sum of equations $(IV.B)$ and $(IV.C)$. From the condition of equilibrium in the dissociative adsorption $(IV.D)$ we obtain

$$c_{\text{As}}^2 (P_{\text{As}_2}^* c_n^2) = K_{\text{As}_2} , \qquad (IV.3)$$

where K_{As_2} represents the equilibrium adsorption constant of arsenic with dissociation, *i.e.* the equilibrium constant of the process $(IV.D)$. Therefrom follows an expression for the concentration of adsorbed atoms of As

$$c_{\text{As}} = c_n K_{\text{As}_2}^{1/2} (p_{\text{As}_2}^*)^{1/2} . \qquad (IV.4)$$

Further on, for a molecular adsorption of gallium chloride

$$GaCl(g) \; + \; n \quad = \quad GaCl(ads) \qquad (IV.E)$$
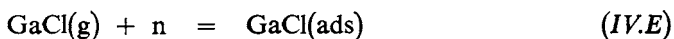
it follows at equilibrium course

$$c_{GaCl} = c_n K_{GaCl} p_{GaCl}^* ,\qquad (IV.5)$$

so that by substituting the expressions $(IV.4)$ and $(IV.5)$ into $(IV.2)$, a relation is obtained for the concentration c_{AsGaCl} as

$$c_{AsGaCl} = c_n^2(s/L)\, K_{As_2}^{1/2} K_{GaCl} (p'_{As_2})^{1/2}\, p_{GaCl}^* . \qquad (IV.6)$$

According to the present mechanism, the hydrogen chloride is adsorbed on a dual centre

$$HCl(g) + n_2 = HCl(ads) \qquad (IV.F)$$
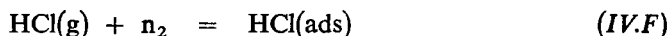
and in this case, the equilibrium relation is of the following form

$$c_{HCl} = c_{n_2} K_{HCl} p_{HCl}^* . \qquad (IV.7)$$

The concentration of unoccupied dual centres, c_{n_2}, will be expressed in the same way as in the preceding mechanism, so that by using the expression $(III.3)$, a relation for the surface concentration of hydrogen chloride is obtained in the form

$$c_{HCl} = c_n^2(s/2L)\, K_{HCl} p_{HCl}^* . \qquad (IV.8)$$

Substituting the expressions for surface concentrations $(IV.6)$ and $(IV.8)$ into the rate equation $(IV.1)$, we obtain after rearranging

$$r = k_+(s/L)\, K_{As_2}^{1/2} K_{GaCl} c_n^2 \big[(p_{As_2}^*)^{1/2}\, p_{GaCl}^* (p_{H_2}^*)^{1/2} -$$
$$- (K_{HCl} p_{HCl}^*/2K' K_{As_2}^{1/2} K_{GaCl}) \big] , \qquad (IV.9)$$

where K' denotes the equilibrium constant of the surface reaction which is equal to the ratio of rate constants $K' = k_+/k_-$. The concentration of unoccupied centres, c_n, appearing in this equation can be eliminated from the balance of active centres

$$c_n + c_{As} + c_{GaCl} + 2c_{HCl} = L, \qquad (IV.10)$$

if the concentration c_{As_2} is neglected against c_{As}. This approximation will be the better the greater the constant of surface dissociation $(IV.C)$ will be in comparison with the equilibrium constant of adsorption $(IV.B)$. Substituting the expressions $(IV.4)$, $(IV.5)$, and $(IV.8)$ into the balance $(IV.10)$, an expression is obtained for the concentration of unoccupied centres

$$c_n = 2L[\alpha + \sqrt{(\alpha^2 + 4sK_{HCl}p_{HCl})}]^{-1} , \qquad (IV.11a)$$

where

$$\alpha = 1 + K_{As_2}^{1/2}(p_{As_2}^*)^{1/2} + K_{GaCl}p_{GaCl}^* , \qquad (IV.11b)$$

and by its substitution into the relation $(IV.9)$, the rate equation for the mechanism IV is obtained in the final form

$$r = \frac{k_+ \, 4sLK_{As_2}^{1/2}K_{GaCl}[(p_{As_2}^*)^{1/2} \, p_{GaCl}^*(p_{H_2}^*)^{1/2} - (p_{HCl}^*/K_D)]}{[\alpha + \sqrt{(\alpha^2 + 4sK_{HCl}p_{HCl})}]^2} , \qquad (IV.12)$$

where α is determined by the relation $(IV.11b)$ and K_D is the equilibrium constant of the reaction (D), which is connected with other equilibrium constants of this mechanism through the relation

$$K_D = K'(2K_{As_2}^{1/2}/K_{HCl}) . \qquad (IV.13)$$

Mechanism V

Here the rate controlling step is the adsorption of gallium chloride, or more specifically the adsorption of one GaCl molecule on a dual centre, so that the stoichiometric equation of the rate controlling step can be written as

$$GaCl(g) + n_2 = GaCl(ads) . \qquad (V.A)$$
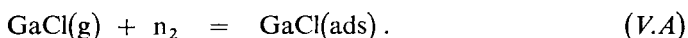
Then, the reaction rate r is equal to the rate of adsorption of the gallium chloride, r_{GaCl}, for which we can write[4,5] in agreement with the equation $(V.A)$

$$r = r_{GaCl} = k_{GaCl} + [p_{GaCl}^*c_{n_2} - c_{GaCl}/K_{GaCl}] . \qquad (V.1)$$

If the rate controlling step is the adsorption of GaCl, the remaining steps such as the surface reaction and the adsorption of HCl will take place at equilibrium. Thus, for the surface reaction

$$\tfrac{1}{2} As_2(g) + GaCl(ads) + \tfrac{1}{2} H_2(g) = GaAs(s) + HCl(ads) \qquad (V.B)$$
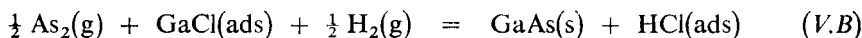
it follows from the condition of equilibrium

$$c_{GaCl} = c_{HCl}/K'(p_{As_2}^* p_{H_2}^*)^{1/2} \qquad (V.2)$$

and for the equilibrium of HCl on a dual centre

$$HCl(g) + n_2 = HCl(ads) \qquad (V.C)$$
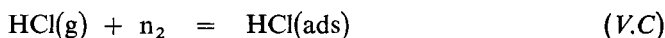
a relation is obtained

$$c_{HCl} = K_{HCl} p^*_{HCl} c_{n_2} . \tag{V.3}$$

The concentration of unoccupied dual centres, c_{n_2}, may be expressed on the basis of the procedure given previously by means of relation $(III.3)$, so that by combining the equations $(V.1)$, $(V.2)$, $(V.3)$, and $(III.3)$, a rate equation is obtained in the form

$$r = k_{GaCl^+}(s/2L) \, c_n^2 [p^*_{GaCl} - (K_{HCl}/K'K_{GaCl}) \, (p^*_{HCl}/p^{*1/2}_{As_2} p^{*1/2}_{H_2})] . \tag{V.4}$$

The concentration of unoccupied single centres, c_n, can be determined from a balance of active centres, which is of the same form here as in the mechanism II, $i.e.$ the form of equation $(II.8)$, from which it follows after combination with the relations $(V.2)$, $(V.3)$, and $(III.3)$, and after rearrangement

$$c_n = 2L\{1 + \sqrt{[1 + (4sK_{GaCl}/K_D) \, (p^*_{HCl}/p^{*1/2}_{As_2} p^{*1/2}_{H_2}) +}$$
$$+ \, 4sK_{HCl}p_{HCl}]\}^{-1} . \tag{V.5}$$

Here K_D is the equilibrium constant of the reaction (D), which is related to other equilibrium constants according to the equation $(V.4)$

$$K_D = K'(K_{GaCl}/K_{HCl}) . \tag{V.6}$$

Substituting the expression $(V.5)$ into the relation $(V.4)$ we arrive at a rate equation in the final form

$$r = k_{GaCl^+} . 2sL \left[p^*_{GaCl} - \frac{p^*_{HCl}}{K_D(p^*_{As_2}p^*_{H_2})^{1/2}} \right] .$$
$$. \left[1 + \sqrt{\left(1 + \frac{4sK_{GaCl}}{K_D} \frac{p^*_{HCl}}{(p^*_{As_2}p^*_{H_2})^{1/2}} + 4sK_{HCl}p^*_{HCl} \right)} \right]^{-2} . \tag{V.7}$$

Mechanism VI

Here the rate controlling step is again the adsorption of gallium chloride, however, the difference consists in the fact that two molecules of GaCl are adsorbed on a dual centre, $i.e.$ one molecule on each centre. The stoichiometric equation of the rate controlling step will be of the form

$$2 \, GaCl(g) + n_2 = 2 \, GaCl(ads) \tag{VI.A}$$
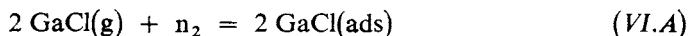
and its rate will be given by the equation

$$r = r_{2GaCl} = k_{2GaCl^+}[(p^*_{GaCl})^2 \, c_{n_2} - (c_{2GaCl}/K_{2GaCl})] , \tag{VI.1}$$

where c_{n_2} denotes the concentration of unoccupied dual centres, and c_{2GaCl} is the concentration of dual sites occupied by two molecules of GaCl. The surface reaction proper

$$\text{As}_2(g) + 2\,\text{GaCl(ads)} + \text{H}_2(g) = 2\,\text{GaAs(s)} + 2\,\text{HCl(ads)} \qquad (VI.B)$$
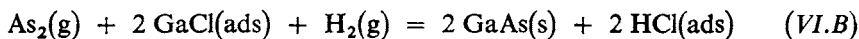
will take place at equilibrium, so that the following relation will be valid

$$c_{2GaCl} = c_{2HCl}/K'p^*_{As_2}p^*_{H_2}. \qquad (VI.2)$$

The adsorption of hydrogen chloride will also take place at equilibrium

$$\text{HCl(g)} + \text{n} = \text{HCl(ads)}, \qquad (VI.C)$$
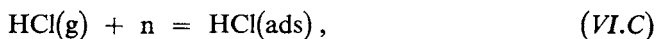
so that from the appropriate condition of equilibrium we obtain

$$c_{HCl} = c_n K_{HCl} p^*_{HCl}. \qquad (VI.3)$$

The concentration of dual centres occupied by two molecules of HCl, appearing in the equation $(IV.2)$, can be expressed assuming a regular arrangement of centres on the surface in an analogous way as previously, and so a relation is obtained

$$c_{2HCl} = (s/2L)\,c^2_{HCl}. \qquad (VI.4)$$

Combining the relations $(VI.2)$ $(VI.3)$, and $(VI.4)$, we obtain an expression

$$c_{2GaCl} = c^2_n(s/2L)\,K^2_{HCl}(p^*_{HCl})^2/(K'p^*_{As_2}p^*_{H_2}), \qquad (VI.5)$$

and after its substitution into the relation $(VI.1)$, the rate equation is transformed to

$$r = k_{2GaCl*}(s/2L)\,c^2_n\left[(p^*_{GaCl})^2 - \frac{K^2_{HCl}}{K'K_{2GaCl}}\frac{(p^*_{As_2})^2}{p^*_{HCl}p^*_{H_2}}\right]. \qquad (VI.6)$$

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

$$c_n + c_{GaCl} + c_{HCl} = L, \qquad (VI.7)$$

where the concentration of single centres occupied by GaCl molecules has to be considered, since not all of these centres are constituents of dual centres, which play

a role in the rate controlling step $(VI.A)$. The relationship between the concentrations c_{GaCl} and c_{2GaCl} is given by an analogous expression as with the hydrogen chloride, *i.e.* by $(VI.4)$, so that the following is valid

$$c_{2GaCl} = (s/2L)\, c_{GaCl}^2 \,. \qquad (VI.8)$$

Substituting this expression into the relation $(VI.5)$, we obtain after a rearrangement

$$c_{GaCl} = c_n \frac{K_{HCl} p_{HCl}^*}{(K' p_{As_2}^* p_{H_2}^*)^{1/2}} \,. \qquad (VI.9)$$

Substituting the expressions $(VI.3)$ and $(VI.9)$ into the balance equation, an expression is obtained for the concentration c_n in the form

$$c_n = L \left[\frac{K_{HCl}}{(K)^{1/2}} \frac{p_{HCl}^*}{(p_{As_2}^* p_{H_2}^*)^{1/2}} + K_{HCl} p_{HCl}^* \right]^{-1} \qquad (VI.10)$$

and after its substitution into the relation $(VI.6)$, we obtain the rate equation for the considered mechanism in the final form as

$$r = k_{2GaCl^+}(sL/2) \left[(p_{GaCl}^*)^2 - \frac{(p_{HCl}^*)^2}{K_D^2 p_{As_2}^* p_{H_2}^*} \right] \left[1 + \frac{K_{AsGaCl}^{1/2}}{K_D} \frac{p_{HCl}^*}{(p_{As_2}^* p_{H_2}^*)^{1/2}} + K_{HCl} p_{HCl}^* \right]^{-2} \,. \qquad (VI.11)$$

The equilibrium constant K_D, which refers to the reaction (D), is related to other equilibrium constants of this mechanism according to the equation

$$K_D^2 = K' K_{2GaCl}/K_{HCl}^2 \,. \qquad (VI.12)$$

Mechanism VII

Even in this mechanism, the rate controlling step is the adsorption of gallium chloride. Here however, an atom of arsenic is adsorbed on one centre of the rate controlling dual centre, and a molecule of GaCl on the other one. The rate of the rate controlling step

$$GaCl(g) + n = GaCl(ads) \qquad (VII.A)$$
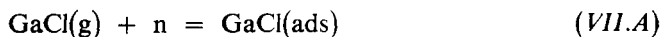
is given by the equation

$$r = r_{GaCl} = k_{GaCl^+} \left[p_{GaCl}^* c_n - c_{GaCl}/K_{GaCl} \right] \,. \qquad (VII.1)$$

The surface reaction proper

$$As(ads) + GaCl(ads) + \tfrac{1}{2} H_2(g) = GaAs(s) + HCl(ads) \qquad (VII.B)$$
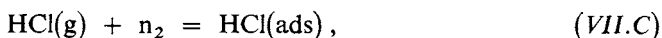
will take place at equilibrium, so that the concentration of dual centres, c_{AsGaCl}, where one centre is occupied by an As atom and the other by a GaCl molecule, will be given by the expression

$$c_{AsGaCl} = c_{HCl}/K'(p_{H_2}^*)^{1/2} . \qquad (VII.2)$$

The adsorption of hydrogen chloride will take place also at equilibrium

$$HCl(g) + n_2 = HCl(ads) , \qquad (VII.C)$$

so that from the condition of equilibrium, it follows

$$c_{HCl} = c_{n_2} K_{HCl} p_{HCl}^* . \qquad (VII.3)$$

The concentrations c_{AsGaCl} and c_{n_2} will be expressed, assuming a regular arrangement of centres, by a procedure described in the mechanism IV, so that we obtain

$$c_{GaCl} = c_{HCl}/[(s/L) K' c_{As}/p_{H_2}^*]^{1/2} \qquad (VII.4)$$

and

$$c_{HCl} = c_n^2(s/2L) K_{HCl} p_{HCl}^* . \qquad (VII.5)$$

Similarly as in the mechanism IV, the dissociation of molecules As_2 into atoms As will be assumed even here according to the summary equation

$$As_2(g) + 2 n = 2 As(ads) , \qquad (VII.D)$$
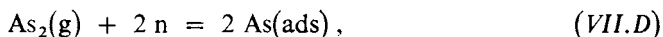
for which the following is valid in the equilibrium course

$$c_{As} = c_n K_{As_2}^{1/2}(p_{As_2}^*)^{1/2} . \qquad (VII.6)$$

Combining the relations $(VII.1)$ and $(VII.6)$, a rate equation is obtained in the form

$$r = k_{GaCl+c_n}\left[p_{GaCl}^* - \frac{K_{HCl}}{2K' K_{As_2}^{1/2} K_{GaCl}} \frac{p_{HCl}^*}{p_{As_2}^* p_{H_2}^*} \right], \qquad (VII.7)$$

where the concentration of unoccupied centres, c_n, is determined by the balance

$$c_n + c_{GaCl} + c_{As} + 2c_{HCl} = L. \qquad (VII.8)$$

Substituting the expressions $(VII.4)$, $(VII.5)$, and $(VII.6)$ into this balance, an expression follows for the concentration c_n

$$c_n = 2L[\beta + \sqrt{(\beta^2 + 4sK_{HCl}p^*_{HCl})}]^{-1}, \qquad (VII.9a)$$

where

$$\beta = 1 + \frac{K_{GaCl}p^*_{HCl}}{K_D(p^*_{As_2}p_{H_2})^{1/2}} + (K_{As_2}p^*_{As_2})^{1/2}. \qquad (VII.9b)$$

The K_D is the equilibrium constant of the reaction (D). A combination with the relation $(VII.7)$ results in the rate equation for the mechanism VII in the final form
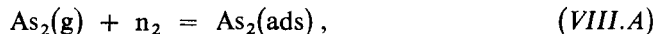
$$r = \frac{k_{GaCl^+} 2L\left[p^*_{GaCl} - \dfrac{p^*_{HCl}}{K_D(p^*_{As_2}p_{H_2})^{1/2}}\right]}{[\beta + \sqrt{(\beta^2 + 4\,sK_{HCl}p^*_{HCl})}]^2}. \qquad (VII.10)$$

In this case, the equilibrium constant K_D is related to other equilibrium constants by

$$K_D = 2K'(2K^{1/2}_{As_2}K_{GaCl}/K_{HCl}). \qquad (VII.11)$$

Mechanism VIII

In this mechanism, the adsorption of diatomic molecules of arsenic on a dual site

$$As_2(g) + n_2 = As_2(ads), \qquad (VIII.A)$$

is considered to be the rate controlling step, so that the resulting rate r will be expressed by the equation

$$r = r_{As_2} = k_{As_2^+} + [p^*_{As_2}c_{n_2} - (c_{As_2}/K_{As_2})]. \qquad (VIII.1)$$

It i considered that the adsorbed diatomic molecules of arsenic dissociate on the sur.ace under participation of two single centres according to the equation

$$As_2(ads) + 2n = 2As(ads) + n_2. \qquad (VIII.B)$$
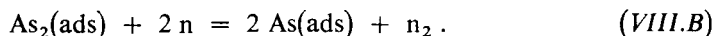
Herefrom we obtain from the condition of equilibrium in this surface dissociation

$$c_{As_2} = c_{As}c_{n_2}/K'_{As}c^2_n, \qquad (VIII.2)$$

where K'_{As} is the equilibrium constant of the dissociation reaction $(VIII.B)$. Using
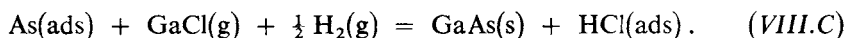
the expression for the concentration of unoccupied dual sites $(III.3)$ and the expression $(VIII.2)$, the rate equation in the following form is obtained

$$r = k_{As_2+}(s/2L) \left[p^*_{As_2} c^2_n - c^2_{As}/K'^2_{As_2} \right], \qquad (VIII.3)$$

where K'_{As_2} is the combined equilibrium constant of adsorption As_2 with dissociation. It is defined by the relation

$$(K'_{As_2})^2 = K_{As_2} K'_{As_2}. \qquad (VIII.4)$$

If the adsorption of arsenic is the rate controlling step, the remaining steps of chemical nature will take place at equilibrium, *i.e.* first the surface reaction proper, which, in the case considered, will take place according to the equation

$$As(ads) + GaCl(g) + \tfrac{1}{2}H_2(g) = GaAs(s) + HCl(ads). \qquad (VIII.C)$$

From its condition of equilibrium, an expression is obtained for the surface concentration of arsenic atoms c_{As} in the form

$$c_{As} = c_{HCl}/K' p^*_{GaCl}(p^*_{H_2})^{1/2}, \qquad (VIII.5)$$

and further on, the adsorption of hydrogen chloride, for which an expression is obtained in agreement with the equation $(VIII.C)$

$$c_{HCl} = c_n K_{HCl} p^*_{HCl}. \qquad (VIII.6)$$

Combining the relations $(VIII.3)$, $(VIII.5)$, and $(VIII.6)$, the rate equation is transformed to the form

$$r = k_{As_2+}(s/2L) c^2_n \left[p^*_{As_2} - \left(\frac{K_{HCl}}{K' K'_{As_2}} \right)^2 \frac{(p^*_{HCl})^2}{(p^*_{GaCl})^2 \, p^*_{H_2}} \right], \qquad (VIII.7)$$

where the concentration of unoccupied single centres c_n is determined again from the balance of active centres in the form

$$c_n + c_{As} + c_{HCl} = L. \qquad (VIII.8)$$

Substituting the expressions $(VIII.5)$ and $(VIII.6)$ into the balance equation $(VIII.8)$, an expression is obtained

$$c_n = L[1 + (K_{HCl}/K) (p^*_{HCl}/p^*_{GaCl} p^*_{H_2})^{1/2} + K_{HCl} p^*_{HCl}]^{-1}, \qquad (VIII.9)$$

and after its substitution into the relation $(VIII.7)$ and after some rearrangement, the rate equation follows in the final form

$$r = k_{As_2+}(sL/2)\left[p^*_{As_2} - \frac{(p^*_{HCl})^2}{K^2_D(p^*_{GaCl})^2\,p^*_{H_2}}\right]\left[1 + \frac{K'_{As_2}}{K_D}\frac{p^*_{HCl}}{p^*_{GaCl}(p^*_{H_2})^{1/2}} + K_{HCl}p^*_{HCl}\right]^{-2},$$

$$(VIII.10)$$

where K_D denotes again the equilibrium constant of the reaction (D), which is related in this case to other equilibrium constants by the equation

$$K_D = K'(K'_{As_2}/K_{HCl}).\qquad\qquad (VIII.11)$$

Mechanism IX

If in addition to diffusion, the joint rate controlling step of chemical nature is represented by the desorption of hydrogen chloride, the resulting rate of the process, r, will be equal to the rate of desorption of the hydrogen chloride, r_{HCl}. In the case, where the rate controlling step takes place by a dual site mechanism,

$$HCl(ads) = HCl(g) + n_2,\qquad\qquad (IX.A)$$
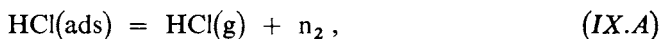
we can write for its velocity

$$r = r_{HCl} = k_{HCl+}\left[(c_{HCl}/K_{HCl}) - p^*_{HCl}c_{n_2}\right].\qquad\qquad (IX.1)$$

The remaining steps of chemical nature will take place at equilibrium, and thus, we obtain for the equilibrium in the surface reaction

$$\tfrac{1}{2}As_2(g) + GaCl(ads) + \tfrac{1}{2}H_2(g) = GaAs(s) + HCl(ads)\qquad (IX.B)$$
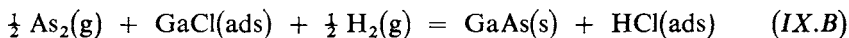
a relation

$$c_{HCl} = K'(p^*_{As_2}p^*_{H_2})^{1/2}\,c_{GaCl},\qquad\qquad (IX.2)$$

and for the equilibrium in the adsorption of gallium chloride on a dual centre

$$GaCl(g) + n_2 = GaCl(ads)\qquad\qquad (IX.C)$$
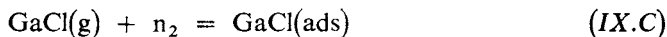
an expression follows

$$c_{GaCl} = c_{n_2}K_{GaCl}p^*_{GaCl}.\qquad\qquad (IX.3)$$

Combining the expressions $(IX.1)$, $(IX.2)$, and $(IX.3)$, the rate equation is obtained

in the form

$$r = k_{HCl^+}(K'K_{GaCl}/K_{HCl})\, c_{n_2} \left[(p_{As_2}^*)^{1/2}\, p_{GaCl}^*(p_{H_2}^*)^{1/2} - \frac{K_{HCl}p_{HCl}^*}{K'K_{GaCl}} \right]. \quad (IX.4)$$

The concentration of unoccupied dual centres, c_{n_2}, will be expressed using the procedure given above as

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

and the concentration of unoccupied single centers, c_n, will be obtained from a balance of active centres, which according to $(IX.B)$, $(IX.A)$, and $(IX.C)$ is of the following form

$$c_n + 2c_{GaCl} + 2c_{HCl} = L. \quad (IX.6)$$

Substituting the expressions $(IX.2)$, $(IX.3)$ and $(IX.5)$ into the balance $(IX.6)$, it follows

$$c_n = 2L\{1 + \sqrt{[1 + 4sK_{GaCl}p_{GaCl}^* + 4sK'K_{GaCl}(p_{As_2}^*)^{1/2}\, p_{GaCl}^*(p_{H_2}^*)^{1/2}]}\}^{-1} \quad (IX.7)$$

and combining this expression with equations $(IX.4)$ and $(IX.5)$, the rate equation is obtained in its final form as

$$r = \frac{k_{HCl} \cdot 2sLK_D[(p_{As_2}^*)^{1/2}\, p_{GaCl}^*(p_{H_2}^*)^{1/2} - p_{HCl}^*/K_D]}{\{1 + \sqrt{[1 + 4sK_{GaCl}p_{GaCl}^* + 4sK_{HCl}K_D(p_{As_2}^*)^{1/2}\, p_{GaCl}^*(p_{H_2}^*)^{1/2}]}\}^2}, \quad (IX.8)$$

where the equilibrium constant K_D of the reaction (D) is given by the relation

$$K_D = K'(K_{GaCl}/K_{HCl}). \quad (IX.9)$$

Mechanism X

Here the rate controlling step is again the desorption of hydrogen chloride, which, however, proceeds here in such a way, that on each centre of the rate controlling dual centre, one molecule of the hydrogen chloride is adsorbed

$$2\,HCl(ads) = 2\,HCl(g) + n_2, \quad (X.A)$$
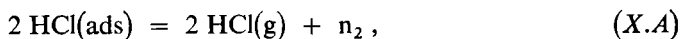
so that in this case, the rate equation will be of the following form

$$r = k_{2HCl^+}[(c_{2HCl}/K_{2HCl}) - p_{HCl}^*)^2\, c_{n_2}]. \quad (X.1)$$

The surface reaction, which is considered in this case as

$$As_2(g) + 2\,GaCl(ads) + H_2(g) = GaAs(s) + 2\,HCl(ads) \qquad (X.B)$$
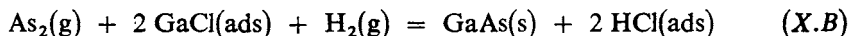
will proceed at equilibrium, so that a relation is obtained for the concentration of dual centres occupied by two HCl molecules, c_{2HCl},

$$c_{2HCl} = K' p^*_{As_2} p^*_{H_2} c_{2GaCl} . \qquad (X.2)$$

The adsorption of gallim chloride

$$2\,GaCl(g) + n_2 = 2\,GaCl(ads) \qquad (X.C)$$
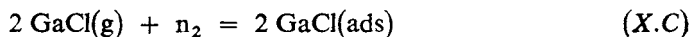
will proceed at equilibrium, so that the following is valid

$$c_{2GaCl} = c_{n_2} K_{2GaCl} (p^*_{GaCl})^2 . \qquad (X.3)$$

Combining relations from $(X.1)$ up to $(X.3)$, the rate equation is obtained in the form

$$r = k_{2HCl^*} \frac{K' K_{2GaCl}}{K_{2HCl}} c_{n_2} \left[p^*_{As_2} (p^*_{GaCl})^2 \, p^*_{H_2} - \frac{K_{2HCl}}{K' K_{2GaCl}} (p^*_{HCl})^2 \right], \qquad (X.4)$$

where the concentration of unoccupied dual centres, c_{n_2}, is given by an expression derived previously (see $(III.3)$). The concentration of single unoccupied centres, c_n, will be determined by the balance of active centres, which is in this case of the following form

$$c_n + 2c_{GaCl} + 2c_{2HCl} = L, \qquad (X.5)$$

and substituting the expressions $(X.2)$, $(X.3)$, and $(III.3)$ into the balance $(X.5)$, the following relation is obtained

$$c_n = 2L\{1 + \sqrt{[1 + 4sK_{2GaCl}(p^*_{GaCl})^2 + 4sK' K_{AsGaCl} p^*_{As_2}(p^*_{GaCl})^2 \, p^*_{H_2}]}\}^{-1} . \qquad (X.6)$$

Combining the relations $(X.4)$, $(III.3)$, and $(X.6)$ the rate equation for mechanism X is obtained in the final form as

$$r = \frac{k_{2HCl^*} . 2sLK_D^2 [p^*_{As_2}(p^*_{GaCl})^2 \, p^*_{H_2} - (p^*_{HCl}/K_D)^2]}{\{1 + \sqrt{[1 + 4sK_{2GaCl}(p^*_{GaCl})^2 + 4sK_{2HCl}K_D^2 p^*_{As_2}(p^*_{GaCl})^2 \, p^*_{H_2}]}\}^2}, \qquad (X.7)$$

where K_D denotes the equilibrium constant of the reaction (D), which is related to

other equilibrium constants of this mechanism in the following way

$$K_D^2 = K'(K_{2GaCl}/K_{2HCl}) \, . \qquad (X.8)$$

Mechanism XI

This mechanism is similar to the mechanism *IX* in that, that the rate controlling step is the desorption of hydrogen chloride, the molecule of which occupies a dual site

$$HCl(ads) = HCl(g) + n_2 \, , \qquad (XI.A)$$
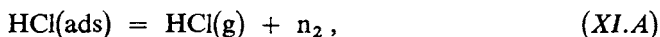
so that the rate equation is of the same form as in the mechanism *IX*

$$r = k_{HCl^+}\left[(c_{HCl}/K_{HCl}) - p_{HCl}^* c_{n_2}\right] \, . \qquad (XI.1)$$

This mechanism, however, differs in that, that in the surface reaction, the reaction dual site is not occupied by a single molecule of GaCl, but on one centre of this dual site, an atom of arsenic is adsorbed, and on the other, a GaCl molecule is adsorbed according to the equation

$$As(ads) + GaCl(ads) + \tfrac{1}{2} H_2(g) = GaAs(s) + HCl(ads) \, . \qquad (XI.B)$$
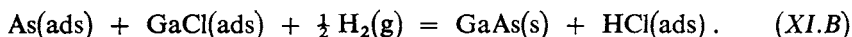
From the condition of equilibrium in the surface reaction $(XI.B)$, a relation follows

$$c_{HCl} = K'(p_{H_2}^*)^{1/2} c_{AsGaCl} \, , \qquad (XI.2)$$

where the symbol c_{AsGaCl} denotes the concentration of the mentioned assymetrically occupied centres. This concentration can be expressed by the following expression assuming a regular arrangement of centres

$$c_{AsGaCl} = (s/L) c_{As} c_{GaCl} \, , \qquad (XI.3)$$

as it has been done in mechanism *IV.* Further on, the dissociative adsorption of di-atomic molecules of arsenic

$$As_2(g) + 2n = 2 As(ads) \, , \qquad (XI.C)$$
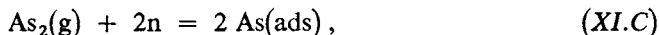
proceeds at equilibrium, and the pertaining condition of equilibrium is of the form

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

The adsorption of gallium chloride

$$GaCl(g) + n = GaCl(ads) \, , \qquad (XI.D)$$
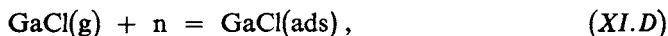
proceeds also at equilibrium, and from the condition of equilibrium, it follows

$$c_{GaCl} = c_n K_{GaCl} p_{GaCl}^* . \qquad (XI.5)$$

Combining the relations from $(XI.1)$ up to $(XI.5)$ and using the expression $(III.3)$, the rate equation assumes after rearrangement the form

$$r = k_{HCl^+}(s/2L) K_D c_n^2 [(p_{As_2}^*)^{1/2} p_{GaCl}^* (p_{H_2}^*)^{1/2} - (p_{HCl}^*/K_D)] , \qquad (XI.6)$$

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

$$K_D = K' \frac{2 K_{As_2}^{1/2} K_{GaCl}}{K_{HCl}} . \qquad (XI.7)$$

The concentration of unoccupied centres, c_n, in the relation $(XI.6)$ will be determined from the balance of active centres, which has in this case the following form

$$c_n + c_{As} + c_{GaCl} + 2c_{HCl} = L . \qquad (XI.8)$$

Substituting the expressions from $(XI.2)$ up to $(XI.5)$ into the balance $(XI.8)$ and combining with the relation $(XI.6)$, the rate equation for the mechanism XI is obtained in its final form as

$$r = \frac{k_{HCl^+} \cdot 2sLK_D[(p_{As_2}^*)^{1/2} p_{GaCl}^* (p_{H_2}^*)^{1/2} - (p_{HCl}^*/K_D)]}{\{\alpha + \sqrt{[\alpha^2 + 4sK_D K_{HCl}(p_{As_2}^*)^{1/2} p_{GaCl}^* (p_{H_2}^*)^{1/2}]}\}^2} , \qquad (XI.9a)$$

where

$$\alpha = 1 + (K_{As_2} p_{As_2}^*)^{1/2} + K_{GaCl} p_{GaCl}^* . \qquad (XI.9b)$$

Mechanism XII

Here the rate controlling step is represented by the desorption of hydogen chloride according to

$$2\,HCl(ads) = 2\,HCl(g) + n_2 \qquad (XII.A)$$
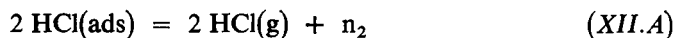
with a rate equation

$$r = k_{2HCl^+}[(c_{2HCl}/K_{2HCl}) - (p_{HCl}^*)^2 c_{n_2}] , \qquad (XII.1)$$

where, however, the gallium chloride does not react in the adsorbed state, but only the arsenic in the form of adsorbed diatomic molecules according to the stoichio-

metry

$$As_2(ads) + 2\,GaCl(g) + H_2(g) = 2\,GaAs(s) + 2\,HCl(ads)\,. \qquad (XII.B)$$
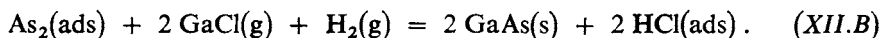
This surface reaction proceeds at equilibrium, so that the following relation is obtained

$$c_{2HCl} = K'(p_{GaCl}^*)^2\, p_{H_2}^* c_{As_2}\,. \qquad (XII.2)$$

Even the adsorption of the As_2 molecules proceeds at equilibrium according to

$$As_2(g) + n_2 = As_2(ads)\,, \qquad\qquad (XII.C)$$
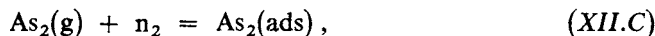
for which the following is valid

$$c_{As_2} = c_{n_2} K_{As_2} p_{As_2}^*\,. \qquad (XII.3)$$

Combining the relations from $(XII.1)$ up to $(XII.3)$, the rate equation is obtained in the form

$$r = k_{2HCl^+}(s/2L)\, K_D^2 c_n^2 [p_{As_2}^*(p_{GaCl}^*)^2\, p_{HCl}^* - (p_{HCl}^*/K_D)^2]\,, \qquad (XII.4)$$

where the equilibrium constant K_D of the reaction (D) relates to other equilibrium constants of this mechanism through

$$K_D^2 = K'(K_{As_2}/K_{2HCl})\,, \qquad (XII.5)$$

where the relation $(III.3)$ was used to express the concentration of unoccupied dual centres. From the balance of active centres, which is in this case of the following form

$$c_n + 2c_{As_2} + 2c_{2HCl} = L\,, \qquad (XII.6)$$

the final rate equation is obtained on substituting the expressions $(XII.2)$ and $(XII.3)$ into the balance $(XII.6)$ using the expression $(III.3)$, and on combining with the relation $(XII.4)$

$$r = \frac{k_{2HCl^+}\,.\,2sLK_D^2[p_{As_2}^*(p_{GaCl}^*)^2\, p_{H_2}^* - (p_{HCl}^*/K_D)^2]}{\{1 + \sqrt{[1 + 4sK_{As_2}p_{As_2}^* + 4sK_{2HCl}K_D^2 p_{As_2}^*(p_{GaCl}^*)^2\, p_{H_2}^*]}\}^2} \qquad (XII.7)$$

RESULTS

The theoretical relations expressing twelve mechanism of the dual site model have been compared with the same experimental set as previously[1,3], however, with regard to the form of these equations, it was necessary to select a different procedure which

is given in the following. To evaluate the rate and equilibrium adsorption constants, the method of least squares was used assuming that the absolute error of the growth rate has a constant dispersion in the whole range of measurements. Since, however, the expressions for the growth rate cannot be linearized in the most cases, the Gauss––Newton's method of nonlinear regression has been used for mathematical treatment. The adjustable parameters in the rate expressions have the significance of rate and equilibrium constants, and, therefore, only non-negative values of these parameters are physically admissible. For that reason, the constants which assumed negative values in the course of computation have been eliminated by equalizing them to zero. By this procedure the number of non-zero constants decreased, but on the other hand, the form of the program for computing the growth rate had to be changed. Therefore, the regression analysis has been carried out once more with the functional dependence of the growth rate varied in the mentioned way, and this procedure was repeated so long until the computation yielded non-negative values for all the constants.

By the procedure given above, all twelve variants of the dual centre model have been evaluated, and for the purpose of comparison, even the five variants of the single centre model which was analyzed previously[1] have been treated in the same way. The results of both series of computations are summarized in Tables II and III. Here, it is necessary to add, that in the previous paper[1], a different procedure has been used to compute the values of constants, where the correlation relations for the growth rate have been linearized first. After that, the method of linear regression was used, and finally, even negative values of constant have been admitted. For that reason, the results for the single centre model, obtained previously[1], are not identical with the results given here, and they are not comparable with the results obtained for the dual centre model.

To appreciate the suitability of individual variants of both model to a correlation of experimental data, the standard deviation has been used defined by the relation

$$s = \sqrt{\left\{ \sum_{i=1}^{n} [v_i(\exp) - v_i(\text{cal})]^2 / (n - m) \right\}} \, .$$

Here, the $v_i(\exp)$ and $v_i(\text{cal})$ are the experimental and calculated values of the growth rate in the i-th experiment, n is the number of experimental points $(n = 20)$, and m is the number of non-zero constants in the pertinent functional dependence of the growth rate.

DISCUSSION

From the twelve dual site mechanisms considered above, at first the mechanisms V, VI, and VII cannot be taken into account, because all the adsorption constants are

equal to zero, so that in these cases, the contribution of any surface centres to the reaction mechanism is excluded, and the rate equations are changed to one-line expressions for the homogeneous reactions. Likewise the high values of standard deviations indicate a low probability of these three mechanisms. Further on, it is necessary to exclude even the mechanism *IV*, where the zero value of the equilibrium adsorption constant K_{As_2} contradicts to the non-zero value of the kinetic term $sLk + K_{As_2}^{1/2}$. For the same reason, the mechanisms *IX* and *XI* will be excluded, too.

From the remaining mechanisms, the experimental data are reproduced best by the mechanisms *I* and *X*, as it is evident from the Table II. In the mechanism *I*,

TABLE II

Computed results of dual centre model

Mechanism	Rate constant		Equilibrium adsorption constant		Standard deviation
	Meaning	Value	Meaning	Value	
I	sLk_+	$1{\cdot}114 \cdot 10^{-4}$	K_{GaCl}	$668{\cdot}8$	
			K_{HCl}	0	$2{\cdot}6$
II	Lk_+	$5{\cdot}544 \cdot 10^{-6}$	sK_{GaCl}	$165{\cdot}8$	
			sK_{HCl}	0	$4{\cdot}1$
III	Lk_+	$1{\cdot}145 \cdot 10^{-2}$	sK_{As_2}	$174{\cdot}9$	$13{\cdot}1$
			K_{HCl}	0	
IV	$sLk_+ K_{As2}^{1/2}$	$5{\cdot}145 \cdot 10^{-6}$	K_{GaCl}	$69{\cdot}68$	
			$K_{As_2} = sK_{HCl}$	0	$4{\cdot}0$
V	sLk_{GaCl+}	$9{\cdot}602 \cdot 10^{-6}$	$sK_{GaCl} = sK_{HCl}$	0	$8{\cdot}9$
VI	sLk_{2GaCl+}	$1{\cdot}302 \cdot 10^{-3}$	$K_{2GaCl} = K_{HCl}$	0	$13{\cdot}4$
VII	Lk_{GaCl+}	$9{\cdot}602 \cdot 10^{-6}$	$K_{GaCl} = K_{As_2} = sK_{HCl}$	0	$8{\cdot}9$
VIII	sLk_{As_2}	$9{\cdot}740 \cdot 10^{-5}$	K_{As_2}	$520{\cdot}3$	$3{\cdot}5$
			K_{HCl}	0	
IX	sLk_{HCl+}	$6{\cdot}205 \cdot 10^{-6}$	sK_{GaCl}	$165{\cdot}8$	
			sK_{HCl}	0	$4{\cdot}1$
X	sLk_{2HCl+}	$9{\cdot}194 \cdot 10^{-4}$	sK_{2GaCl}	$193{\cdot}3 \cdot 10^3$	
			sK_{2HCl}	0	$2{\cdot}6$
XI	sLk_{HCl+}	$4{\cdot}841 \cdot 10^{-6}$	K_{GaCl}	$69{\cdot}68$	
			$K_{As_2} = 4sK_{HCl}$	0	$4{\cdot}0$
XII	sLk_{2HCl+}	$4{\cdot}919 \cdot 10^{-4}$	sK_{2HCl}	$4\,378$	
			sK_{As_2}	0	$5{\cdot}2$

in addition to diffusion the rate controlling step is the surface reaction, where the reaction dual centre is occupied by two molecules of gallium chloride, whereas the arsenic and the hydrogen are taking part in the formation of the activated complex directly from the gas phase. This mechanism reproduces the measured growth rates with a standard deviation of $2 \cdot 6 \, \mu m/h$, which represents a twofold of the accuracy of experimental data proper, which has been estimated to $1 \cdot 3 \, \mu m/h$ as an average error of measurement. The experimental data are reproduced with the same standard deviation even by the mechanism X, where however, the zero value of the equilibrium adsorption constant is not physically compatible with the non-zero value of the kinetic term s k_{2HCl^+}, by considering the validity of the relation $K_{2HCl} = = k_{2HCl^+}/k_{2HCl^-}$. For this reason, the mechanism X seems as a less probable one. Thus the mechanism I seems to be the most probable one of the dual centre model.

By an analogous argumentation as in the dual centre model, it is possible to eliminate the mechanisms II, III, and V of the single centre model, as follows from the values of constants given in Table.III. The remaining mechanisms I and IV are not significantly different, their standard deviations being $4 \cdot 0$ and $3 \cdot 6$, so that their probability will not be greatly different.

If the single centre model is compared with the dual centre one, the standard deviations of optimum mechanisms in both cases ($2 \cdot 6$ and $3 \cdot 6$ or $4 \cdot 0 \, \mu m/h$) indicate a significantly higher probability of the dual centre model. The importance of this conclusion is emphasized by the fact, that the quantitative description of both models contains the same number of adjustable parameters, *i.e.* two.

TABLE III

Results of single centre model

Mechanism	Rate constant		Equilibrium adsorption constant		Standard deviation
	Meaning	Value	Meaning	Value	
I	Lk_+	$1 \cdot 862 \cdot 10^{-6}$	K_{GaCl}	$220 \cdot 2$	
			K_{HCl}	0	$4 \cdot 0$
II	$Lk_+ (K'_{As_2})^{1/2}$	$1 \cdot 747 \cdot 10^{-4}$	$K'_{As_2} = K_{HCl}$	0	$6 \cdot 5$
III	Lk_{GaCl^+}	$4 \cdot 801 \cdot 10^{-6}$	$K_{GaCl} = K_{HCl}$	0	$8 \cdot 9$
IV	$Lk_{As_2^+}$	$5 \cdot 15 \cdot 10^{-5}$	K'_{As_2}	$195 \cdot 2 \cdot 10^4$	
			K_{HCl}	0	$3 \cdot 6$
V	Lk_{HCl^+}	$2 \cdot 769 \cdot 10^{-6}$	K_{GaCl}	$220 \cdot 2$	
			K_{HCl}	0	$4 \cdot 0$

In comparison with previous results[1], it can be stated that the approach described above leads to the achievement of physical plausibility by eliminating the negative values of the equilibrium constants, whereby the number of adjustable parameters is decreased from three to two. From this point of view, the previous equations[1] do appear as semiempirical correlation equations, even though a higher precision of reproduction has been obtained in one case.

With regard to individual rate controlling steps, it can be concluded from Table II, that the surface reaction appears as the most probable rate controlling step, followed by the adsorption of arsenic and by the desorption of hydrogen chloride, and that the adsorption of gallium chloride appears as the significantly least probable rate controlling step. It is interesting, that the same probability sequence holds roughly even in the single centre model, which follows from Table III.

In passing from the single centre model to the dual centre one, a distinct increase of the accuracy in reproducing experimental date is observed, in agreement with theoretical ideas, according to which the adsorption mechanism should predominate over the impact mechanism. In this direction, a quantitative investigation of the effect of increasing the number of active centres seems promising. Further on, it is necessary to realize, that only one kind of active centers has been considered in all the models up to now. Therefore, the direction to a greater number of kinds of these centers appears as an additional trend in the theoretical study. It is necessary to add, that in the literature of the branch[6], a situation is frequently met, when only one model or mechanism is proposed and quantitatively studied, and that the direction characterized by a systematic comparative study of a series of mechanisms and of models has no precedent in the literature.

From the present study, the following conclusion can be drawn:

1. The introduction of the dual site model for the epitaxial layers growth of gallium arsenide from the gas phase and the application of a new method of mathematical treatment of data has led to a physical plausibility, whereby a simultaneous decrease of the number of adjustable parameters was achieved.

2. As the most probable mechanism is the variant in which the rate controlling step of chemical nature (in addition to diffusion) is the surface reaction, where the adsorbed gallium chloride and the arsenic react with the hydrogen from the gas phase. This variant is leading to a relation for the growth rate, which reproduces the experimental data with a standard deviation which is equal to the twofold of accuracy of the experiments.

3. The dual centre model is distinctly more probable than the single centre model.

4. The obtained rate equation represents a physically founded relation, applicable in controlling and optimizing the preparation and properties of epitaxial layers of the gallium arsenide.

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