AN INHOMOGENEOUS GROWTH MODEL OF GALLIUM ARSENIDE EPITAXIAL LAYERS FROM THE GAS PHASE

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Dedicated to late Academician Eduard Hála.

This paper represents a continuation and ending of the kinetic study of the gallium arsenide formation, where a so-called inhomogeneous model is proposed and quantitatively formulated in five variants, in which two kinds of active centres appear. This model is compared both with the experimental data and with the previous sequence of homogeneous models.

In the last papers[1-3], a sequence of growth models of the gallium arsenide epitaxial layers from the gas phase has been described with increasing complexity from the one centre model through the dual centre- and the triple centre models up to the quadruple centre model. In all these models, it has been supposed that the surface of the solid is homogeneous in the sense that only one kind of active centres occurs on the surace. This homogeneity consists first in that the same surface processes such as adsorption or chemical reaction are taking place on all centres. Thus it appears as desirable to abandon the assumption of homogeneity and to investigate the consequences to which the inhomogeneity of active centres can lead. In this paper, therefore, a growth model of the epitaxial gallium arsenide is proposed and quantitatively treated, in which two different kinds of active centres appear. At the same time, the cases are considered, where the total number of centres taking part in the activated complex formation in the rate controlling surface reaction is equal to two, three, or four. The model of this type is here denoted for brevity sake as an inhomogeneous one.

THEORETICAL

BASIC MODEL IDEAS

All ideas from the previous models[1-3] concerning the metastable equilibrium in the gas phase and the existence of two rate controlling steps remain here conserved, together with the set of three chemical reaction which can take place in the system. In addition to that, all the equations concerning the diffusion of individual components and the steady state conditions remain valid here. The essential difference, however, will consist in all equations, in which the concentrations of active centres appear, since, in the present model, two kinds of active centres are appearing, which will be denoted by subscripts of 1 and 2. Thus, the changes will concern the equations describing adsorption and surface reaction which will be considered as the second rate controlling step, in agreement with the knowledge obtained previously[2,3]. In addition to that, it will be considered, that from the gaseous reactants, the arsenic only will be adsorbed on centres of the first kind, and the gallium monochloride only will be adsorbed on centres of the second kind. The hydrogen chloride, which is the gaseous product, will be assumed to be adsorbed on centres of the second kind or on a mixed centre of both kinds. Finally, it will be considered, that the rate controlling surface reaction can take place by the dual centre-, triple centre- or quadruple centre mechanism. All the considered variants, which are treated quantitatively in the following, are summarized in Table I. Here, the symbol (ads 1) denotes the adsorption on a centre of the first kind, the (ads 2) denotes the adsorption on a centre of the second kind, the (ads 11) denotes the adsorption on a dual centre, where both

TABLE I

Variants of the inhomogeneous model

Variant	Mechanism	Rate controlling surface reaction
A	dual centre	$As(ads\ 1) + GaCl(ads\ 2) + \frac{1}{2}H_2(g) = GaAs(s) + HCl(ads\ 12)$
B	dual centre	$As(ads\ 1) + GaCl(ads\ 2) + \frac{1}{2}H_2(g) = GaAs(s) + HCl(ads\ 2) + + n1$
C	triple centre	$As_2(ads\ 1) + 2\ GaCl(ads\ 2) + H_2(g) = 2\ GaAs(s) + + 2\ HCl(ads\ 2) + n1$
D	quadruple centre	$2\ As(ads\ 1) + 2\ GaCl(ads\ 2) + H_2(g) = 2\ GaAs(s) + + 2\ HCl(ads\ 2) + (n1)_2$
E	quadruple centre	$As_2(ads\ 11) + 2\ GaCl(ads\ 2) + H_2(g) = 2\ GaAs(s) + + 2\ HCl(ads\ 2) + (n1)_2$

centres are of the first kind, the (ads 12) denotes the adsorption on a mixed dual centre, where one centre is of the first- and the other centre is of the second kind, the symbol n1 denotes an unoccupied centre of the first kind, and the $(n1)_2$ denotes an unoccupied dual centre, where both centres are of the first kind. The rate equations for all variants given in Table I are derived in the following.

RATE EQUATIONS

Variant A

The surface reaction (A) takes place by the dual centre mechanism and its rate in the forward direction will be proportional to the concentration of mixed dual centres, $c(AsGaCl)$, in which the centre of the first kind is occupied by an atom of arsenic and the centre of the second kind by a molecule of the gallium monochloride. The rate of this reaction in the backward direction is proportional to the concentration of mixed dual centre, $c(HCl)$, occupied by a molecule of the hydrogen chloride, so that the resulting rate, r, will be given by the equation

$$r = k_+ c(AsGaCl) \left[p^*(H_2)\right]^{1/2} - k_- c(HCl), \qquad (A.1)$$

where k_+ and k_- are the rate constants and $p^*(H_2)$ is the partial pressure of hydrogen closely at the surface of the solid. With regard to the equilibrium condition, it is possible to rewrite Eq. $(A.1)$ into a compact form

$$r = k_+ \left\{ c(AsGaCl) \left[p^*(H_2)\right]^{1/2} - c(HCl)/K' \right\}, \qquad (A.2)$$

where K' denotes the equilibrium constants of the surface reaction (A), for which the following relationship is valid

$$K' = k_+/k_- . \qquad (A.3)$$

The concentration of mixed dual centres, $c(AsGaCl)$, appearing in Eq. $(A.2)$, may be expressed in terms of simple centre concentrations under assumption of a regular arrangement of centres on the solid surface. The regularity of arrangement means, that every centre of the first kind has the same number of vicinal centres of the second kind, denoted as s_{12} and vice versa. In a regular arrangement, every centre of the first kind will have naturally also the same number of vicinal centres of the first kind, i.e. the value of s_{11} will be the same for all centres, etc. The meaning of what has been said is that the quantities of s_{11}, s_{21}, s_{12} and s_{22} are constants, the numerical values of which can generally differ one from another, however, an additional assumption concering their values is not necessary to proceed further.

Thus, let us select one centrer of the first kind, occupied by an arsenic atom, which has s_{12} vicinal centres of the second kind, on which molecules of the gallium mono-chloride can be adsorbed. If the fraction of centres of the second kind, occupied by the molecules of gallium monochloride, is denoted as $\Theta(\text{GaCl})$, it is possible to write

$$\Theta(\text{GaCl}) = c(\text{GaCl})/L_2 \,, \qquad\qquad (A.4)$$

where L_2 denotes the total concentration of centres of the second kind. Therefore, in the vicinity of the considered centre of the first kind, occupied by an arsenic atom, there will exist on the average $s_{12}\Theta(\text{GaCl})$ centres of the second kind, occupied by the GaCl molecules. This means, that one adsorbed atom of arsenic can form $s_{12}\Theta(\text{GaCl})$ mixed dual centres AsGaCl. Since the number of such adsorbed arsenic atoms on a unit surface is equal to $c(\text{As})$, the total concentration of mixed dual centres AsGaCl will be given by an expression of

$$c(\text{AsGaCl}) = s_{12}\Theta(\text{GaCl}) \, c(\text{As}) \,, \qquad\qquad (A.5)$$

or on substituting from the relationship $(A.4)$

$$c(\text{AsGaCl}) = (s_{12}/L_2) \, c(\text{As}) \, c(\text{GaCl}) \,. \qquad\qquad (A.6)$$

In these calculations, it is also possible to proceed in a reversed way, i.e. to select a centre of the second kind, occupied by a GaCl molecule, which will have s_{21} vicinal centres of the first kind, on which the arsenic atoms can be adsorbed. If we denote the fraction of centres of the first kind, occupied by the As atoms, as $\Theta(\text{As})$, i.e. $\Theta(\text{As}) = c(\text{As})/L_1$, we arrive in an analogous way at an expression for the concentration of mixed dual centres AsGaCl in the form

$$c(\text{AsGaCl}) = (s_{21}/L_1) \, c(\text{As}) \, c(\text{GaCl}) \,. \qquad\qquad (A.7)$$

By comparing the relations $(A.6)$ and $(A.7)$, we arrive at a conclusion, that the following equality must be valid

$$s_{12}/L_2 = s_{21}/L_1 \,. \qquad\qquad (A.8)$$

This result may be understood more easily, if Eq. $(A.8)$ is rewritten into the form

$$s_{12}L_1 = s_{21}L_2 \,, \qquad\qquad (A.9)$$

where the product $s_{12}L_1$ indicates the total concentration of mixed dual centres 12,

i.e. the quantity c_{12}, and the product $s_{21}L_2$ is equal to c_{21}, i.e. to the total concentration of mixed dual centres 21. And since the dual centre 12 is equivalent to the dual centre 21, the following equation is valid

$$c_{12} = c_{21} , \qquad (A.10)$$

which is in agreement with Eq. $(A.9)$. It is also evident from Eq. $(A.9)$, that the values of s_{12} and s_{21} will be equal only in a speical case, if $L_1 = L_2$, i.e. if concentrations of centres of both kinds will be equal. In other cases, the values of s_{12} and s_{21} will be different even with a regular arrangement.
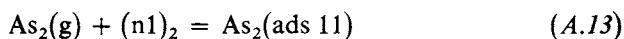
If the rate controlling step is the chemical reaction, then the remaining steps of chemical nature, i.e. the chemisorption of gaseous reactants and products will take place at equilibrium. Consequently, for adsorption of gallium monochloride which is adsorbed molecularly on centres of the second kind
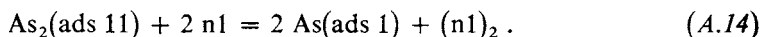
$$\text{GaCl(g)} + \text{n2} = \text{GaCl(ads 2)} \qquad (A.11)$$
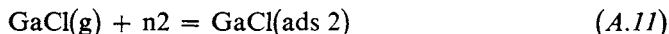
we obtain from the equilibrium condition[3]

$$c(\text{GaCl}) = c_{n2}(K\text{GaCl})\, p^*(\text{GaCl}) , \qquad (A.12)$$
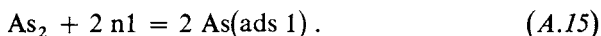
where the $K(\text{GaCl})$ is the adsorption equilibrium constant of the gallium monochloride, and c_{n2} is the concentration of unoccupied centres of the second kind. The arsenic is adsorbed according to Eq. (A) on centres of the first kind in an atomic form, whereas, in the gas phase, it is present predominantly in the form of diatomic molecules, according to previous analyses. Thus, let us consider, that the adsorption of arsenic takes place in two steps so that an As_2 molecule is adsorbed first on a dual centre of the second kind, and in the second step, a dissociation occurs under participation of two simple centres of the same kind, or

$$\text{As}_2(\text{g}) + (\text{n1})_2 = \text{As}_2(\text{ads 11}) \qquad (A.13)$$

and

$$\text{As}_2(\text{ads 11}) + 2\,\text{n1} = 2\,\text{As(ads 1)} + (\text{n1})_2 . \qquad (A.14)$$

Since the adsorption of arsenic takes place at equilibrium, it is sufficient to consider the summary equation $(A.15)$ which results by summing up Eqs $(A.13)$ and $(A.14)$

$$\text{As}_2 + 2\,\text{n1} = 2\,\text{As(ads 1)} . \qquad (A.15)$$

For this adsorption step, we obtain from the equilibrium condition

$$c(\text{As}) = c_{n1}[K(\text{As}_2)]^{1/2} \, [p^*(\text{As}_2)]^{1/2} \,, \qquad (A.16)$$

where c_{n1} is the concentration of unoccupied centres of the first kind, and $K(\text{As}_2)$ is the adsorption equilibrium constant in the summary equation $(A.15)$. Combining Eqs $(A.6)$, $(A.12)$, and $(A.16)$, an expression is obtained for the concentration of mixed dual centres AsGaCl in the form

$$c(\text{AsGaCl}) = (s_{12}/L_2) \, [K(\text{As}_2)]^{1/2} \, K(\text{GaCl}) \, [p^*(\text{As}_2)]^{1/2} \, p^*(\text{GaCl}) \, c_{n1}c_{n2} \,. \quad (A.17)$$

In the backward reaction, the hydrogen chloride is adsorbed according to Eq. (A) on a mixed dual centre

$$\text{HCl(g)} + \text{n12} = \text{HCl(ads 12)} \qquad (A.18)$$
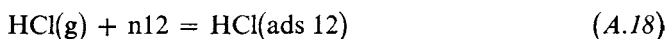
and at adsorption equilibrium, the following will be valid

$$c(\text{HCl}) = c_{n12}K(\text{HCl}) \, p^*(\text{HCl}) \,, \qquad (A.19)$$

where the concentration of unoccupied mixed dual centres, c_{n12}, can be expressed in terms of simple centres, if a regular arrangement is assumed. Let us select one unoccupied centre of the first kind, in the vicinity of which there will be s_{12} centres of the second kind in total. If the fraction of unoccupied centres of the second kind is denoted as Θ_2, i.e.

$$\Theta_2 = c_{n2}/L_2 \,, \qquad (A.20)$$

then the number of unoccupied centres of the second kind in the vicinity of the considered centre will be equal to $s_{12}\Theta_2$ on the average. At the same time, the value of $s_{12}\Theta_2$ gives the number of mixed unoccupied dual centres, which can be formed by one unoccupied centre of the first kind. And since there exist c_{n1} such centres on a unit surface, the concentration of unoccupied mixed dual centres will be given by the relationship

$$c_{n12} = s_{12}\Theta_2 c_{n1} \,, \qquad (A.21)$$

or on substituting from Eq. $(A.20)$

$$c_{n12} = (s_{12}/L_2) \, c_{n1}c_{n2} \,. \qquad (A.22)$$

In a reversed procedure, i.e. if we would start with a centre of the second kind, we would arrive at the result

$$c_{n12} = (s_{21}/L_1) \, c_{n1}c_{n2} \,, \qquad (A.23)$$

and on comparing with Eq. $(A.22)$, we would obtain again Eq. $(A.9)$, which must be satisfied even here, if the rate equation is to be consistent for both directions of the reaction. By substituting Eq. $(A.22)$ into $(A.19)$, an expression is obtained for the concentration of the adsorbed hydrogen chloride

$$c(\text{HCl}) = (s_{12}/L_2)\, K(\text{HCl})\, p^*(\text{HCl})\, c_{n1}c_{n2}\,. \qquad (A.24)$$

Combining Eqs $(A.2)$, $(A.17)$, and $(A.24)$, we obtain an expression for the rate of the surface reaction in the form

$$r = k_+(s_{12}/L_2)\, [K(\text{As}_2)]^{1/2}\, K(\text{GaCl})\, c_{n1}c_{n2}\, \{[p^*(\text{As}_2)]^{1/2}\, p^*(\text{GaCl})\, [p^*(\text{H}_2)]^{1/2} -$$
$$- [p^*(\text{HCl})/K_F]\}\,, \qquad (A.25)$$

where K_F is the thermodynamic equilibrium constant of the reaction

$$1/2\ \text{As}_2(\text{g}) + \text{GaCl}(\text{g}) + 1/2\ \text{H}_2(\text{g}) = \text{GaAs}(\text{s}) + \text{HCl}(\text{g})\,, \qquad (F)$$
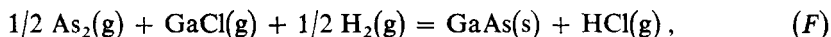
and its relationship to other equilibrium constants is given by the expression

$$K_F = K'[K(\text{As}_2)]^{1/2}\, K(\text{GaCl})/K(\text{HCl})\,. \qquad (A.26)$$

The concentrations of unoccupied centres of the first and of the second kind, i.e. the quantities c_{n1} and c_{n2} appearing in Eq. $(A.25)$, can be eliminated by means of material balances. Consequently, for centres of the first kind, an equation is obtained

$$c_{n1} + c(\text{As}) + c(\text{HCl}) = L_1 \qquad (A.27)$$

and for centres of the second kind, the following is valid

$$c_{n2} + c(\text{GaCl}) + c(\text{HCl}) = L_2\,. \qquad (A.28)$$

Substituting the expressions $(A.12)$, $(A.16)$, and $(A.24)$ into these equations, the balances assume the following forms

$$c_{n1} + [K(\text{As}_2)\, p^*(\text{As}_2)]^{1/2}\, c_{n1} + (s_{12}/L_2)\, K(\text{HCl})\, p^*(\text{HCl})\, c_{n1}c_{n2} = L_1 \quad (A.29)$$

and

$$c_{n2} + K(\text{GaCl})\, p^*(\text{GaCl})\, c_{n2} + (s_{12}/L_2)\, K(\text{HCl})\, p^*(\text{HCl})\, c_{n1}c_{n2} = L_2\,. \quad (A.30)$$

By a simultaneous solution of both quadratic equations $(A.29)$ and $(A.30)$ and by

substitution into Eq. $(A.25)$, the final form/of the rate equation is obtained

$$r = \frac{2k_+ s_{12} L_1 [K(\text{As}_2)]^{1/2} K(\text{GaCl}) \{[p^*(\text{As}_2)]^{1/2} p^*(\text{GaCl}) [p^*(\text{H}_2)]^{1/2} - {} - p^*(\text{HCl})/K_\text{F}\}}{\{\{1 + [K(\text{As})_2 \, p^*(\text{As})_2)]^{1/2}\} [1 + K(\text{GaCl}) \, p^*(\text{GaCl})] + {} + (1 + R) \, s_{12} K(\text{HCl}) \, p^*(\text{HCl})\}[1 + (1 - x^2)^{1/2}]},$$

$$(A.31)$$

where the constant R denotes the ratio of concentrations of both kinds of active centres

$$R = L_1/L_2 , \qquad\qquad (A.32)$$

and the quantity x has the following meaning

$$x = R^{1/2} \frac{2s_{12} K(\text{HCl}) \, p^*(\text{HCl})}{\{1 + [K(\text{As}_2) \, p^*(\text{As}_2)]^{1/2}\} [1 + K(\text{GaCl}) \, p^*(\text{GaCl})] + {} + (1 + R) \, s_{12} K(\text{HCl}) \, p^*(\text{HCl})} . \quad (A.33)$$

In a special case, where the concentrations of both kinds of centres are equal, $R = 1$, and the rate equation $(A.31)$ contains one adjustable parameter less.

Variant B

The variant B differs from the preceeding variant in that the hydrogen chloride is here adsorbed on a simple centre of the second kind, so that the rate equation in the forward direction remains unchanged, and the rate of the backward reaction will be proportional to the concentration of mixed centres, in which the centre of the second kind is occupied by a molecule of hydrogen chloride and the centre of the first kind is unoccupied. Thus we can write

$$r = k_+ c(\text{AsGaCl}) [p^*(\text{H}_2)]^{1/2} - k_- c_{\text{HCln}} , \qquad (B.1)$$

or

$$r = k_+ \{c(\text{AsGaCl}) [p^*(\text{H}_2)]^{1/2} - c_{\text{HCln}}/K'\} . \qquad (B.2)$$

Consequently, the concentration of dual centres AsGaCl will be given by the expression $(A.17)$

$$c(\text{AsGaCl}) = (s_{12}/L_2) [K(\text{As}_2)]^{1/2} K(\text{GaCl}) [p^*(\text{As}_2)]^{1/2} p^*(\text{GaCl}) \, c_{n1} c_{n2} , \quad (B.3)$$

and the relationship for the concentration of dual centres HCln is obtained under assumption of regular arrangement of centres in the following way. Let us consider

one centre of the second kind, which is occupied by a molecule of hydrogen chloride and which possesses s_{21} vicinal centres of the first kind. If the fraction of unoccupied centres of the first kind is denoted as Θ_1, i.e.

$$\Theta_1 = c_{n1}/L_1 \,, \tag{B.4}$$

there will be $s_{21}\Theta_1$ unoccupied centres in the vicinity of the considered centre, with which the last named centre can form dual centres of the type HCln. And since the number of centres occupied by a hydrogen chloride molecule on the unit surface is equal to $c(HCl)$, the concentration/of dual centres c_{HCln} will be given by the expression

$$c_{HCln} = s_{21}\Theta_1 c(HCl) \,, \tag{B.5}$$

or on substituting the relation $(B.4)$

$$c_{HCln} = (s_{21}/L_1)\, c_{n1} c(HCl) \,. \tag{B.6}$$

The adsorption of hydrogen chloride on centres of the second kind, i.e. the process

$$HCl(g) + n2 = HCl(ads\ 2) \,, \tag{B.7}$$
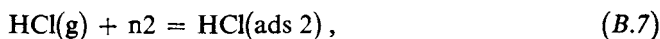
will take place at equilibrium, so that we obtain for the concentration $c(HCl)$

$$c(HCl) = c_{n2} K(HCl)\, p^*(HCl) \,, \tag{B.8}$$

and on substituting into Eq. $(B.6)$, it follows

$$c_{HCln} = (s_{21}/L_1)\, K(HCl)\, p^*(HCl)\, c_{n1} c_{n2} \,. \tag{B.9}$$

Combining the relations $(B.2)$, $(B.3)$, and $(B.9)$ and after rearrangeing, the rate equation is obtained in the form

$$r = k_+(s_{12}/L_2)\, [K(As_2)]^{1/2}\, K(GaCl)\, c_{n1} c_{n2}\{[p^*(As_2)]^{1/2}\, p^*(GaCl)\, [p^*(H_2)]^{1/2} -$$
$$- p^*(HCl)/K_F\} \,, \tag{B.10}$$

where the relationship $(A.8)$ has been used, which is valid naturally even here, as it can be easily shown by reversing the procedure, by which the relationship $(B.6)$ has been derived. The quantity K_F is the thermodynamic equilibrium constant of the reaction (F), and its relation to other constants is given again by the expression $(A.26)$. For concentrations of unoccupied centres c_{n1} and c_{n2}, two material balances

are valid in the form

$$c_{n1} + c(As) = L_1 \qquad (B.11)$$

and

$$c_{n2} + c(GaCl) + c(HCl) = L_2 . \qquad (B.12)$$

On substitution of relationships for the equilibrium adsorption of gas components $(A.6)$, $(A.12)$, and $(B.8)$, the balances $(B.11)$ and $(B.12)$ will assume the form

$$c_{n1} + c_{n2}[K(As_2) \, p^*(As_2)]^{1/2} = L_1 \qquad (B.13)$$

and

$$C_{n2} + c_{n2}K(GaCl) \, p^*(GaCl) + c_{n2}K(HCl) \, p^*(HCl) = L_2 . \qquad (B.14)$$

The final form of the rate equation is obtained by combining the Eqs $(B.10)$, $(B.13)$, and $(B.14)$

$$r = \frac{k_+ s_{12} L_1 [K(As_2)]^{1/2} \, K(GaCl) \, \{[p^*(As_2)]^{1/2} \, p^*(GaCl) \, [p^*(H_2)]^{1/2} - p^*(HCl)/K_F\}}{\{1 + [K(As_2) \, p^*(As_2)]^{1/2}\} \, [1 + K(GaCl) \, p^*(GaCl) + K(HCl) \, p^*(HCl)]} .$$

$$(B.15)$$

Variant C

In both preceeding variants, the rate controlling surface reaction took place by a dual centre mechanism, however, in the variant C, a triple centre is involved in the formation of the activated complex. This triple centre consists of one centre of the first kind and of two centres of the second kind. In the forward direction, the reaction centre is occupied by one As_2 molecule and by two GaCl molecules, and in the backward direction, two HCl molecules are adsorbed on two centres of the second kind and the centre of the first remains unoccupied. The rate equation of this variant may be consequently written in the form

$$r = k_+[c(As_2 2 \, GaCl) \, p^*(H_2) - c(2 \, HCl n1/K)] , \qquad (C.1)$$

where K' denotes again the equilibrium constant of the surface equation, which is equal to the ratio of rate constants of both opposing reactions, i.e. $K' = k_+/k_-$. The concentration of triple centre of type $As_2 2$ GaCl will be expressed by the following procedure under assumption of regular arrangement of centres. Let us consider one centre of the first kind occupied by an As_2 molecule, in the vicinity of which there are s_{12} vicinal centres of the second kind. On these s_{12} centres, a GaCl

molecule can be adsorbed, and on the remaining $(s_{12} - 1)$ centres, an additional GaCl molecule is adsorbed, so that in the vicinity of the considered centre of the first kind, there will be $s_{12}\Theta(\text{GaCl})\,(s_{21} - 1)\,\Theta(\text{GaCl})/2$ couples occupied by two GaCl molecules, where

$$\Theta(\text{GaCl}) = c(\text{GaCl})/L_2 . \qquad (C.2)$$

Consequently, the concentration of triple centres of the type $\text{As}_2 2\,\text{GaCl}$ will be given by the relationship

$$c(\text{As}_2 2\,\text{GaCl}) = \left[s_{12}(s_{12} - 1)/2L_2^2\right] c(\text{As}_2)\left[c(\text{GaCl})\right]^2 . \qquad (C.3)$$

The factor of one half appears here, since in this way of computation, each couple of GaCl molecules is counted twice. The surface concentrations of As_2 and of GaCl are given by equilibrium conditions of adsorption

$$\text{As}_2(g) + n1 = \text{As}_2(\text{ads } 1) \qquad (C.4)$$

and

$$\text{GaCl}(g) + n2 = \text{GaCl}(\text{ads } 2) , \qquad (C.5)$$

i.e. by the relationship

$$c(\text{As}_2) = c_{n1} K(\text{As}_2)\, p^*(\text{As}_2) \qquad (C.6)$$

and

$$c(\text{GaCl}) = c_{n2} K(\text{GaCl}) p^*(\text{GaCl}) . \qquad (C.7)$$

By substitution of equilibrium conditions $(C.6)$ and $(C.7)$ into the expression $(C.3)$, a relation is obtained for the concentration of triple centres $\text{As}_2 2\,\text{GaCl}$

$$c(\text{As}_2 2\,\text{GaCl}) = \left[s_{12}(s_{12} - 1)2L_2^2\right] K(\text{As}_2)\, K(\text{GaCl})\, p^*(\text{As}_2)\left[p^*(\text{GaCl})\right]^2 c_{n1} c_{n2}^2 . \qquad (C.8)$$

The expression for the concentration of triple centres $2\,\text{HCln1}$ in the backward direction is obtained in an analogous way, if an unoccupied centre of the first kind is considered, in the vicinity of which two molecules of hydrogen chloride are adsorbed. In this way, an expression is obtained

$$c(2\,\text{HCln1}) = \left[s_{12}(s_{12} - 1)/2L_2^2\right] c_{n1}\left[c(\text{HCl})\right]^2 , \qquad (C.9)$$

where the equilibrium concentration of hydrogen chloride is given by the relation

$$c(\text{HCl}) = c_{n2} K(\text{HCl})\, p^*(\text{HCl}) . \qquad (C.10)$$

Combining both last equations, an expression is obtained for the concentration of triple centres in the backward direction as

$$c(2 \text{ HCln1}) = \left[s_{12}(s_{12} - 1)/2L_2^2\right] \left[K(\text{HCl}) \, p^*(\text{HCl})\right]^2 c_{n1} c_{n2}^2 . \qquad (C.11)$$

Substituting the expressions $(C.8)$ and $(C.11)$ into the relation $(C.1)$ and after re-arrangeing, the rate equation is obtained in the form

$$r = k_+\left[s_{12}(s_{12} - 1)/2L_2^2\right] K(\text{As}_2) \left[K(\text{GaCl})\right]^2 c_{n1} c_{n2}^2 \{p^*(\text{As}_2) \left[p^*(\text{GaCl})\right]^2 .$$
$$. \, p^*(\text{H}_2) - \left[p^*(\text{HCl})/K_F\right]^2\} , \qquad (C.12)$$

where the equilibrium constant K_F of the reaction (F) is given by the relation

$$K_F^2 = K'K(\text{As}_2) \left[K(\text{GaCl})/K(\text{HCl})\right]^2 . \qquad (C.13)$$

The concentrations of unoccupied centres of the first and of the second kind will be determined from balance relations, which are here of the following form

$$c_{n1} + c(\text{As}_2) = L_1 \qquad (C.14)$$

and

$$c_{n2} + c(\text{GaCl}) + c(\text{HCl}) = L_2 . \qquad (C.15)$$

Combining these both balances with the equilibrium conditions $(C.4)$, $(C.5)$, and $(C.10)$, we obtain expressions for the quantities c_{n1} and c_{n2}, and substituting them into the relation $(C.12)$, we arrive at the final form of rate equation

$$r = \frac{k_+\left[s_{12}(s_{12} - 1)/2\right] L_1 K(\text{As}_2) \left[K(\text{GaCl})\right]^2 \{p^*(\text{As}_2) \left[p^*(\text{GaCl})\right]^2 p^*(\text{H}_2) - \left[p^*(\text{HCl})/K_F\right]^2\}}{\left[1 + K(\text{As}_2) \, p^*(\text{As}_2)\right] \left[1 + K(\text{GaCl}) \, p^*(\text{GaCl}) + K(\text{HCl}) \, p^*(\text{HCl})\right]^2} . \qquad (C.16)$$

Variant D

In this variant, the surface reaction takes place according to the Table I by a qua-druple centre mechanism, consisting of two centres of the first kind and of two centres of the second kind. In the forward direction, the quadruple centre is occupied by two arsenic atoms and by two gallium chloride molecules, and in the backward direction, by two hydrogen chloride molecules, while the dual centre of the first kind remains unoccupied. Consequently, the rate equation of the surface reaction

will be of the form

$$r = k_+[c(2 \text{ As2 GaCl}) \, p^*(\text{H}_2) - c(2 \text{ HCl2 n1})/K'] \,. \qquad (D.1)$$
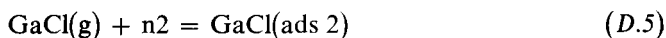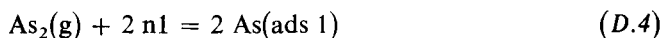
Let us start with one centre of the first kind, on which an arsenic atom is adsorbed, and which possesses s_{11} neighbours of the first kind, on which an additional arsenic atom is adsorbed, and which besides possesses s_{12} vicinal centres of the second kind, on which GaCl molecules are adsorbed. By extending the procedure used in the preceding variant, we arrive at an expression for the surface concentration of quadruple centres of the type 2 As2 GaCl, assuming a regular arrangement

$$c(2 \text{ As2 GaCl}) = [s_{11}s_{12}(s_{12} - 1)/4L_1L_2^2] \, [c(\text{As}) \, c(\text{GaCl})]^2 \,. \qquad (D.2)$$
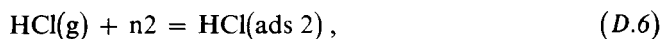
In a similar way, it is possible to obtain an expression even for the quadruple centre of the type 2 HCl2 n1, which appears in the reversed reaction, in the following form

$$c(2 \text{ HCl2 n1}) = [s_{11}s_{12}(s_{12} - 1)/4L_1L_2^2] \, [c_{n1}c(\text{HCl})]^2 \,. \qquad (D.3)$$

The surface concentrations of centres occupied by molecules or atoms of gas components are given by equilibrium conditions in adsorption steps, where it is necessary to take into account, that the As_2 molecules dissociate into atoms during the adsorption. Here, the following adsorption steps are involved

$$\text{As}_2(\text{g}) + 2 \text{ n1} = 2 \text{ As(ads 1)} \qquad (D.4)$$

$$\text{GaCl}(\text{g}) + \text{n2} = \text{GaCl(ads 2)} \qquad (D.5)$$

and

$$\text{HCl}(\text{g}) + \text{n2} = \text{HCl(ads 2)} \,, \qquad (D.6)$$

with the corresponding equilibrium conditions

$$c(\text{As}) = c_{n1}[K(\text{As}_2) \, p^*(\text{As}_2)]^{1/2} \,, \qquad (D.7)$$

$$c(\text{GaCl}) = c_{n2}K(\text{GaCl})p^*(\text{GaCl}) \qquad (D.8)$$

and

$$c(\text{HCl}) = c_{n2}K(\text{HCl}) \, p^*(\text{HCl}) \,. \qquad (D.9)$$

In this case, the material balance over active centres of the first and of the second kind are of the following form

$$c_{n1} + c(\text{As}) = L_1 \qquad (D.10)$$

and

$$c_{n2} + c(GaCl) + c(HCl) = L_2 \,, \tag{D.11}$$

so that combining the equations from $(D.1)$ up to $(D.3)$ and from $(D.7)$ up to $(D.11)$, we obtain the rate equation of the surface reaction in its final form as

$$r = \frac{k_+ \left[s_{11}s_{12}(s_{12} - 1)/4\right] L_1 K(As_2) \left[K(GaCl)\right]^2 \left\{p^*(As_2) \left[p^*(GaCl)\right]^2 p^*(H_2) - \left[p^*(HCl)/K_F\right]^2\right\}}{\left\{1 + \left[K(As_2) \, p^*(As_2)\right]^{1/2}\right\}^2 \left[1 + K(GaCl) \, p^*(GaCl) + K(HCl) \, p^*(HCl)\right]^2} \,. \tag{D.12}$$

The thermodynamic equilibrium constant K_F of the reaction (F) is given in this case by a relation which is identical with Eq. $(C.13)$.

Variant E

The rate controlling surface reaction takes place in this variant again by a quadruple centre mechanism and the difference from the preceding variant consists in that the diatomic arsenic molecules do not dissociate in atoms during the adsorption, but they are adsorbed molecularly on dual centres of the first kind. The rate equation of the surface reaction will be consequently of the following form

$$r = k_+ [c(As_2 2 \, GaCl) \, p^*(H_2) - c(2 \, HCl2 \, n1)/K'] \,. \tag{E.1}$$
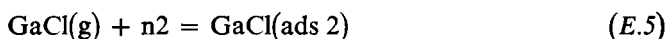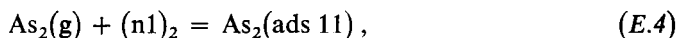
To derive a suitable expression for the concentration of quadruple centres of the type $As_2 2 \, GaCl$, we will start from a dual centre of the first kind, on which an As_2 molecule is adsorbed. The considered dual centre will possess s_{112} vicinal centres of the second kind, on which the GaCl molecules will be adsorbed, and by an analogous procedure as above, we obtain for the concentration of quadruple centres the expression

$$c(As_2 2 \, GaCl) = [s_{112}(s_{112} - 1)/2L_2^2] \, c(As_2) \, [c(GaCl)]^2 \,. \tag{E.2}$$

In the backward reaction, let us start from an unoccupied dual centre of the first kind, in the vicinity of which there are s_{112} centres of the second kind, on which the HCl molecules will be adsorbed, and by an analogous procedure, we obtain an expression for the concentration of quadruple centres of the type $2 \, HCl2 \, n1$ in the form

$$c(2 \, HCl2 \, n1) = [s_{112}(s_{112} - 1)/2L_2^2] \, c_{(n1)_2}[c(HCl)]^2 \,. \tag{E.3}$$

The adsorption steps take place in this variant according to the equations

$$As_2(g) + (n1)_2 = As_2(ads\ 11), \qquad (E.4)$$

$$GaCl(g) + n2 = GaCl(ads\ 2) \qquad (E.5)$$

and

$$HCl(g) + n2 = HCl(ads\ 2), \qquad (E.6)$$
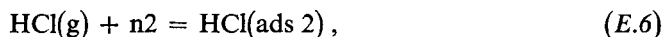
to which the following equilibrium conditions correspond

$$c(As_2) = c_{(n1)_2}K(As_2)\,p^*(As_2), \qquad (E.7)$$

$$c(GaCl) = c_{n2}K(GaCl)\,p^*(GaCl) \qquad (E.8)$$

and

$$c(HCl) = c_{n2}K(HCl)\,p^*(HCl). \qquad (E.9)$$

The concentration of unoccupied dual centres of the first kind, $c_{(n1)_2}$, appearing in Eqs $(E.3)$ and $(E.7)$ can be expressed in terms of simple centres as

$$c_{(n1)_2} = (s_{11}/2L_1)\,c_{n1}^2 \qquad (E.10)$$

and the material balances of active centres of the first and of the second kind are of the following form

$$c_{n1} + 2c(As_2) = L_1 \qquad (E.11)$$

and

$$c_{n2} + c(GaCl) + c(HCl) = L_2. \qquad (E.12)$$

Combining the equations from $(E.1)$ up to $(E.3)$ and from $(E.7)$ up to $(E.12)$, we obtain the rate equation of the rate controlling surface reaction in its final form

$$r = k_+ \frac{\begin{array}{c} s_{112}(s_{112} - 1)\,L_1 s_{11}K(As_2)\,[K(GaCl)]^2\,.\\ \cdot\{p^*(As_2)\,[p^*(GaCl)]^2 p^*(H_2) - [p^*(HCl)/K_F]^2\} \end{array}}{\{1 + [1 + 4s_{11}K(As_2)\,p^*(As_2)]^{1/2}\}^2\,[1 + K(GaCl)\,p^*(GaCl) + {}\atop{} + K(HCl)\,p^*(HCl)]^2},$$

$$(E.13)$$

where the equilibrium constant K_F of the reaction (F) is given again by a relation, which is identical with the equation $(C.13)$.

RESULTS

The resulting rate equations expressing individual variants of the inhomogeneous model, given in Table I, have been compared with the same experimental set as in the previous paper[3], and likewise the same procedure[3] has been used in evaluating the rate- and equilibrium constants, so that the results are mutually comparable. The final results are contained in Table II, where the kinetic term represents an effective rate constant in rate equations and its meaning in individual variants is given in the Table III.

DISCUSSION

It is evident at first sight from the Table II, that the variants C, D, and E are distinctly more probable than the variants A and B. However, with regard to the physical meaning of the kinetic term in the Table III and to the values of adsorption equilibrium constants given in the Table II, it is evident that the zero values of adsorption constants of arsenic are incompatible with nonzero values of the kinetic term in all variants except the variant C. Consequently, from all the variants considered here, only the variant C appears as physically acceptable, and this variant is shown also as the most probable from the viewpoint of the statistical treatment of data, since it presents the least value of the standard devation. Both these facts lead to the conclusion, that the most probable mechanism in the inhomogeneous model is the triple centre mechanism, where an As_2 molecule, adsorbed on one adsorption centre of the first kind, reacts with two GaCl molecules which are adsorbed on two centres of the second kind.

It is of course necessary to compare this conclusion with the previous results, obtained with homogeneous models[1-3]. It follows from this comparison, that the inhomogeneous model in the variant C is only slightly more probable than the homogeneous models[1-3] studied up to now, as it is evident from the standard deviation 2·5 and the previous[3] value 2·6. With respect to the accuracy of the experimental data which has been estimated to 1·3, however, this difference is in no way significant, so that we can conclude that the level of reproducing experimental data by the inhomogeneous model is practically the same as by the homogeneous models. In addition, this level of reproduction is achieved here with three adjustable parameters, i.e. with the same number of parameters as in the polycentric homogeneous models, i.e. in the triple centre and quadruple centre models[3]. Therefrom, it follows, that both inhomogeneous and homogeneous models are of equal probability and it is not possible to prefer some of them even on the ground of complexity of the form of rate equation. In general, it remains only one criterion from the standpoint of practical applicability, i.e. the number of adjustable parameters. And from this point of view, it appears, that the most suitable model is still the

homogeneous dual centre model[2], where two parameters are sufficient to achieve the same level of accuracy.

Table II

Computed results of inhomogeneous models

Variant	Kinetic term[a]	Equilibrium adsorption constant		Standard deviation
		meaning	value	
A	$4{\cdot}102 \cdot 10^{-4}$	$K(\text{GaCl})$	$220{\cdot}4$	$4{\cdot}0$
		$K(\text{As}_2)$	0	
		$s_{12}K(\text{HCl})$	0	
B	$4{\cdot}102 \cdot 10^{-4}$	$K(\text{GaCl})$	$220{\cdot}4$	$4{\cdot}0$
		$K(\text{As}_2)$	0	
		$K(\text{HCl})$	0	
C	$14{\cdot}46$	$K(\text{GaCl})$	$668{\cdot}8$	$2{\cdot}5$
		$K(\text{As}_2)$	$171{\cdot}6$	
		$K(\text{HCl})$	0	
D	$12{\cdot}46$	$K(\text{GaCl})$	$669{\cdot}1$	$2{\cdot}6$
		$K(\text{As}_2)$	0	
		$K(\text{HCl})$	0	
E	$49{\cdot}85$	$K(\text{GaCl})$	$669{\cdot}1$	$2{\cdot}6$
		$s_{11}K(\text{As}_2)$	0	
		$K(\text{HCl})$	0	

[a] See Table III.

Table III

Meaning of the kinetic term

Variant	Kinetic term
A	$2s_{12}L_1k_+[K(\text{As}_2)]^{1/2}\,K(\text{GaCl})$
B	$s_{12}L_1k_+[K(\text{As}_2)]^{1/2}\,K(\text{GaCl})$
C	$0{\cdot}5s_{12}(s_{12}-1)\,L_1k_+K(\text{As}_2)\,[K(\text{GaCl})]^2$
D	$0{\cdot}25s_{11}s_{12}(s_{12}-1)\,L_1k_+K(\text{As}_2)\,[K(\text{GaCl})]^2$
E	$s_{112}(s_{112}-1)\,L_1k_++s_{11}K(\text{As}_2)\,[K(\text{GaCl})]^2$

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