

CVD-grown Boron Phosphides: A Thermodynamical Adsorption Model to Understand the Growth of Different Kinds of Boron Phosphides

E.M. Kelder, P. van der Put, J. Schoonman

Laboratory for Inorganic Chemistry,
Delft University of Technology,
Julianalaan 136, NL-2628 BL Delft,
The Netherlands

ABSTRACT

The surface equilibrium concentration on BP has been calculated using thermodynamics and assuming Langmuir adsorption behavior, for the system B-P-H-Br. Thermodynamic constants for several adspecies are constructed, in order to calculate the surface concentrations of the adspecies, using the program SOLGASMIX [1]. Adsorption of gases on a surface is caused by a change in enthalpy and entropy. This change in enthalpy is characterized by the adsorption bond energy, whereas the entropy change is characterized by a loss of translation and rotation on adsorption, and gaining an equal number of vibrations. Enthalpy values were derived using experimental as well as reported bond energies. Entropy as well as heat capacity values were derived from the partition function, using available spectroscopic data, or data calculated empirically. The surface of BP was divided into B and P surface sites, b- and p-, respectively. The thermodynamic calculations were performed for several different temperatures as well as several different input partial pressures of BBr₃ and PBr₃ at atmospheric H₂ pressure. The calculations reveal the surface to be predominantly covered by PH₂ on b- as well as on p- sites. However, at very low PBr₃ input partial pressure the surface was mainly covered with BH₂. A ratio of the surface concentrations of BH₂ and PH₂ was defined. This ratio was used to explain the observed transition from cubic BP to amorphous B_xP (3 < x < 12) in the experimental CVD diagram. Both calculated surface concentrations of BH₂ and PH₂ depend strongly on temperature. The surface concentrations of the other adspecies depend strongly on the temperature as well as the surface concentration of the predominant adspecies BH₂ and PH₂. The concentrations of the free surface sites b- and p- increase with increasing temperature in the entire temperature range under study.

1 INTRODUCTION

In Ref. [2-4] an experimental CVD diagram was observed with either polycrystalline cubic boron monophosphide or amorphous boron phosphide B_xP with x ranging from 3 to 12. The thermodynamical CVD diagram calculated in Ref. [4], however, reveals a difference for especially high temperatures and high β₁ ($\beta_1 = \frac{p(\text{BBr}_3)}{p(\text{BBr}_3) + p(\text{PBr}_3)}$) values. The kinetics of the deposition growth rate for the BP deposits reveal a Langmuir-Hinshelwood mechanism [3]. In this mechanism heats of adsorption were derived from a least squares fit to the results. Unfortunately, all these measurements could not explain, by means of a change in free energy of the system, the observed transition in the experimental CVD diagram from BP → B_xP either on going to higher temperatures or for higher β₁ values. In order to understand this transition, thermodynamic calculations are performed to determine the surface concentrations of the adspecies. In this paper the gas-surface equilibrium reactions

are used to obtain these surface concentrations. The calculations are performed using the program SOLGASMIX [1] adapted for PC. However, to calculate these equilibrium concentrations, the thermodynamical properties of the gaseous species, the adspecies, as well as the surface sites must be known. Those values were calculated from the partition function, derived from reported spectroscopic data. If there were no spectroscopic data available, the values were estimated empirically. Results of these calculations were used in Ref. [3] to support the reaction model.

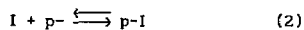
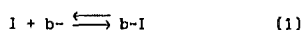
2. THE ADSORPTION MODEL

The adsorption model follows the assumptions for the Langmuir and Langmuir-Hinshelwood isotherms, which can be summarized as follows. Adsorption takes place only at free adsorption sites and forms monolayers only. In the present approximation the adspecies do not perturb neighboring sites and neighboring adspecies, though it is

generally accepted that perturbation of neighboring sites is possible [5]. As a consequence the perturbation leads to a dependency of the heat of adsorption on the surface concentration. However, this dependency is difficult to calculate from first principles, and will further be ignored here. In our approximation it is allowed to treat the free and occupied surface sites as independent species having their own thermodynamic constants. Furthermore, single bonds of the adspecies are assumed, which are perpendicular to the surface. Physisorption is also excluded, since it would not be expected to be important at these high operating temperatures [6]. The bond energies involved in physisorption are much smaller than those involved in chemisorption. Hence, the surface concentration will be dominated mainly by chemisorbed species. In order to calculate the surface concentration the thermodynamic constants $\Delta_r H^\circ$, S° , and $c_p(T)$ have to be known for all the species which could participate. In Eq. (1) or Eq. (2). Note that the species b-I and p-I, which represent the adspecies I on a boron site b- and a phosphorus site p-, respectively, should be treated as virtual gaseous species in order to obtain a distribution of the different adspecies. If the b-I and p-I species were to be treated as solid species having activities of one, only the presence or absence of solid phases is observed and no distribution of the adspecies. The thermodynamic constants of the gaseous species are taken from Ref. [4]. The thermodynamic constants for the free adsorption sites b- and p-, and those for the adspecies are calculated using several different approximations which will be presented when required. The evaluation of the three thermodynamic constants, i.e. $\Delta_r H^\circ$, S° , and c_p is discussed separately in the next Sections. The input amount of the free surface sites is taken to be small compared to the input amount of the gaseous species BBr₃ and PBr₃. In this case the observed surface concentration of the adspecies will not depend on the input amount of the free surface sites.

3. THERMODYNAMICS OF ADSORBED SPECIES

A necessary condition for adsorption of a gaseous species will be a negative value of the free energy ΔG between the initial state and the final state [6]. We consider the adsorption equilibrium reactions (1) and (2) of any gaseous species I on boron b- as well as on phosphorus p- sites. The gaseous species I represents any gaseous species calculated to be present in the gas phase [4]. The species mentioned in the text all refer to the gaseous species if not indicated otherwise.



The free energy change ΔG is given by the well-known equation:

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

where ΔH is the change in enthalpy and ΔS the change in entropy of the entire system. The change in enthalpy on adsorption depends on the process involved. The adsorption processes are either physisorption or chemisorption, both with their own adsorption heat range [5,6]. The adsorption assumed here is dictated by chemi-

sorption involving chemical bond formation between the surface and the gaseous species [6]. In contrast, the adsorption energies involved in physisorption are merely caused by VanderWaals forces and are, therefore, much smaller, and consequently the surface concentration of physisorbed adspecies will be much smaller. The heat of adsorption is derived from known bond energies as expected from chemical bond formation. The change in entropy on adsorption depends mainly on the loss and gain of translational, rotational, and vibrational degrees of freedom [7]. The change in entropy due to change in electronic levels is small, but will be taken into account in some instances. The possibility of surface diffusion is not taken into account. Therefore, the translation contribution to the entropy of the adspecies is zero. The surface concentration of each adspecies is assumed to be in equilibrium with its gaseous species. Hence, the surface equilibrium concentrations of these species are determined by their thermodynamic constants. In the next section the adsorption model will be described, while the evaluation of the thermodynamic constants of gaseous species I, the adsorption sites b- and p-, and the adspecies b-I and p-I are given in Section 4.

3.1. ENTHALPY OF FORMATION OF ADSPECIES

The actual value of the enthalpy of formation $\Delta_r H^\circ$ of the adspecies is calculated from the following equation:

$$\Delta_r H^\circ(s-I) = \Delta_r H^\circ(I) + \Delta_r H^\circ(s) - E_{(s-1)} \quad (4)$$

Where s means a surface site and $E_{(s-1)}$ the bond energy between the surface site and a species I. The meaning of the other symbols has already presented. The bond energy $E_{(s-1)}$ can be taken from fit results of experimental data, or by calculating its value from similar bonds.

3.2. THE ENTROPY OF THE ADSPECIES

The entropy of a gaseous species is determined by its translation, rotation, vibration, and electronic levels [8]. On chemisorption, gaseous species will loose at least their three translational degrees of freedom. The rotational degrees of freedom of poly-atomic species, however, can also disappear, either entirely in the event of perpendicular adsorption of a linear molecule, or partly in all other cases as will be discussed later on. Note that the bond of the adspecies to the surface is perpendicular by definition but the species itself need not be perpendicular to the surface. We assume that the molecule is not disturbed on chemisorption. Hence, the vibration frequencies of the adspecies are assumed to remain the same as for the gaseous species. The assignments of the vibrations of the gaseous species have been reported in the literature [9]. The vibrations of the gaseous species which are assumed to be unchanged in the adspecies are called internal vibrations, since the center of mass of the adspecies I remains at rest.

The electronic contribution to the entropy of the adspecies is estimated by considering the electronic levels and their degeneracy if one hydrogen or bromine atom is attached to the corresponding gaseous species [10]. For instance, the adspecies of atomic phosphorus will be treated electronically as a PH gaseous species. The rotational, vibrational and electronic

contributions to the entropy of the adspecies are called S_r^0 , S_v^0 , and S_e^0 , and are calculated using the partition function as summarized in Eqs. (5)-(9), respectively [8].

$$S_r^0/R = \frac{1}{2} \times \ln(I_z) + \frac{1}{2} \times \ln(T) - \ln(\sigma) - 0.523 \quad (5)$$

$$S_v^0/R = \sum_{j=1}^n \left\{ \frac{U_j \times \exp(-U_j)}{1 - \exp(-U_j)} - \ln[1 - \exp(-U_j)] \right\} \quad (6)$$

$$U_j = c_2 \nu_j / T; \quad n = 3 \times N - \Delta \quad (7)$$

$\Delta = 1, 0$ for adspecies with or without rotation, respectively.

$$S_e^0/R = T \frac{d(\ln(Q))}{dT} + \ln(Q) \quad (8)$$

$$Q = \sum_{j=1}^m g_j \times \exp[-c_2 \epsilon_j / kT] \quad (9)$$

with S_r^0 , S_v^0 , and S_e^0 the entropy value of rotation, vibration, and the electronic levels, respectively, R the gas constant, I_z the moment of inertia, T the absolute temperature, σ the symmetry number, U_j a parameter defined by Eq. (7), n the number of possible vibrations, N the number of atoms present in the adspecies, Δ an integer equal to 0 or 1 for adspecies with or without rotation, respectively, c_2 the second radiation constant, ν_j the j^{th} number of the vibration frequency, Q a parameter defined by Eq. (9), g_j the degeneration number of the electronic level, m the number of electronic levels, ϵ_j the energy value of the electronic level relative to the ground state, and k Boltzmann's constant.

The degrees of translational and rotational freedom, lost upon adsorption, are replaced by an equal number of additional vibrational degrees of freedom of the adspecies. The vibrations gained due to the loss of the three translations will be called external vibrations since the center of mass of adspecies I will vibrate (Fig. 1).

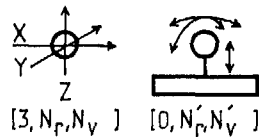


Fig. 1. Schematic representation of the vibrations of adsorbed species due to loss of translation. The three degrees of translation freedom of the gaseous species are suppressed on adsorption by the bond formation resulting in one stretching ν_t and a two-fold degenerate bending β_t vibration. Note that the figure could represent either monoatomic or polyatomic adspecies. $X, Y,$ and Z represent the three principal axes. The numbers between the square brackets denote the degrees of translation freedom, the degrees of rotational freedom, and the degrees of vibrational freedom of either the gas species or the adspecies.

The gain of the vibrations due to the loss of rotational freedom (Fig. 2) will also be called internal vibrations, since in this event the center of mass remains at rest. The new vibrations of the adspecies due to adsorption will be discussed along with their number of atoms and their structure. The values of the individual vibration

frequencies, however, will be discussed in Section 4.2. The loss of the three translations which occurs for every gaseous species once adsorbed results in the gain of an equal number of vibrations, i.e. the external vibrations. The loss of translation on adsorption is shown in Figure 1 for a monoatomic species. The same vibrations occur for the poly-atomic species.

A listing of possible vibrations resulting upon adsorption, and compiled according to the number of atoms present, is given below.

Monoatomic adsorption. In the case of monoatomic adsorption the three translations transform to one stretching vibration ν_t and a two-fold degenerate bending vibration β_t (Fig. 1).

Di-atomic linear adsorption. For diatomic linear adsorption (Fig. 2) the two lost rotations return as a two-fold degenerate rocking vibration ρ_r .

GAS SPECIES	ADSPECIES	
 linear [3,2,0+0+1]	 linear [0,0,3+2+1]	 non-linear [0,1,3+1+1]
 linear [3,2,0+0+4]	 non-linear [3,3,0+0+3]	 planar [0,1,3+2+3]
 planar [3,3,0+0+6]	 pyramidal [3,3,0+0+6]	 tetrahedral [0,1,3+2+6]

Fig. 2. Schematic representation of the vibrations replacing rotations after adsorption. The numbers between the square brackets, i.e. $[N_t, N_r, N_{v,t} + N_{v,r} + N_{v,v}]$ represent:
 N_t : degrees of translational freedom.
 N_r : degrees of rotational freedom.
 $N_{v,t}$: degrees of vibrational freedom due to loss of translation of the gas species.
 $N_{v,r}$: degrees of vibrational freedom due to loss of rotation of the gas species.
 $N_{v,v}$: degrees of vibrational freedom derived from the degrees of vibrational freedom of the gas species.

Di-atomic non-linear adsorption. One of the two lost rotations shows up as a rocking vibration ρ_r , whereas the other rotation remains a rotation around the adsorption bond (Fig. 2).

Tri-atomic adsorption. Linear adsorption of the tri-atomic gaseous species is assumed not to occur. Linear tri-atomic gaseous species are assumed to bend on adsorption to a planar or a pyramidal configuration. Note that linear gaseous species contain only two rotations, while non-linear gaseous species contain three rotations. However, the difference in degrees of rotational freedom is compensated by an extra vibration in the linear gaseous species along the axis of the molecule. Hence, a linear molecule loses two rotations and one vibration on adsorption and gains one new rotation along the adsorption bond and two new vibrations. Non-linear tri-atomic molecules, however, lose their three rotations and gain one new rotation around the adsorption bond and two new vibrations. The observed vibrations of the two different tri-atomic molecules on adsorption are a rocking vibration ρ_r and a wagging vibration ω_r (Fig.2). Although the adsorption of the tri-atomic molecules can occur either in a plane perpendicular to the surface or in a plane under a certain angle (but not perpendicular) the assignments of the new vibrations are the same. The assignments of the new vibrations of tri-atomic gaseous species on adsorption hold irrespective of the atoms near the central atom, i.e. B or P (Fig.2).

Tetra-atomic adsorption. For tetra-atomic molecules which are planar or pyramidal, the three rotations disappear on adsorption, yielding one new rotation along the adsorption bond and two new vibrations. The planar gaseous species are assumed to bend from a planar to a pyramidal configuration on adsorption. If the three atoms near the central atom, i.e. B or P, are the same the new vibration becomes a two-fold degenerate rocking vibration ρ_r (Fig.2). In the case of two different atoms near the central atom the degeneration is lost resulting in one wagging vibration ω_r and one rocking vibration ρ_r . These wagging and rocking vibrations can be coupled, but this will not be taken into account. The case of three different atoms near the central atom is not considered here.

The entropy of the empty surface sites b- and p- is taken as the entropy of the corresponding solids B and P, respectively, and added to the electronic contribution of the entropy S_e^0 . S_e^0 is determined by dangling bond states which are assumed to have a two-fold degenerate ground state due to the two spin states of the electron. Hence, according to Eqs.(8) and (9), S_e^0 is calculated to be 5.67 J/mole K.

3.3. HEAT CAPACITY C_p OF ADSPECIES

The heat capacity c_p for gaseous species as well as adspecies is determined by translation, rotation, vibration, and the electronic levels [8]. Translation for adspecies, however, was assumed to be absent. This holds also for rotation of certain adspecies. As was mentioned in Ref.[4], the electronic contribution to c_p is very small and, therefore, will be neglected. Hence, in order to calculate c_p as a function of temperature we have to calculate c_p for rotation $c_{p,r}$ and vibration $c_{p,v}$ as a function of temperature. With Eqs.(10) and (11), c_p can be calculated for the individual contributions at several temperatures,

$$c_{p,r}/R = \frac{1}{2} \quad (10)$$

$$c_{p,v}/R = \sum_{j=1}^n \left(\frac{U_j^2 \exp(-U_j)}{(1 - \exp(-U_j))} \right) \quad (11)$$

The value of c_p is calculated for several temperatures by summation of the individual contributions. A polynomial function (Eq.(12)), with fit parameters A-F, is used to fit the calculated c_p value as a function of temperature.

$$c_p = A + BxT + CxT^{-2} + DxT^2 + ExT^{-3} + FxT^{-1/2} \quad (12)$$

4. DETERMINATION OF THE THERMODYNAMICAL CONSTANTS OF THE ADSPECIES PRESENT IN THE SYSTEM B-P-H-Br

4.1. DETERMINATION OF THE ADSORPTION BOND ENERGIES AND THE ENTHALPIES OF FORMATION

The bond energy of the adspecies are taken from the calculated fit results of Ref.[3], i.e. 248 kJ/mole for B-P, and 89 kJ/mole for B-PBr₃ and P-PBr₃. The bond energy for B-B is estimated to be 225 kJ/mole representing the vaporization of solid boron into mono-atomic boron [8] taking an average of 2½ bond per atom, based on the crystal structure of solid boron, into account. The bond energy for P-P is estimated to be 220 kJ/mole representing the vaporization of solid black phosphorus into mono-atomic phosphorus taking 1½ bond per atom into account, based on the crystal structure. The adsorption bond energy B-B of the three-coordinated planar boron gaseous species is estimated taking a deformation energy, necessary to deform the planar boron gaseous species to pyramidal boron gaseous species, into account (see Appendix I). The deformation will be necessary since four-atomic planar boron species are probably not able to adsorb chemically but only physically. However, if the planar species deformed to pyramidal species, there is no room for a chemical bond to be formed. The phosphorus containing gaseous species are already pyramidal, and hence, do not need this extra deformation energy as is necessary for the planar boron containing gaseous species. The bond energies of B-H, P-H, B-Br, and P-Br are estimated, assuming pyramidal geometry, from BH₄ [8,11] and PBr₄ [8,12] (see Appendix I). The enthalpy of formation of the free surface sites b- and p- is taken to be half the value of the chemical bond of B-B [8] and P-P [8] plus the enthalpy of formation of the corresponding solid [8], i.e. B and P, respectively. The results of the adsorption bond energies are shown in Table 1. The enthalpies of formation of the adspecies are gathered in Tables 2 and 3.

Table 1. Energies of association [kJ/mole] between surface sites b- or p- and gaseous species i.

bond	$E(i-s)$	From:
b-B	225.0	sublimation of solid boron: B(s) → B(g) [8]
b-Br	100.0	BBr ₃ (g) + Br(g) → BBr ₄ (g) (see Appendix I)
b-H	102.0	BH ₃ (g) + H(g) → BH ₄ (g) (see Appendix I)
b-P	247.0	E _{ad} : fit result taken from Eq. (31)
p-B	247.0	E _{ad} : fit result taken from Eq. (31)
p-Br	56.4	PBr ₃ (g) + Br(g) → PBr ₄ (g) (see Appendix I)
p-H	112.0	PH ₃ (g) + H(g) → PH ₄ (g) (see Appendix I)
p-P	220.0	sublimation of solid phosphorus: P(s) → P(g) [8]
b-BX ₃ ¹⁾	84.7	B-BH ₃ [13]
b-PX ₃ ¹⁾	89.0	ΔH _f : fit result taken from Ref. [3]
p-BX ₃ ¹⁾	89.0	ΔH _f : fit result taken from Ref. [3]
p-PX ₃ ¹⁾	89.0	ΔH _f : fit result taken from Ref. [3]

¹⁾X stands for either hydrogen or a halogen.

Table 2. Enthalpy of formation $\Delta_r H^\circ(b-l)$ for the individual adspecies on boron b- sites. l stands for the gaseous species.

adspecies	$\Delta_r H^\circ(b-l)$ kJ/mole	$\Delta_r H^\circ(l)$ kJ/mole	$E(b-l)$ kJ/mole	$E_{def}^{(1)}$ kJ/mole	$\Delta_r H^\circ(b-l)$ kJ/mole
b-H	0.0	218.0	102.3	0.0	115.7
b-Br	0.0	96.4	99.8	0.0	-3.4
b-B	0.0	560.0	225.0	0.0	335.0
b-BH	0.0	442.7	225.0	0.0	217.7
b-BBr	0.0	218.8	225.0	0.0	-6.2
b-BH2	0.0	200.8	225.0	0.0	-24.2
b-BBr2	0.0	31.9	225.0	0.0	-193.1
b-BHBr	0.0	116.3 ²⁾	225.0	0.0	-108.7
b-BH3	0.0	106.7	84.7	226.0	248.0
b-BH2Br	0.0	-51.4	84.7	226.0	89.9
b-BHBr2	0.0	-135.5	84.7	226.0	5.8
b-BBr3	0.0	-250.5	84.7	226.0	-109.2
b-P	0.0	316.4	247.0	0.0	69.4
b-PH	0.0	236.1	247.0	0.0	10.9
b-PBr	0.0	147.1	247.0	0.0	-99.9
b-PH2	0.0	119.6	247.0	0.0	-127.4
b-PBr2	0.0	-20.4	247.0	0.0	-267.4
b-PH3	0.0	5.4	89.0	0.0	-83.6
b-PBr3	0.0	-192.4	89.0	0.0	-281.4
b-P4	0.0	58.9	89.0	0.0	-30.1
b-	112.5 ³⁾	0.0	0.0	0.0	112.5

¹⁾ E_{def} represents a deformation energy as defined in the text.
²⁾ $\Delta_r H^\circ(BHBr)$ is estimated as follows:
 $BH_2 \rightarrow B + 2H; E(B-H) = 397.6 \text{ kJ/mole}$
 $BBr_2 \rightarrow B + 2Br; E(B-Br) = 360.5 \text{ kJ/mole}$
 $BHBr \rightarrow B + H + Br; \Delta_r H^\circ(BHBr) = 116.3 \text{ kJ/mole}$
 i.e. $\Delta_r H^\circ(BHBr) = \Delta_r H^\circ(B) + \Delta_r H^\circ(H) + \Delta_r H^\circ(Br) - E(B-H) - E(B-Br)$.
³⁾ $\Delta_r H^\circ(b-) = \Delta_r H^\circ(B_2) + \frac{1}{2} \times E(b-B) = 0 + \frac{1}{2} \times 225 = 112.5 \text{ kJ/mole}$.

4.2. DETERMINATION OF THE ENTROPIES OF THE ADSPECIES

The entropy of the adspecies is calculated from rotation, vibration, and electronic levels. Here we shall discuss the evaluation of the values which contribute to the entropy separately. The standard entropy S° is calculated by summation of the entropy due to rotation, vibration, and electronic levels, and the entropy of the solid phase surface site, i.e. b- or p-.

Entropy due to rotation. The rotation is assumed to occur along the adsorption bond. In order to determine the rotation entropy (Eq.(5)) the moments of inertia along the adsorption bond perpendicular to the surface were calculated. The direction of the adsorption bond is taken to be the z-axis. Other rotations for the adspecies are not possible. The moment of inertia, I_z , is calculated using:

$$I_z = \sum_{j=1}^N r_j^2 \times m_j \quad (13)$$

where r_j is the distance of atom j to the z-axis, and m_j the atomic mass. The moments of inertia along with the geometric information of the individual adspecies are given in Tables A1 and A2.

Entropy due to vibration. The entropy due to vibration of adspecies is calculated using Eqs. (6) and (7). The vibration frequency ν_j in the approximation of a harmonic oscillator is often given by [14]:

$$\nu_j = K_j \sqrt{k_j/\mu} \quad (14)$$

$$K_j = 2 \times E(X-Y) / (r(X-Y)^2) \quad (15)$$

Where ν_j is the j^{th} vibration frequency, K_j a dimensionless constant, k_j the force constant, μ the reduced mass, $E(X-Y)$ the bond energy between atoms X and Y, and $r(X-Y)$ is the bond length between the atoms X and Y.

Table 3. Enthalpy of formation $\Delta_r H^\circ(p-l)$ for the individual adspecies on phosphorus p- sites. l stands for gaseous species.

adspecies	$\Delta_r H^\circ(p-l)$ ¹⁾ kJ/mole	$\Delta_r H^\circ(l)$ kJ/mole	$E(p-l)$ kJ/mole	E_{def} ²⁾ kJ/mole	$\Delta_r H^\circ(p-l)$ kJ/mole
p-H	-12.4	218.0	112.0	0.0	93.6
p-Br	-12.4	96.4	56.3	0.0	28.0
p-B	-12.4	560.0	247.0	0.0	300.6
p-BH	-12.4	442.7	247.0	0.0	183.3
p-BBr	-12.4	218.8	247.0	0.0	-40.6
p-BH2	-12.4	200.8	247.0	0.0	-58.6
p-BBr2	-12.4	31.9	247.0	0.0	-227.5
p-BHBr	-12.4	116.3 ³⁾	247.0	0.0	-143.1
p-BH3	-12.4	106.7	89.0	226.0	231.3
p-BH2Br	-12.4	-51.4	89.0	226.0	73.2
p-BHBr2	-12.4	-135.5	89.0	226.0	-10.9
p-BBr3	-12.4	-250.5	89.0	226.0	-125.9
p-P	-12.4	316.4	220.0	0.0	84.0
p-PH	-12.4	236.1	220.0	0.0	3.7
p-PBr	-12.4	147.1	220.0	0.0	-85.3
p-PH2	-12.4	119.6	220.0	0.0	-112.8
p-PBr2	-12.4	-20.4	220.0	0.0	-252.8
p-PH3	-12.4	5.4	89.0	0.0	-96.0
p-PBr3	-12.4	-192.4	89.0	0.0	-293.8
p-P4	-12.4	58.9	89.0	0.0	-42.5
p-	97.6 ⁴⁾	0.0	0.0	0.0	97.6

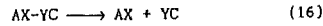
¹⁾ $\Delta_r H^\circ(p-)$ is taken from red phosphorus IV [8] since this agrees most with the tetrahedrally coordinated phosphorus p- sites.
²⁾ See footnote ¹⁾ Table 2.
³⁾ See footnote ²⁾ Table 2.
⁴⁾ $\Delta_r H^\circ(p-) = \Delta_r H^\circ(P_4) + \frac{1}{2} \times E(p-P) = -12.4 + \frac{1}{2} \times 220 = 97.6 \text{ kJ/mole}$.

The three translational degrees of freedoms of the molecule in the gas phase are lost on adsorption. This loss of translations will be compensated for by a gain of three vibrations, which we shall call the external vibrations since the center of mass of the adspecies will shift during vibration. The real center of mass, i.e. adspecies plus substrate does not shift. The gain of external vibrations will be observed as one stretching vibration along the adsorption bond and a two-fold degenerate bending vibration of the complete adspecies. The number of rotations will also be affected on adsorption as already discussed in Section 3.2. The loss of degrees of rotational freedom is compensated for by a gain of the same number of vibrations. The vibrations resulting from the loss of rotation are observed as rocking and twisting vibrations of the adspecies and occur without shift of the center of mass, and hence are called internal vibrations. The vibration frequencies of the gaseous species are assumed not to change on adsorption, and are, therefore, also called internal vibrations since these vibrations do not shift the center of mass of the adspecies. Hence, in most cases the frequencies of the internal vibrations are taken from the known gaseous species. In a few cases, however, the vibration frequencies are taken from equivalent species.

The main objective here is to determine the individual frequencies of the adspecies. In order to determine those individual vibration frequencies which could not be taken from the corresponding gaseous species or from equivalent species, the approximation of Eqs. (14) and (15) will be used by first deriving the constant K_j from known reported data. The value K_j is determined by using several different reported equivalent vibration frequencies and by taking a mean value. The results of the K_j values and the data of the frequencies to be calculated are summarized in the Tables 4 to 11. A # represents a fit parameter reported for Eqs.(17) and (29). The columns, numbered by 1 to 7, of Tables 4 to 11 are compiled as follows,

1. The bond involved in the vibration.
2. The bond energy $E(X-Y)$ [kJ/mole] involved in the vibration (see Table 1). The bond energies

being unknown at this stage are calculated assuming the following dissociation reaction:



with X and Y being either B or P and A and C being any ligand. Note that the case of no ligands is also included in Eq. (16).

- The bond length $r(X-Y)$ (Å) between the atoms involved in the vibration. $r_{1,B}$ and $r_{1,P}$ represent the bond length of the adspecies 1 and the surface site b- or p-, respectively.
- The reduced mass μ (amu) involved in the vibration. $M_{1,B}$ and $M_{1,P}$ represent the reduced mass of the adspecies on either b- or p- sites, respectively.
- The vibration frequency $\nu(X-Y)$ (cm^{-1}) is taken from the literature or calculated. The vibration frequencies printed between braces are calculated as needed using the tabulated values.
- The constants K_j defined by Eq. (14) and calculated from known parameters are taken from the literature as mentioned in the last column.
- The references (Ref.) per individual bond are given in the order: bond, $E(X-Y)$, $r(X-Y)$, $\nu(X-Y)$, respectively.

At first the external vibrations, i.e. the stretching (Tables 4-8) and the two-fold degenerate bending vibrations (Table 9) are evaluated for each individual adspecies and for both adsorption sites, i.e. b or p. After discussing the external vibrations the internal vibrations will be described for the individual adspecies, separately.

External vibrations

Table 4. External stretching vibration frequencies ν of one-, two-, and three-coordinate boron adspecies on boron.

bond	$E(B-B)$	$r(B-B)$	$\mu(B-B)$	$\nu(B-B)$	K_j	Ref.
H ₂ B-BH ₂	255.2	1.669	6.41	872	163.1	15; 16; 15; 15
B ₂	290.3	1.589	5.41	1062	162.8	8; 8; 8; 8
b-B	225.0	1.70	$M_{1,B}$	ν	163	-; 8; -

Table 5. External stretching vibration frequencies ν of one-, two-, and three-coordinate phosphorus adspecies on phosphorus.

bond	$E(P-P)$	$r(P-P)$	$\mu(P-P)$	$\nu(P-P)$	K_j	Ref.
P ₂	489.1	1.894	15.49	780	186.0	8; 8; 8; 8
HP-PH	363.2	2.004	15.99	699	207.8	17; 17; 18; 18
H ₂ P-P ₂ H	196.0	2.218	16.50	437	198.9	19; 19; 20; 21
p-P	220.0	2.22	$M_{1,P}$	ν	198	-; 8; -

Table 6. External stretching vibration frequencies ν of four-coordinate boron adspecies on boron.

bond	$E(B-B)$	$r(B-B)$	$\mu(B-B)$	$\nu(B-B)$	K_j	Ref.
4B-B ¹⁾	84.7	1.702	57.95	1061	1065	22; 13; 22; 22
BB-BB ²⁾	84.7	1.80	50.40	1065	1045	23; 13; 23; 23
b-B	84.7	1.80	$M_{1,B}$	ν	1050	-; 13; -

¹⁾ represents the ligands -Cl₂PH₃.
²⁾ represents the ligands -H₂PF₃.

Internal vibrations

Two-atomic adspecies.

The stretching vibration frequencies B-H, B-Br, P-H, and P-Br in the adspecies BH, BBr, PH, and PBr are taken from the corresponding gaseous species [8]. The deformation vibration frequencies of BH and PH adspecies are calculated using Eqs. (14) and (15) with parameters given in Table 10 and

Table 7. External stretching vibration frequencies ν of boron adspecies on phosphorus, phosphorus adspecies on boron, and four-coordinate phosphorus adspecies on phosphorus.

bond	$E(X-Y)$ ¹⁾	$r(X-Y)$ ¹⁾	$\mu(X-Y)$ ¹⁾	$\nu(X-Y)$ ¹⁾	K_j	Ref.
H ₂ B-PH ₂ ²⁾	89.0	1.937	9.929	564	257.9	24; 8; 25; 24
H ₂ B-PH ₂ ³⁾	..	1.937	9.417	577	256.9	24; 8; 25; 24
D ₂ B-PH ₂	..	1.937	11.271	515	251.1	26; 8; 25; 26
H ₂ B-PD ₂	..	1.937	10.071	549	253.0	26; 8; 25; 26
D ₂ B-PD ₂	..	1.937	11.585	510	252.1	26; 8; 25; 26
H ₂ B-PH ₂	..	1.937	9.833	551	250.9	26; 8; 25; 26
H ₂ B-PHMe ⁴⁾	..	1.93	10.741	557	264.1	27; 8; 27; 27
D ₂ B-PHMe ⁴⁾	..	1.93	12.48	509	256.9	27; 8; 27; 27
H ₂ B-PHMe ₂ ⁴⁾	..	1.93	11.313	561	273.0	27; 8; 27; 27
D ₂ B-PHMe ₂ ⁴⁾	..	1.93	13.258	506	266.6	27; 8; 27; 27
H ₂ B-PHMe ₃ ⁴⁾	..	1.93	11.313	556	270.6	27; 8; 27; 27
D ₂ B-PHMe ₃ ⁴⁾	..	1.93	13.258	507	267.1	27; 8; 27; 27
H ₂ B-PHEt ⁵⁾	..	1.93	11.99	557	279.1	27; 8; 27; 27
D ₂ B-PHEt ⁵⁾	..	1.93	14.203	506	275.9	27; 8; 27; 27
b-P ⁶⁾	..	1.93	$M_{1,P}$	ν	263	-; 8; -
p-P ⁶⁾	..	1.93	$M_{1,B}$	ν	263	-; 8; -
b-P ⁷⁾	..	2.22	$M_{1,P}$	ν	263	-; 8; -
p-P ⁷⁾	..	2.22	$M_{1,B}$	ν	263	-; 8; -
b-P ⁷⁾	47.0	1.90	$M_{1,P}$	ν	263	-; 8; -
p-P ⁷⁾	47.0	1.90	$M_{1,B}$	ν	263	-; 8; -

¹⁾ X-Y represents either B-P or P-P bond.
²⁾ values given for isotope B¹⁰.
³⁾ values given for isotope B¹¹.
⁴⁾ Me represents the ligand methyl (-CH₃).
⁵⁾ Et represents the ligand ethyl (-CH₂CH₃).
⁶⁾ bond represents four-coordinate adspecies.
⁷⁾ bond represents one-, two-, and three-coordinate adspecies.

Table 8. External stretching vibration frequencies ν of H and Br adspecies on boron and phosphorus

bond	$E(X-Y)$	$r(X-Y)$	$\mu(X-Y)$	$\nu(X-Y)$	K_j	Ref.
B-H	335.3 ¹⁾	1.233	0.922	2368	108.2	8; 8; 8; 8
b-H	302.4 ²⁾	1.23	1.008	(2155)	108.2	11; 11; 28; -
b-Br	-	-	-	200 ³⁾	-	-; 28; 28
P-H	263.4 ⁴⁾	1.47	0.980	2304	146.1	4; -; 28; 28
p-H	263.4 ⁴⁾	1.47	1.008	(2272) ⁵⁾	146.1	-; 28; -
P-Br	265.6 ⁶⁾	2.23	23.04	400	185.8	8; 8; 8; 8
p-Br	213.6 ⁷⁾	2.20 ⁸⁾	79.909	(195)	185.8	-; 12; 8; -

¹⁾ E(B-H) is calculated from BH \rightarrow B + H.
²⁾ E(b-H) is calculated from BH₂ \rightarrow B + 4H.
³⁾ E(b-Br) is taken to be 200 cm^{-1} as is approximated from $\nu(p-Br)$.
⁴⁾ E(p-H) is calculated from PH₂ \rightarrow P + 4H.
⁵⁾ This value agrees well the P-H stretching vibration frequency observed with NREEL in InP, i.e. 280 meV (=2258 cm^{-1}), [29].
⁶⁾ E(P-Br) is calculated from PBr \rightarrow P + Br.
⁷⁾ E(p-Br) is calculated from PBr₂ \rightarrow P + 4Br.
⁸⁾ r(p-Br) is taken from PBr₂ or PBr₃, i.e. 2.20 Å.

Table 9. Two-fold degenerate external bending vibration frequencies β of adspecies on boron and phosphorus.

bond	$E(X-Y)$	$r(X-Y)$ ¹⁾	$\mu(X-Y)$	$\nu(X-Y)$	K_j	Ref. ²⁾
Si-H	321.9 ³⁾	1.481	1.008	637 ¹⁾	37.32	8; 8; 8; 30
b-B ⁴⁾	225.0	$r_{1,B}$	$M_{1,B}$	β	37.32	-; 8; -
b-P ⁵⁾	204.7	$r_{1,P}$	$M_{1,P}$	β	37.32	-; 8; -
p-P ⁵⁾	204.7	$r_{1,B}$	$M_{1,B}$	β	37.32	-; 8; -
p-P ⁶⁾	224.5	$r_{1,P}$	$M_{1,P}$	β	37.32	-; 8; -
b-B ⁶⁾	84.73	$r_{1,B}$	$M_{1,B}$	β	37.32	-; 8; -
b-P ⁶⁾	88.96	$r_{1,P}$	$M_{1,P}$	β	37.32	-; 8; -
p-P ⁶⁾	88.96	$r_{1,B}$	$M_{1,B}$	β	37.32	-; 8; -
p-P ⁶⁾	88.96	$r_{1,P}$	$M_{1,P}$	β	37.32	-; 8; -
b-H	302.4 ⁴⁾	1.23	1.008	(743)	37.32	29; 8; 30; -
b-Br	299.9 ⁷⁾	1.89	79.909	(54)	37.32	-; 8; 8; -
p-H	269.2 ¹⁰⁾	1.47	1.008	(587)	37.32	-; 8; 30; -
p-Br	213.6	2.20	79.909	(39)	37.32	8; 8; 8; -

¹⁾ r is taken to be the distance between the surface and the center of mass of the adspecies. (See Table A1 and A2 for geometrical data).
²⁾ β means data are taken from Table 8.
³⁾ bond energy is taken from the reaction SiH₄ \rightarrow Si + 4H.
⁴⁾ the Si-H bending vibration frequency agrees quite well with the observed Si-H wagging vibration frequency, i.e. 650 cm^{-1} , in hydrogenated amorphous silicon [31].
⁵⁾ one-, two or three-coordinate boron adspecies.
⁶⁾ four-coordinate adspecies.
⁷⁾ see ²⁾ for Table 8.
⁸⁾ E(p-Br) is taken to be $1/4(3E_{B-Br} + E_{B-Br})$.
⁹⁾ (b) see notes ¹⁾, ⁶⁾, respectively, given at Table 8.

assuming the boron and phosphorus atoms to be at rest. Hence, the vibrations are characterized by hydrogen bound to either boron or phosphorus atoms. The bond energies are taken from BH₂ and PH₂, respectively.

Table 10. Internal rocking vibration frequencies ν_r for BH and PH adspecies.

bond	$E(x-y)^{1)}$	$r(x-y)^{2)}$	$\mu(x-y)^{3)}$	$\nu(x-y)^{4)}$	K	Ref. 2)
b-H	302.4	1.22	1.008	743	37.32	11; 11; 28; 2
B-H	397.6 ³⁾	1.20	1.008	(874) ⁴⁾	37.32	8; 8; -
p-H	269.2	1.47	1.008	587	37.32	2; 2; 28; 2
P-H	322.0 ⁵⁾	1.19	1.008	(793) ⁶⁾	37.32	8; 8; -

¹⁾X-Y represents either B-H or P-H bond.
²⁾ means the value is taken from Table 9.
³⁾E(x-y) is calculated from the reaction $BH_2 \rightarrow B + 2H$.
⁴⁾ ν_r is two-fold degenerate since the adspecies is adsorbed linearly.
⁵⁾E(x-y) is calculated from the reaction $PH_2 \rightarrow P + 2H$.
⁶⁾ ν_r is not degenerate since the adspecies is not adsorbed linearly.
 Note that the degeneration disappears to form a rotation.

For the bending vibrations of BBr and PBr adspecies we assume the heavy bromine atoms to be at rest. Hence, the reduced mass equals the mass of boron or phosphorus. The vibration frequencies are calculated from the deformation vibration frequencies of the gaseous species BBr₂ and PBr₂, respectively, by assuming complex bond energies and bond lengths as shown in Table 11. The bond energies and bond lengths are approximated by the average of the bond energies as well as the bond lengths involved in the deformation vibration as shown in Table 11.

Table 11. Internal rocking vibrations ν_r of BBr and PBr adspecies.

bond	$E(x-y)^{1)}$	$r(x-y)^{2)}$	$\mu(x-y)^{3)}$	$\nu(x-y)^{4)}$	K	Ref.
BBr ₂	388.5	1.87	10.811 ³⁾	150	34.35	8; 8; 8; 8
p-B-Br	349.5	1.86	10.811 ³⁾	(137)	35.35	-; 8; 8; -
b-B-Br	388.5	1.87	10.811 ³⁾	(142)	34.35	-; 8; 8; -
PBr ₂	352.4	2.38	30.974 ⁴⁾	114	60.56	8; 8; 8; 8
p-P-Br	355.6	2.38	30.974 ⁴⁾	(108)	60.56	-; 8; 8; -
b-P-Br	355.6	2.38	30.974 ⁴⁾	(120)	60.56	-; 8; 8; -

¹⁾E(x-y) is calculated as an average of the bond energies of either b-B, b-P, p-B, or p-P (upper value) with either B-Br or P-Br (lower value).
²⁾r(x-y) is calculated as an average of the bond lengths of either b-B, b-P, p-B, or p-P (upper value) with either B-Br or P-Br (lower value).
³⁾the reduced mass is assumed to be the atomic mass of the boron atom due to the high atomic mass of bromine.
⁴⁾the reduced mass is assumed to be the atomic mass of the phosphorus atom due to the high atomic mass of bromine.

Three-atomic adspecies.

The vibration frequencies of BH₂ adspecies, i.e. δ_{sc} , ω_r , ν_r , ν_{as} are taken from diborane(4) [15]. The vibration frequencies for the PH₂ adspecies are taken from diphosphine with the same assignments as given for the BH₂ adspecies. The evaluation of the vibration frequencies of the BBr₂ adspecies are made in a similar way using B₂Br₄ [32]. The observed vibration frequencies taken from B₂Br₄ equal almost the corresponding vibration frequencies of BBr₃. The corresponding phosphorus species, i.e. P₂Br₄, is only mentioned in the literature [33], but no vibrational data are available. Hence, we will take for PBr₂ adspecies the vibration frequencies of PBr₃. The possible vibrations derived from PBr₃ are ν_{as} , ω_r , and δ_{sc} , while, ν_r is not obtained. For P₂Cl₄ δ_{sc} and ν_r are almost equal [34], and, therefore, this will be assumed also to be the case for PBr₂ adspecies. The vibration frequencies of BHBr adspecies are for the same reason taken equal to those in BHBBr₂.

Four-atomic adspecies.

The stretching and deformation vibration frequencies of BH₃ adspecies are taken from (phenyl)₃P-BH₃ [35] since this is the heaviest

adduct of BH₃ without halogens reported in the literature. Halogens are known to affect the bond energies and hence the vibration frequencies due to electron shifts. However, the observed vibration frequencies do not depend strongly on the nature of the adduct, and these will be assumed not to depend on the nature of the surface site as adspecies.

The two-fold degenerate rocking vibration frequency, however, depends strongly on the nature of the adduct. The dependency itself is not easily understood from Eqs. (14) and (15). Hence, to observe the rocking vibration frequency of BH₃ adspecies the rocking vibration frequencies of different adducts are plotted versus their reduced mass over their respective B-P bond and fitted to a polynomial function (see Fig.3). The calculated vibration frequency is 748 cm⁻¹.

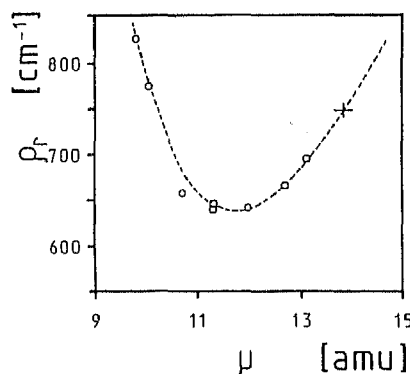


Fig.3. Rocking vibration ν_r as a function of the reduced mass μ for several H₃B:PY₃ species to obtain the rocking vibration ν_r for BH₃ adspecies. The adduct PY₃ represents several adducts observed in the literature. A polynomial fit along with a reduced mass which equals the mass of BH₃ yields $\nu_r=748$ cm⁻¹.

The individual vibration frequencies of the adspecies BHBr₂ are unknown since no values have been reported in the literature. Although this adspecies is tetrahedral many vibration frequencies have been taken from the planar BHBBr₂ gaseous species. The assignments of the vibrations however, are taken from PBr₂ adspecies along with a two-fold bending vibration and one stretching vibration due to the extra hydrogen atom. This approximation seems to be plausible as the adspecies of PBr₂ is pyramidal, in contrast to the adspecies of BBr₂ which is planar. The hydrogen atom is assumed to vibrate relative to the boron atom since the boron atom to which it is bound, is stationary. In line with this assumption the stretching and bending₁ vibration frequencies, i.e. 2155 and 743 cm⁻¹, respectively, can be taken from b-H since the boron atom is also tetrahedrally bound. The wagging vibration frequency ω_r is taken from the BBr₂ adspecies. The rocking vibration frequency ν_r is determined in a similar way as is the rocking vibration frequency of the PBr₂ adspecies, i.e. from the scissoring vibration frequency of PBr₂ adspecies. The individual vibration frequencies of BH₂Br adspecies are also unknown. Here too, many vibration frequencies are taken from the corresponding gaseous species [4]. An extra problem is the

heavy bromine atom, since the approximation of the boron atom being at rest will not hold anymore. Hence, the B-Br stretching vibration frequency is taken from the BBr adspecies. However, the bending vibration frequency, i.e. 54 cm^{-1} is taken from b-Br. The scissoring vibration frequency is taken from B₂H₄. The wagging vibration frequency ω_r is taken from gaseous BH₂Br [4]. The rocking vibration frequency ρ_r is assumed to be equal to the scissoring vibration frequency as is also assumed for BHBr₂ adspecies. The BBr₃ stretching vibration frequencies are almost independent on the nature of the adduct. This is assumed to hold also for adspecies. However, the vibration frequencies are chosen from an adduct with high molecular mass, i.e. "Dabco" [36] (see Fig. 4). The deformation vibration frequencies are also not affected by the adduct, though again we take the deformation vibration frequencies of BBr₃ adspecies with the heaviest adduct found in the literature. Note that the deformation vibrations for the "Dabco" adduct are not observed. In contrast to the BH₃ rocking vibration frequency the BBr₃ rocking vibration frequency depends linearly on the square root of the reduced mass of the adduct over the B-P bond (see Fig. 5). The observed rocking vibration frequency is calculated to be 63 cm^{-1} .

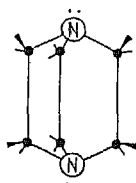


Fig. 4. The adduct Dabco (1,4-diazabicyclo[2.2.2]octane) [36] for obtaining the vibrations of BBr₃ adspecies. Closed circles represent carbon atoms.

None of the PH₃ vibration frequencies depends on the nature of the adduct. We take the reported vibration frequencies of the heaviest adduct, i.e. I₃BPH₃ [37].

The Ni(PBr₃)₃ vibration frequencies [38] are used for PBr₃.

The vibration frequencies of P₄ adspecies are assumed to be equal to those of gaseous P₄ species [8], whereas the two-fold degenerated rocking vibration frequency is estimated to be 460 cm^{-1} . This value is derived from the most degenerate vibration observed in the gaseous P₄ species.

Entropy due to electronic levels. As is mentioned in section 3.2. the electronic contribution to the entropy of the adspecies is estimated by taking the electronic levels ϵ_i and their degeneracies g_i of a molecule, which is the corresponding gaseous species with one hydrogen or bromine atom attached. The observed levels are assumed not to depend strongly on the nature of the surface site. The entropy contribution of electronic levels with energies above 10^4 cm^{-1} is very small, and hence these levels are assumed not to contribute to the entropy. In Table 12 the results are listed. The adspecies H, Br, BH₂, BBr₂, BH₃, BH₂Br, BHBr₂, BBr₃, PH₂, PBr₂, PH₃, PBr₃, and P₄ are assumed to have no electronic levels contributing to the entropy due to full coordination.

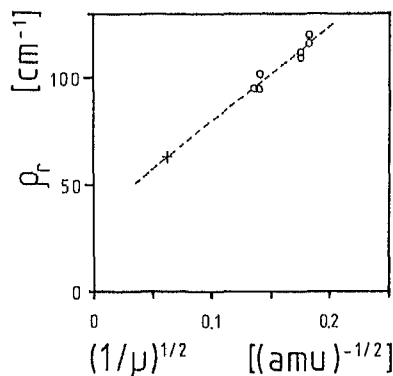


Fig. 5. Rocking vibration ρ_r as a function of the reciprocal square root of the reduced mass μ for several Br₃B:PY₃ species to obtain the rocking vibration ρ_r for BBr₃ adspecies. The adduct PY₃ represents several adducts observed in the literature. A linear least squares fit according to Eq. (A19) and (A20) along with a reduced mass which equals the mass of BBr₃ yields $\rho_r = 63 \text{ cm}^{-1}$.

Results of the entropy due to rotation, vibration and the electronic levels.

In Tables 13 and 14 the results are listed for the individual contributions to the entropy of rotation and vibration, electronic, and the surface site b- or p-. The last column shows the summation of the individual contributions.

4.3. DETERMINATION OF THE SPECIFIC HEAT OF THE ADSPECIES

In this Section the fit parameters are listed for the C_p polynomial function of Eq. (12). The results are shown in Tables 15 and 16 for b- and p- sites, respectively.

Table 12. Electronic levels in cm^{-1} of adspecies and their degeneracy derived from certain gas species. $\epsilon_i=0$ corresponds to the ground state.

adspecies	ϵ_1, g_1	ϵ_2, g_2	From: (Ref.)
-B	0, 1	-	BH ; [8]
-BH	0, 2	-	BH ₂ ; [8]
-BBr	0, 2	-	BBr ₂ ; [8]
-P	0, 3	7650, 2	PH ; [8]
-PH	0, 2	-	PH ₂ ; [8]
-PBr	0, 2	-	PBr ₂ ; [4]

5. RESULTS AND DISCUSSION

As has already been mentioned in the introduction it is our aim to understand the difference between the thermodynamic CVD diagram and the experimental CVD diagram (see Fig. 6) for temperatures beyond 1200 K. In Ref. [3] a contribution to this difference due to depletion of reactant gases as a result of a side reaction of PBr₃ with H₂ forming P₂ and P₄, which are the thermodynamically stable gaseous species as was calculated in Ref. [4].

Langmuir-Hinshelwood kinetics were used to describe the reaction mechanism [2-4]. With the calculated fit results, it is possible to calculate the surface concentration of the boron containing

Table 13. Standard entropy S° for the individual adspecies on boron b- sites.

adspecies	$S^\circ + S^\circ_f$ J/mole K	S°_f J/mole K	$S_b^{(1)}$ J/mole K	S° J/mole K
b-H	2.166	0.0	5.834	8.00
b-Br	47.964	0.0	5.834	53.80
b-B	25.075	0.0	5.834	30.91
b-BH	27.744	5.76	5.834	39.34
b-BHR	112.380	5.76	5.834	123.97
b-BH2	48.217	0.0	5.834	54.05
b-BHR2	148.623	0.0	5.834	154.46
b-BHBr	113.055	0.0	5.834	119.69
b-BH3	52.884	0.0	5.834	59.72
b-BH2Br	137.954	0.0	5.834	143.79
b-BHR2	140.184	0.0	5.834	146.02
b-BBR3	181.213	0.0	5.834	187.05
b-P	37.193	9.13	5.834	52.16
b-PH	61.289	5.76	5.834	72.88
b-PBr	119.074	5.76	5.834	130.67
b-PH2	65.647	0.0	5.834	71.48
b-PBR2	156.257	0.0	5.834	162.09
b-PH3	71.367	0.0	5.834	77.20
b-PBR3	178.216	0.0	5.834	184.05
b-P4	125.209	0.0	5.834	131.04
b-	0.0	5.76	5.834	11.59

¹⁾ S_b represents the entropy of the surface site b-, which corresponds to solid boron.

Table 14. Standard entropy S° for the individual adspecies on phosphorus p- sites.

adspecies	$S^\circ + S^\circ_f$ J/mole K	S°_f J/mole K	$S_p^{(1)}$ J/mole K	S° J/mole K
p-H	3.950	0.0	23.197	27.15
p-Br	52.516	0.0	23.197	75.71
p-B	26.485	0.0	23.197	49.68
p-BH	29.144	5.76	23.197	58.10
p-BHR	118.414	5.76	23.197	147.37
p-BH2	49.423	0.0	23.197	72.62
p-BHR2	148.095	0.0	23.197	171.29
p-BHBr	112.593	0.0	23.197	135.79
p-BH3	57.360	0.0	23.197	80.56
p-BH2Br	147.904	0.0	23.197	171.10
p-BHR2	151.007	0.0	23.197	174.20
p-BBR3	193.008	0.0	23.197	216.21
p-P	41.270	9.13	23.197	73.60
p-PH	65.429	5.76	23.197	94.39
p-PBr	122.530	5.76	23.197	151.49
p-PH2	69.841	0.0	23.197	93.04
p-PBR2	160.239	0.0	23.197	183.44
p-PH3	74.787	0.0	23.197	97.98
p-PBR3	182.892	0.0	23.197	206.08
p-P4	128.879	0.0	23.197	152.08
p-	0.0	5.76	23.197	28.96

¹⁾ S_p represents the entropy of the surface site p-, which corresponds to solid phosphorus.

Table 15. Fit parameters for the c_p polynomial function of Eq. (11) for boron b- sites.

adspecies	A	B 10^{-2}	C 10^5	D 10^{-6}	E	F 10^3
b-H	106.01	-1.675	6.797	3.97	0.0	-1.577
b-Br	98.268	-2.094	4.1315	5.733	0.0	-1.0637
b-B	112.03	-2.751	4.80	7.47	0.0	-1.351
b-BH	145.6	-2.794	8.08	5.80	0.0	-1.93
b-BHR	136.0	-2.384	5.12	7.79	0.0	-1.423
b-BH2	133.4	0.142	6.63	-1.0	0.0	-1.666
b-BHR2	164.4	-3.105	4.48	8.20	0.0	-1.497
b-BHR2	161.3	-2.42	5.78	6.50	0.0	-1.774
b-BH3	136.7	3.18	11.62	-10.4	0.0	-2.014
b-BH2Br	190.7	-1.07	12.68	1.25	0.0	-2.435
b-BHR2	220.6	-3.87	7.93	9.34	0.0	-2.507
b-BBR3	211.4	-4.24	5.01	11.04	0.0	-1.955
b-P	106.77	-2.54	4.34	6.86	0.0	-1.238
b-PH	111.2	-1.1	3.55	3.06	0.0	-1.227
b-PBr	124.55	-2.389	3.239	6.49	0.0	-1.1746
b-PH2	144.1	-0.418	7.53	0.22	0.0	-1.834
b-PBR2	153.1	-2.584	2.29	6.99	0.0	-1.247
b-PH3	150.0	1.41	7.72	-4.82	0.0	-1.874
b-PBR3	185.9	-3.00	0.9	8.07	0.0	-1.406
b-P4	224.6	-5.02	1.63	13.2	0.0	-2.199
b-	72.9	-2.07	4.64	5.67	0.0	-1.055

Table 16. Fit parameters for the c_p polynomial function of Eq. (11) for phosphorus p- sites.

adspecies	A	B 10^{-2}	C 10^5	D 10^{-6}	E	F 10^3
p-H	36.9	2.346	-0.67	-2.66	0.0	-0.215
p-Br	42.821	1.3917	-0.5379	0.091	0.0	-0.0127
p-B	62.81	0.489	2.072	2.14	0.0	-0.462
p-BH	97.14	0.843	5.32	0.64	0.0	-1.05
p-BHR	81.5	0.496	0.34	2.29	0.0	-0.391
p-BH2	85.4	3.326	3.18	-6.02	0.0	-0.792
p-BHR2	110.7	0.326	0.14	2.63	0.0	-0.492
p-BHR2	107.0	1.0	0.98	1.03	0.0	-0.745
p-BH3	115.5	4.14	7.55	-9.06	0.0	-1.353
p-BH2Br	115.9	3.34	5.63	-6.54	0.0	-0.98
p-BHR2	152.8	0.25	2.70	2.11	0.0	-1.201
p-BBR3	148.0	-0.34	0.50	4.33	0.0	-0.742
p-P	45.01	1.274	-0.789	0.395	0.0	-0.0566
p-PH	46.63	2.917	-1.914	-4.07	0.0	-0.0
p-PBr	61.9	1.591	-1.906	-0.66	0.0	-0.0
p-PH2	82.7	3.38	2.48	-6.2	0.0	-0.661
p-PBR2	97.11	0.931	-2.14	1.27	0.0	-0.186
p-PH3	96.11	4.71	3.49	-9.80	0.0	-0.854
p-PBR3	130.2	0.49	-3.70	2.39	0.0	-0.351
p-P4	168.8	-1.52	-2.95	7.5	0.0	-1.142
p-	17.25	1.4267	0.0	0.0	0.0	-0.0

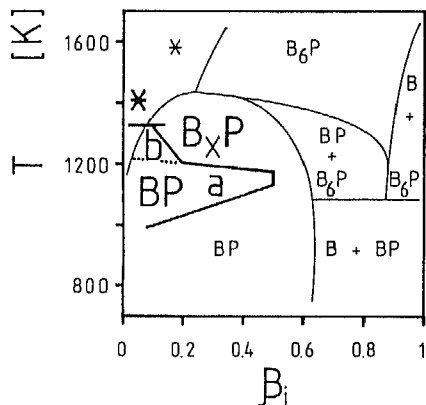


Fig. 6. Thermodynamic [4] (—) and experimental [2-4] CVD (---) diagram. Bold symbols refer to the experimental CVD diagram, whereas small symbols refer to the thermodynamic CVD diagram. * represents no solid phase formation, and x in B_xP is ranging from 3 to 12. a represents the regime of smooth BP films, whereas b represents the regime of grain-like BP films.

adspecies as well as the concentration of the phosphorus containing adspecies. The adsorption constants of BBr, PBr₃, and P₂ which are K_B, K_P, and K_{P2}, respectively, are taken from Ref. [3]. The surface concentrations, calculated using Eqs. (17) to (20) [39] and using the fit results taken from Ref. [3], are shown in Figures 7 and 8.

$$\theta_B = K_B x_{pB} / (1 + K_B x_{pB} + K_P x_{pP}) \quad T < 1200 \text{ K} \quad (17)$$

$$\theta_P = K_P x_{pP} / (1 + K_B x_{pB} + K_P x_{pP}) \quad T < 1200 \text{ K} \quad (18)$$

$$\theta_B = K_B x_{pB} / (1 + K_B x_{pB} + (K_P x_{pP})^{1/2}) \quad T > 1200 \text{ K} \quad (19)$$

$$\theta_{P2} = (K_P x_{pP})^{1/2} / (1 + K_B x_{pB} + (K_P x_{pP})^{1/2}) \quad T > 1200 \text{ K} \quad (20)$$

From these figures it is obvious that the calculated surface concentration of phosphorus is larger than that of boron. Hence, from these surface concentrations it is difficult to understand why a transition of BP to B_xP occurs, as was already mentioned in the introduction.

In order to understand the transition of BP to B_xP formation thermodynamic calculations are carried out to estimate surface concentrations according to Eqs. (1) and (2). The observed thermodynamic constants are used to calculate thermodynamic equilibrium concentrations with the program SOLGASHIX [1] adapted for PC. In splitting the surface into b- and p- sites, it should

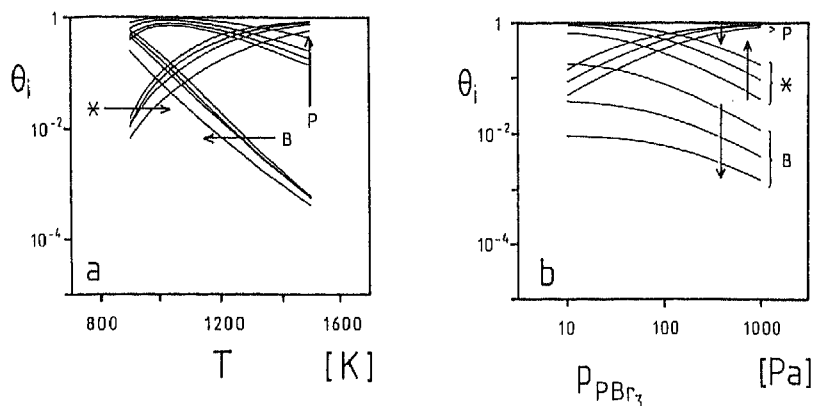


Fig. 7. Surface concentration as a function of temperature (a) and PBr_3 input partial pressure (b) calculated with Eqs. (19) and (20), and parameters taken from Ref. [3]. B, P, and * represent the boron adspecies concentration, the phosphorus adspecies concentration, and the free surface site concentration, respectively. In Fig. 7a the arrows show the direction of increasing PBr_3 input partial pressure, i.e. 10, 50, 100, and 500 Pa, respectively. In Fig. 7b the arrows show the direction of increasing temperature, i.e. 1000, 1100, and 1200 K, respectively.

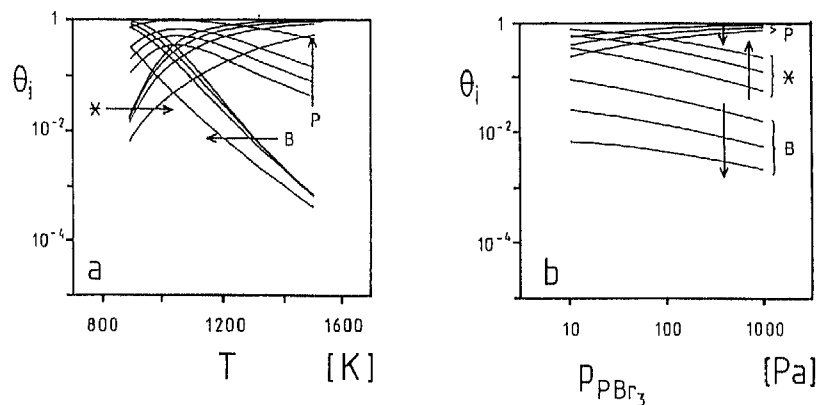


Fig. 8. Surface concentration as a function of temperature (a) and PBr_3 input partial pressure (b) calculated with Eqs. (19) and (20), and parameters taken from Ref. [3]. B, P, and * represent the boron adspecies concentration, the phosphorus adspecies concentration, and the free surface site concentration, respectively. In Fig. 8a the arrows show the direction of increasing PBr_3 input partial pressure, i.e. 10, 50, 100, and 500 Pa, respectively. In Fig. 8b the arrows show the direction of increasing temperature, i.e. 1000, 1100, and 1200 K, respectively.

first be shown which are the consequences of adspecies on either b- or p- sites. BP will be formed if boron adspecies are present on p- sites as well as phosphorus adspecies on b- sites. If b- as well as p- sites are occupied by phosphorus adspecies, there will be no solid phase formation, i.e. solid phosphorus, since the temperature under study is higher than the boiling point of solid phosphorus. If b- as well as p- sites are occupied by boron adspecies, however, solid boron is assumed to be formed. Boron adspecies on p- sites and phosphorus adspecies on b- sites are necessary for BP formation. Since we are dealing with equilibrium surface concentrations, either b- or p- sites are partially occupied by either boron or phosphorus adspecies. To observe a transition from BP to B_xP formation, we have to take only the b- sites and their adspe-

cies into account, since on p- sites BP is the only possible solid which can be formed. Before describing the most relevant results for the b- sites, some general aspects of the less important p- sites will be discussed. At room temperature the low-lying vibration frequency levels of the adspecies contribute substantially to the total entropy of the adspecies, contrary to the high-lying levels, which do not contribute much to this entropy at room temperature. However, at elevated temperatures this latter contribution strongly increases. Moreover, the value of the heat capacity of the adspecies is dependent also on these vibration frequencies, and as a consequence also on temperature. Therefore, it is necessary to evaluate first the number of possible vibrations. However, no strong dependence of the calculated surface concentration due to small

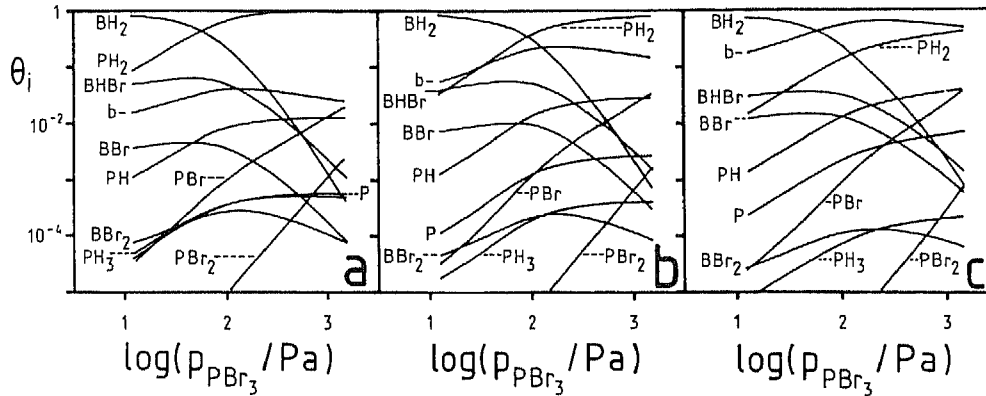


Fig. 9. Calculated surface concentration θ_i on boron b- sites as a function of PBr_3 input partial pressure at three different temperatures, i.e. 1000 K (a), 1100 K (b), and 1200 K (c), respectively. The index i of θ at the ordinate represents the adspecies indicated in the Figure. The surface concentrations are calculated using the adsorption model described in the text and assuming thermodynamic equilibrium.

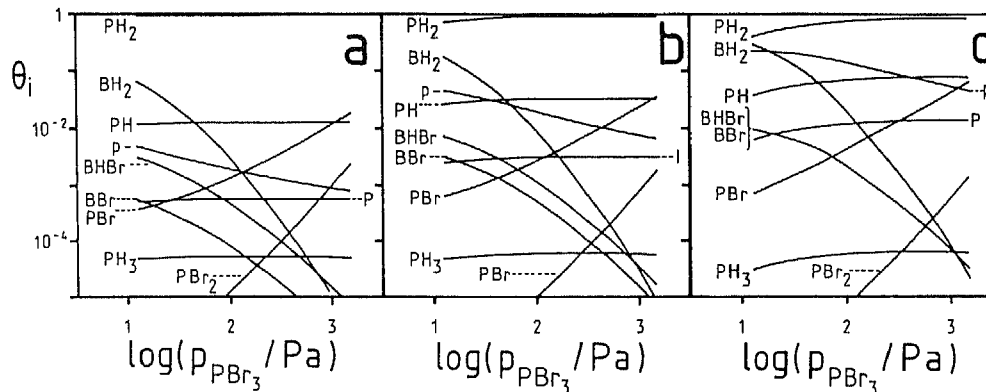


Fig. 10. Calculated surface concentration θ_i on phosphorus p- sites as a function of PBr_3 input partial pressure at three different temperatures, i.e. 1000 K (a), 1100 K (b), and 1200 K (c), respectively. The index i of θ at the ordinate represents the adspecies indicated in the figure. The surface concentrations are calculated using the adsorption model described in the text and assuming thermodynamic equilibrium.

Introduced variations of these vibration frequencies was observed, while minor dependencies were observed upon ignoring several vibration frequency levels. The strongest impact on the surface concentrations was observed by varying the bond energies of the adspecies with the surface sites. However, the main features which will be discussed next remain the same.

The most striking result of the thermodynamic equilibrium calculation is the high surface concentration of both BH_2 and PH_2 , i.e. $\theta(BH_2)$ and $\theta(PH_2)$, respectively, on either b- or p- sites. In the following discussion of the surface concentration these two adspecies will play the most important role. The calculated surface concentrations of the other adspecies are low. The surface concentration of chemically bonded adspecies with bond energies in excess of 200 kJ/mole, however, are generally higher than those having bond energies lower than 100 kJ/mole (Figs.9-12). Only PH_3 adspecies with a bond energy of 89 kJ/mole show a considerable surface concentration (Figs.9-12).

The decrease of $\theta(PH_2)$ with increasing temperature (Figs.11 and 12) is expected for chemisorption. A consequence of this strong decrease of $\theta(PH_2)$ with temperature may be the increase in surface concentrations of many other adspecies. However, at certain temperatures the surface concentrations of these adspecies will also decrease as discussed for $\theta(PH_2)$. Another consequence of decreasing surface concentrations of the adspecies is the increase of free surface sites. The surface concentrations of the other adspecies could be important because they may be involved in the reaction controlling step. Consequently, as many as possible adspecies in this model should be considered and may be used to explain certain phenomena reported in the literature. Still bearing in mind that not only BH_2 and PH_2 can determine the BP and BxP formation we prefer to discuss the formation mechanism of BP and BxP based on these two adspecies.

The results of the thermodynamical equilibrium calculations for the adspecies on p- sites are

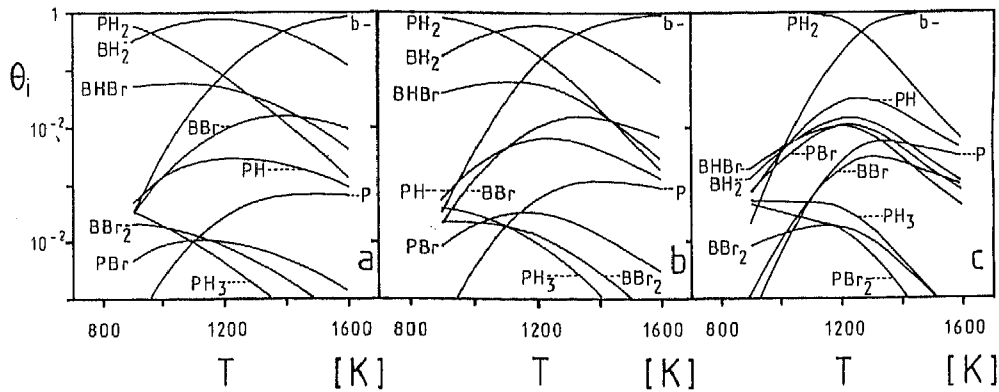


Fig. 11. Calculated surface concentration θ_i on boron b- sites as a function of temperature at three different PBr_3 input partial pressures, i.e. 10 Pa (a), 50 Pa (b), and 500 Pa (c), respectively. The index i of θ at the ordinate represents the adspecies indicated in the figure. The surface concentrations are calculated using the adsorption model described in the text and assuming thermodynamic equilibrium.

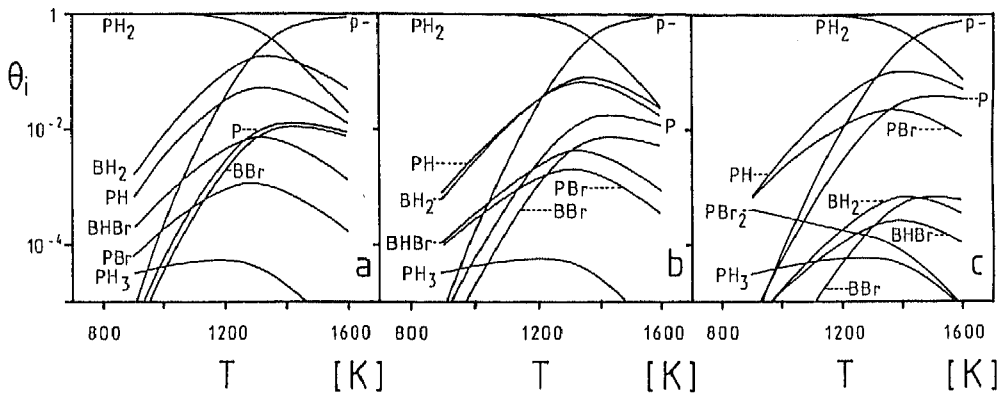


Fig. 12. Calculated surface concentration θ_i on phosphorus p- sites as a function of temperature at three different PBr_3 input partial pressures, i.e. 10 Pa (a), 50 Pa (b), and 500 Pa (c), respectively. The index i of θ at the ordinate represents the adspecies indicated in the figure. The surface concentrations are calculated using the adsorption model described in the text and assuming thermodynamic equilibrium.

shown in Figs. 10 and 12. As already mentioned, the most striking result is the very high coverage of the p- sites with PH_2 . Upon increasing PBr_3 partial pressures the surface concentrations of the adspecies P, PH, PH_2 , and PH_3 increase very slowly. However, the surface concentrations of bromine containing phosphorus adspecies increase exponentially with increasing PBr_3 input partial pressure. Consequently, the concentrations of the sites occupied with boron containing adspecies as well as the free surface sites decrease. On going to higher temperature $\theta(PH_2)$ will decrease and simultaneously the free surface site concentration $\theta(p^-)$ increase as expected. The decrease of $\theta(PH_2)$ with increasing temperature is faster than that of $\theta(BH_2)$. Only at low PBr_3 input partial pressures and high temperatures the strong decrease of $\theta(PH_2)$ compared to $\theta(BH_2)$ results in $\theta(PH_2) < \theta(BH_2)$ (see Fig. 9a).

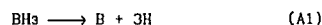
In order to discriminate between BP and B_xP formation according to the calculated surface concentrations, we have to define a certain ratio of the surface concentrations of the main boron and main phosphorus containing adspecies on the b- sites, i.e. $\theta_b(BH_2)$ and $\theta_b(PH_2)$, respectively. The ratio $y = \theta_b(PH_2) / \theta_b(BH_2)$ will determine whether there is BP or B_xP formation. In a first approximation we shall take the ratio y being unity, assuming at $y < 1$ B_xP formation and at $y > 1$ BP formation. However, we must keep in mind that the transition from BP to B_xP could be established already at even higher y ratios. This seems even more plausible since boron adspecies on b- sites cause boron formation and hence, in order to prevent solid boron formation the b- sites should be occupied completely by phosphorus containing adspecies or remain empty. Hence, already small amounts of boron containing adspecies on the b- sites and phosphorus containing adspecies on b- sites could cause B_xP formation.

these adspecies decrease exponentially with increasing temperature.
 -The concentrations of the free surface sites b- and p- increase with increasing temperature over the entire temperature range involved.
 -The transition from cubic BP to amorphous ExP (3<x<12) formation in the experimental CVD diagram agrees with a calculated surface concentration ratio of PH₂ and BH₂ of 10.

APPENDIX 1. DETERMINATION OF THE ENTHALPY OF FORMATION FOR ADSPECIES

In this Appendix the enthalpies of formation of the individual adspecies $\Delta rH^\circ(s-1)$, with s- being either b- or p-, and species I, will be discussed. The enthalpy values for the atomic species are calculated relative to the reference state and taken from JANAF [8].

In Table 1 the bond energies involved in the heat of adsorption are presented. The bond energies for the hydrogen and bromine on both different surface sites are not directly taken from the bond energies observed in the gaseous species BH, BBr, PH, and PBr since the bond energy is affected by the coordination number of the central atom, i.e. B or P. The enthalpy of formation of gaseous B, BH₃, BBr₃, Br, H, P, PH₃, and PBr₃ are taken from JANAF [8]. The enthalpy of formation of BH₄ and PBr₄ are taken from Symons et al. [11], and Dittler and Niemann [12], respectively. The average bond energy $E(b-h)$ of B-H is determined by:



$$E(b-h)^{(3)} = \frac{1}{3} \times (\Delta rH^\circ(B) + 3\Delta rH^\circ(H)) - \Delta rH^\circ(BH_3) = 369.1 \text{ kJ/mole} \quad (A2)$$

The average bond energy $E(b-h)^{(3)}$ is used to calculate the bond energy $E(b-h)^{(4)}$ of the fourth B-H bond in the tetrahedral configuration of BH₄. In BH₄ we assume three bonds with energy $E(b-h)^{(3)}$ and one bond having energy $E(b-h)^{(4)}$:

$$E(b-h)^{(4)} = \Delta rH^\circ(B) + 4\Delta rH^\circ(H) - \Delta rH^\circ(BH_4) - 3E(b-h)^{(3)} = 102.3 \text{ kJ/mole} \quad (A3)$$

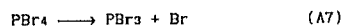
The difference between $E(b-h)^{(3)}$ and $E(b-h)^{(4)}$, i.e. 266.8 kJ/mole will be used as a very rough estimation for the evaluation of the B-Br bond energy $E(b-br)^{(4)}$ in boron tetrabromide. The energy $E(b-br)^{(4)}$ is calculated using the equation:



$$E(b-br)^{(3)} = \frac{1}{3} (\Delta rH^\circ(B) + 3\Delta rH^\circ(Br)) - \Delta rH^\circ(BBr_3) = 366.6 \text{ kJ/mole} \quad (A5)$$

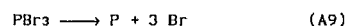
$$E(b-br)^{(4)} = E(b-br)^{(3)} - 266.8 = 99.8 \text{ kJ/mole} \quad (A6)$$

The P-Br bond energy of the fourth Br atom to the central P atom is calculated from the following equation:



$$E(p-br)^{(4)} = \Delta rH^\circ(PBr_3) + \Delta rH^\circ(Br) - \Delta rH^\circ(PBr_4) = 56.3 \text{ kJ/mole} \quad (A8)$$

The P-Br bond energies in PBr, PBr₂, and PBr₃ are the same, irrespective of the coordination of the central P atom. However, the actual value is obtained from the dissociation of PBr₃.



$$E(p-br)^{(3)} = \frac{1}{3} (\Delta rH^\circ(P) + 3\Delta rH^\circ(Br)) - \Delta rH^\circ(PBr_3) = 266.0 \text{ kJ/mole} \quad (A10)$$

Hence, the difference between $E(p-br)^{(3)}$ and $E(p-br)^{(4)}$ is 209.7 kJ/mole. This difference in bond energy will also be used to calculate the P-H bond energy assuming the unknown species PH₄. The P-H bond energies in PH₃ and PH₂ are almost the same, whereas this energy in PH is different. Hence the P-H bond energy $E(p-h)^{(3)}$, i.e. 321.7 kJ/mole is obtained from the dissociation reaction:



$$E(p-h)^{(3)} = \frac{1}{3} (\Delta rH^\circ(P) + 3\Delta rH^\circ(H)) - \Delta rH^\circ(PH_3) = 321.7 \text{ kJ/mole} \quad (A12)$$

The P-H bond energy $E(p-h)^{(4)}$ assuming four H atoms near the central P atom is estimated by subtracting a same amount observed for the difference in P-Br bond energies $E(p-br)^{(3)}$ and $E(p-br)^{(4)}$, i.e. 209.7 kJ/mole, from $E(p-h)^{(3)}$, i.e. 321.7 kJ/mole. Hence the P-H bond energy $E(p-h)^{(4)}$ will become 112.0 kJ/mole.

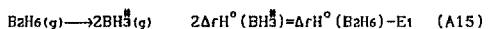
The actual value of the enthalpy of formation ΔrH° of the adspecies is calculated from the following equations:

$$\Delta rH^\circ(b-I) = \Delta rH^\circ(I) + \Delta rH^\circ(b) - E(b-I) \quad (A13)$$

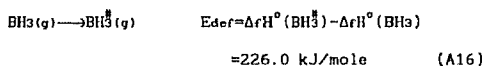
$$\Delta rH^\circ(p-I) = \Delta rH^\circ(I) + \Delta rH^\circ(p) - E(p-I) \quad (A14)$$

In Tables 2 and 3 these values are gathered.

The boron containing gaseous species BH₃, BH₂Br, BHBr₂, and BBr₃ are planar. Hence, these gaseous species will be deformed upon adsorption. The planar to pyramidal deformation energy E_{def} is estimated as follows. The interaction energy E_i of B-BH₃ is taken from Forcada et al. [13], i.e. 84.7 kJ/mole. From Dill et al. [16] the enthalpy of formation of B₂H₆ $\Delta rH^\circ(B_2H_6)$ with the ethane structure, i.e. 580.7 kJ/mole is calculated. B₂H₆ with the ethane structure is assumed to dissociate into pyramidal BH₃, i.e. BH₃^{*}, by bond breaking with a bond energy equal to the reported interaction energy E_i [13]. The enthalpy of formation of BH₃^{*} $\Delta rH^\circ(BH_3^*)$ is calculated using Eq. (A15), while E_{def} is calculated using Eq. (A16).



$$\Delta rH^\circ(BH_3^*) = 580.7 \text{ kJ/mole}$$



From Eqs. (A15) and (A16) and the interaction energy E_i we calculated the deformation energy E_{def} of BH₃ → BH₃^{*} to be 226.0 kJ/mole. The deformation energy E_{def} , which is a very rough estimate, is taken to be the same for all the planar three coordinated boron containing gaseous species, irrespective of the nature of the atoms attached to the central boron atom. The phosphorus containing gaseous species already have a pyramidal configuration.

In Figs.9 and 11 the surface concentrations of the adspecies on the b- sites are shown as a function of temperature (Fig.11) and as a function of PBr_3 input partial pressure (Fig.9). The general aspects mentioned above are obvious, i.e.:

- the surface is covered almost entirely by adspecies with bond energies higher than 200 kJ/mole.
- the surface concentration of the main adspecies decreases with increasing temperature.
- the initial increase of the surface concentrations of most of the other adspecies stops and decreases on further increasing temperatures.
- the concentration of the free surface sites increases with increasing temperature.

The main difference, however, between the surface concentrations of the p- and b- sites is the high surface concentration of $BH_2\theta_bBH_2$. Upon increasing PBr_3 partial pressure $\theta_b(BH_2)$, however, will become smaller than $\theta_b(PH_2)$. With increasing temperature $\theta_b(PH_2)$ decreases and initially $\theta_b(BH_2)$ increases, goes through a maximum, and finally decreases exponentially.

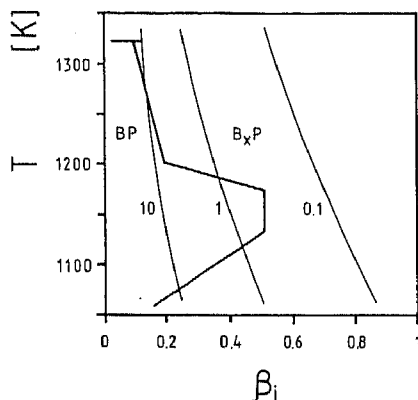


Fig.13. Experimental CVD diagram. The bold lines represent the boundaries of BP to B_xP formation. The thin lines represent ratios $y = \theta_b(PH_2)/\theta_b(BH_2)$. The ratios $y=0.1$, 1, and 10 are drawn in the figure. Note that for $y=10$ the calculated surface concentration ratio y fits quite well with the experimentally observed $BP \rightarrow B_xP$ transition.

In order to discriminate between BP and B_xP formation we have defined a ratio $y = \theta_b(PH_2)/\theta_b(BH_2)$ which was assumed in a first approximation to be unity. The ratio y is assumed to determine the transition points of BP to B_xP formation. If $y=1$, and thus $\theta_b(BH_2)$ equals $\theta_b(PH_2)$ the conditions are easily obtained from Figs.9 and 11. In Fig.13 the curve with $y=1$ is plotted as a function of the parameters also used in the CVD diagrams, i.e. temperature, and molar reactant fraction β_1 , with $\beta_1 = p(BBr_3)/(p(BBr_3)+p(PBr_3))$. In the same diagram (Fig.13) the experimentally observed solid phases are plotted also. The dependence of the curve with $y=1$, which is assumed to determine the transition from BP to B_xP , on temperature as well as on β_1 , has also been observed experimentally. However, the curve with $y=1$ does not agree exactly with the experimentally observed curve. Hence, the approximation $y=1$ needs to be reviewed. If curves are plotted for different y values, i.e. 10 and 0.1, a very good agreement is observed with the experimentally observed curve

for $y=10$. Hence, the transition of BP to B_xP is probably already established at $\theta(PH_2)$ values 10 times higher than $\theta(BH_2)$, i.e. $y=10$.

The $y=10$ value agrees approximately with $\beta_1=0.2$ in Fig.13. The ratio $x = \theta_p(PH_2)/\theta_p(BH_2)$ for p-sites is about 100 (Figs.10 and 12). Hence, the surface of BP determined by b- and p- sites is almost completely covered with PH_2 adspecies, though B_xP formation will occur.

There was also an excess of a phosphorus containing adspecies observed compared to the boron containing adspecies on the BP surface from the fit parameters presented in Ref.[3] where a Langmuir-Hinshelwood adsorption model was assumed. The results were already shown in Figs.7 and 8. From the fits to the Langmuir-Hinshelwood model, the ratio of surface concentrations of the P-containing and B-containing adspecies is calculated to be about 100. The ratios of the calculated surface concentrations in both models are in agreement. Hence, with the model described above it is possible to understand the transition of BP to B_xP formation. However, the problem of defining a correct ratio y , which determines the transition point needs further research.

6. CONCLUSIONS

In the present model of Langmuir adsorption together with calculated thermodynamic constants, i.e. ΔH° , S° , and c_p for adspecies it is possible to obtain surface concentrations of adspecies. In this model adsorption of gaseous species on a surface is assumed to be caused by a change in Gibbs free energy. The change in enthalpy is characterized by the adsorption bond energies which were taken from experiment or from the literature. The entropy as well as the heat capacity of the adspecies were derived from the partition function, using spectroscopic data, or data calculated empirically. The conclusions can be summarized as follows:

- The calculated surface concentrations of the adspecies strongly depend on the assumed adsorption bond energies. The surface concentrations of the adspecies bound to the surface with an adsorption bond energy lower than about 100 kJ/mole are practically zero. However, only PH_3 with an adsorption bond energy of 89 kJ/mole seems to be an exception.
- The mutual ratios of the surface concentrations of adspecies, having the same adsorption bond energy, do not vary much with this adsorption bond energy.
- The calculated surface concentrations strongly depend upon the specific heat.
- In order to estimate the specific heat, the number of the vibrations of the adspecies needs to be determined.
- The boron as well as the phosphorus surface sites, b- and p-, respectively, are predominantly covered with PH_2 and BH_2 . However, in most instances PH_2 is in excess.
- Only at low PBr_3 input partial pressure BH_2 is in excess over PH_2 .
- The surface concentration of predominantly PH_2 adspecies on b- as well as on p- sites decreases exponentially with increasing temperature.
- The surface concentrations of adspecies besides predominantly PH_2 on b- as well as on p- sites initially increase with increasing temperature due to the strong decrease of the PH_2 surface concentration. However, upon further increasing the temperature the surface concentrations of

APPENDIX 11. TABLES CONTAINING GEOMETRICAL DATA OF THE ADSPECIES

Table A1. Geometrical data of the adspecies on b- sites. Data were taken from JANAF [8], or from sources as indicated.

adspecies	l_x [amuÅ ²]	q	σ	bond distances (Å); bond angles (deg)
b-H	0	1	-	b-H=1.23
b-Br	0	1	-	b-Br=1.887
b-B	0	1	-	b-B=1.7
b-BH	0	2	-	b-B=1.7, B-H=1.2; b-B-H=180°
b-BBr	213	2	1	b-B=1.7, B-Br=1.887; b-B-Br=120°
b-BH ₂	2.04	1	2	b-B=1.7, B-H=1.16; b-B-H-H-B-H=120°
b-BBr ₂	419	1	2	b-B=1.7, B-Br=1.87; b-B-Br=Br-B-Br=120°
b-BHBr	211	1	1	b-B=1.7, B-H=1.2, B-Br=1.87; b-B-H-H-B-Br=Br-B-H=120°
b-BH ₃	4.18	1	3	b-B=1.8, B-H=1.212; b-B-H=104° [40]
b-BH ₂ Br	292	1	1	b-B=1.8, B-H=1.212, B-Br=2.02; b-B-H=104° [40], b-B-Br=109.5 [41]
b-BHBr ₂	581	1	1	b-B=1.8, B-H=1.212, B-Br=2.02; b-B-H=104° [40], b-B-Br=109.5 [41]
b-BBr ₃	869	1	1	b-B=1.8, B-Br=2.02 [41]; b-B-Br=109.5° [41]
b-P	0	3	-	b-P=1.9
b-PH	2.02	2	1	b-P=1.9, P-H=1.419; b-P-H=93.7°
b-PBr	367	2	1	b-P=1.9, P-Br=2.2; b-P-Br=106° [4]
b-PH ₂	4.04	1	1	b-P=1.9, P-H=1.419; b-P-H-H-P-H=93.7°
b-PBr ₂	715	1	1	b-P=1.9, P-Br=2.2; b-P-Br=Br-P-Br=106°
b-PH ₃	4.7	1	3	b-P=1.93, P-H=1.4; b-P-H=117°, H-P-H=101.1° [42]
b-PBr ₃	1017	1	3	b-P=1.93, P-Br=2.2; b-P-Br=110.5°, Br-P-Br=108° [43]
b-P ₄	135	1	3	b-P=1.93, b-P-P=109.5°

Table A2. Geometrical data of the adspecies on p- sites. Data were taken from JANAF [8], or from sources as indicated.

adspecies	l_x [amuÅ ²]	q	σ	bond distances (Å); bond angles (deg)
p-H	0	1	-	p-H=1.47
p-Br	0	1	-	p-Br=2.2
p-B	0	1	-	p-B=1.9
p-BH	0	2	-	p-B=1.9, B-H=1.2; p-B-H=180°
p-BBr	213	2	1	p-B=1.9, B-Br=1.887; p-B-Br=120°
p-BH ₂	2.04	1	2	p-B=1.9, B-H=1.16; p-B-H-H-B-H=120°
p-BBr ₂	419	1	2	p-B=1.9, B-Br=1.87; p-B-Br=Br-B-Br=120°
p-BHBr	211	1	1	p-B=1.9, B-H=1.2, B-Br=1.87; p-B-H-H-B-Br=Br-B-H=120°
p-BH ₃	4.18	1	3	p-B=1.93, B-H=1.212; p-B-H=104° [40]
p-BH ₂ Br	292	1	1	p-B=1.93, B-H=1.212, B-Br=2.02 [41]; p-B-H=104° [40], p-B-Br=109.5 [41]
p-BHBr ₂	581	1	1	p-B=1.93, B-H=1.212, B-Br=2.02 [41]; p-B-H=104° [40], p-B-Br=109.5° [41]
p-BBr ₃	869	1	1	p-B=1.93, B-Br=2.02 [41]; p-B-Br=109.5° [41]
p-P	0	3	-	p-P=2.22
p-PH	2.02	2	1	p-P=2.22, P-H=1.419; p-P-H=93.7°
p-PBr	367	2	1	p-P=2.22, P-Br=2.2; p-P-Br=106° [4]
p-PH ₂	4.04	1	1	p-P=2.22, P-H=1.419; p-P-H-H-P-H=93.7°
p-PBr ₂	715	1	1	p-P=2.22, P-Br=2.2; p-P-Br=Br-P-Br=106°
p-PH ₃	4.7	1	3	p-P=2.22, P-H=1.4; p-P-H=117°, H-P-H=101.1° [42]
p-PBr ₃	1017	1	3	p-P=2.22, P-Br=2.2; p-P-Br=110.5°, Br-P-Br=108° [43]
p-P ₄	135	1	3	p-P=2.22, p-P-P=109.5°

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