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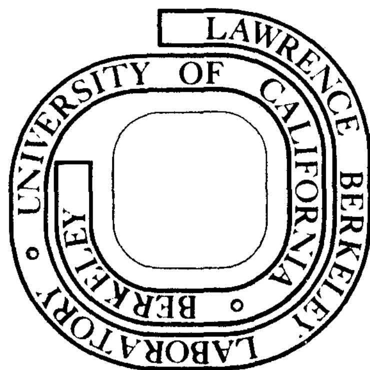

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Thermodynamics of Phase Equilibria for Chemical Vapor Deposition of $GaAs_{1-x}P_x$

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Abstract

The thermodynamics of phase equilibria in the Ga-As-P-Cl-H system is studied for the chemical vapor deposition of $GaAs_{1-x}P_x$ solid solutions from $Ga_{(\ell)}$, AsH_3 , PH_3 , HCl and H_2 source chemicals. The properties of reaction equilibria and the predominant chemical species are deduced for each zone of the reactor. Analytical procedures are described for calculating multi-component phase equilibria in terms of reduced variables. The composition of the $GaAs_{1-x}P_x$ alloy is calculated as a function of temperature and the arsine-phosphine ratio. These calculations provide a basis for efficient III-V compound reactor design and operation. The results of experimental studies are reported to provide confirmation of the phase equilibria for alloy compositions near $x = 0.4$.

Introduction

The production of $GaAs_{1-x}P_x$ by chemical vapor deposition (CVD) has become very important in the recent years. The chief use of these compounds is in the electronic industry where the compositions of commercial applications are $x = 0.4$ and 0.19. The first composition is required in the manufacture of light emitting diodes and second in solid state heterojunction lasers. The expansion of commercial applications of $GaAs_{1-x}P_x$ crystals and epitaxial thin films has been so great in recent years that the supply has become the limiting factor. The main reason why this compound is preferred over classes of electronic materials lies in its relatively easy and low cost of synthesis and epitaxial growth on a supporting substrate. The industrial applications of epitaxial III-V compound alloys has established a need for better understanding of the gas phase, and gas-solid reactions and their equilibria. The purpose of this work is to provide a comprehensive study of these reaction equilibria in the Ga-As-P-Cl-H system as they relate to the $GaAs_{1-x}P_x$ chemical vapor deposition reactor.

Although many experimental studies of III-V alloy growth by chemical vapor deposition have been reported, only recently has this process been the subject of theoretical study. For example the growth process for GaAs has been studied in great detail following the inspiring work of Newman (1961). Reactors with varying designs were employed in these experimental studies. However the theoretical aspects of the growth process were not studied until

Hurle and Mullin (1966) outlined a general approach to the calculation of phase equilibria in the Ga-As-H-Cl system on the basis of which the feasibility of the reaction could be assessed from thermodynamic data. Seki and Araki (1967) and Seki et al. (1968) used a similar approach to solve the system Ga-P-H-Cl. Later studies extended these calculations to phase equilibria involving $GaAs_{1-x}P_x$ by Seki and Eguchi (1971) and Amron (1971). Kirwan (1970) and others have aided these calculations by measuring the equilibrium constants for reactions which can take place in the Ga-As-P-Cl-H system.

The GaAs controlled growth process has been studied by Goettler (1970) whose approach coupled the thermodynamic constraint with diffusion processes in the deposition zone to obtain the growth rate for the process. Chemical vapor deposition of $GaAs_{1-x}P_x$ alloys is achieved by processes analogous to that of GaAs and it is anticipated that future work will concentrate on analyzing more and more complex systems after sufficient experimental work has been reported.

The first study of $GaAs_{1-x}P_x$ growth was reported by Finch and Mehal (1969) and since then many experimentalists have grown this alloy in all compositions. However the thermodynamics of the system were only recently analyzed by Manabe (1972) and by Bleicher (1972). These two workers neglected the growth process itself and concentrated more on phase equilibria in the reactor. Further analysis of chemical vapor deposition is essential if the optimum efficiency and product uniformity is to be achieved commercially, where the primary interest is on lower cost and higher yield.

The present study examines the overall chemical vapor deposition process in three parts: In the first part, the reactions taking part

in the formation of the volatile gallium compound GaCl from liquid gallium and HCl in H_2 is explored. In the second part a thermodynamic study of general gas phase equilibria in the Ga-As-P-Cl-H system is presented. Finally, the gas solid equilium between the gas phase and $GaAs_{1-x}P_x$ is examined toward deducing the various equilibrium properties of the system. These calculations provide a basis from which the reactor can be designed and the driving forces available for the deposition process can be predicted. These three parts give a comprehensive picture of the thermodynamics of the chemical $GaAs_{1-x}P_x$ reactor through fundamental analysis of each part of the reactor. The results of the study should provide a foundation for better reactor design, improved reaction control and greater uniformity of the deposition of $GaAs_{1-x}P_x$ solid solutions.

The Chemical Vapor Deposition Reactor

Processes for the growth of epitaxial layers of GaAs, GaP and $GaAs_{1-x}P_x$ by chemical vapor deposition (CVD) have been known since the early 1960's, and are essentially the same for either of the two pure compounds or their alloy, but different chemical reactions are involved. Many of these processes utilize chemical transport reactions as developed by Schaefer (1964), but many of the consequences apply to chemical vapor deposition as well.

A basic transport process consists of reacting liquid gallium (source) with an oxidizing agent to form a volatile compound of gallium which is mixed with a volatile form of arsenic and/or phosphorous and transported to a zone where the gas phase is supersaturated with respect to the solid. Growth takes place at surfaces where the gases react to condense the III-V compound. Because the number of volatile compounds is large, so is the number of possible ways of reacting them. Many reactor designs have been developed to explore this process.

Owing to the high costs of reactants for the chemical vapor deposition of $GaAs_{1-x}P_x$ -- and for other III-V compounds -- the deposition reaction must be carried out in the diffusion-controlled regime. Hot wall reactors are used for III-V compound deposition in order to prevent condensation of GaCl which is volatile only at high temperatures. This choice is contrary to reactors used for silicon where the silane transport species are relatively more volatile at lower temperatures and cold wall, heated substrate conditions can be used.

Essentially all of the GaAs , GaP or $GaAs_{1-x}P_x$ reactors are open flow types (constant pressure). A sealed tube reactor (constant-volume) is not usual due to the large number of reactants involved and difficulty in controlling the growth. The open flow reactors are semi-continuous batch type in which a number of substrates can be placed for epitaxial growth with an infinite choice of conditions.

Early reactors used both arsenic and gallium in the solid form as starting materials but later AsH_3 or $AsCl_3$ replaced solid arsenic as a transport species. The advantages of introducing a gaseous species at the input instead of a solid as a source of arsenic are so great in terms of ease and controllability that few reactor studies have used arsenic in the solid form.

AsH_3 is a gas at standard temperature and pressure and can be introduced at precise flow rates. Therefore control of the growth process is much easier and precise. Tietjen (1966) first used AsH_3 as a source of arsenic in 1966 and reacted gallium with HCl to form GaCl and $GaCl_3$.

Thus, the preferred source compounds are gaseous AsH_3 , PH_3 and HCl passed over gallium to obtain GaCl and $GaCl_3$. The combined gases are then transported to the substrate for deposition. Commercial reactors for CVD of $GaAs_{1-x}P_x$ has been reported by Ruherwein (1968) and by Pelser and Benzing (1972). Both of these reactors employing PH_3 , AsH_3 , HCl and Ga(ℓ) as source chemicals in this process.

Calculations of Phase Equilibria in the Ga-As-P-Cl-H System

The principles of analysis of multicomponent multiphase equilibria were established early in the development of chemical thermodynamics. J. Willard Gibbs (1931) developed a fundamental differential form of the combined first and second laws, known as "Gibbs equation 97," and also, the celebrated Gibbs phase rule. Equilibria in high temperature gases over solids or liquids have been studied extensively by Gurry (1950) who developed techniques to establish limits for processes such as the heat treatment of steel.

Lever (1964) applied these techniques to equilibria in the Si-H-Cl system important to semiconductor processing. A general analysis of the Ga-As-H-Cl system important in the growth of GaAs from the gas phase was later outlined by Hurle and Mullin (1966). This approach was followed Seki and Araki (1967) to calculate equilibrium properties of the Ga-P-H-Cl system.

Chemical reactions equilibria in the Ga-As-P-H-Cl system known to take place in the gas phase and with $Ga(\ell)$ and $GaAs_{1-x}P_x(s)$ alloys are summarized in Table I along with equilibrium constants, K_i and the reactor zone where the equilibrium is expected to apply. The magnitude of $\log K_i$ for these reactions is shown in Fig. 1 over the temperature range expected in the reactor for each of the three reactor zones.

A schematic of the $GaAs_{1-x}P_x$ reactor using AsH_3 , PH_3 and $Ga(\ell)/HCl$ as reactants in a H_2 carrier gas is shown in Fig. 2. When HCl in H_2 is introduced into a liquid gallium saturator, and the products mixed with AsH_3 and PH_3 , the gas phase species appearing as a result of chemical reaction are shown in Fig. 2 for each of the reactor zones. By a comparison of the relative magnitudes of the equilibrium constants, the following species can be eliminated at the temperature of interest:

a. Cl , Cl_2 in the gallium saturator zone

b. Cl , Cl_2 , $AsCl_3$, PCl_3 , in the reaction zone

c. Cl , Cl_2 , $AsCl_3$, PCl_3 , AsH_3 , PH_3 in the deposition zone.

Table I. Reaction equilibria in the Ga-As-P-H-Cl system

Reaction number	Reaction	$\log_{10}K_i$ (atm units)	Zone	Reference
1	$Ga(\ell)+\frac{1}{2}Cl_2 \rightarrow GaCl_{(g)}$	$6.46+3.69\times10^3/T-0.47\ \ell n\,T$	Saturation	a,b,c,d† (calculated)
2	$Ga(\ell)+\frac{3}{2}Cl_2 \rightarrow GaCl_{3(g)}$	$-1.96+2.25\times10^4/T-0.17\ \ell n\,T$	Saturation	e† (calculated)
3	$GaCl+Cl_2 \rightarrow GaCl_{3(g)}$	$-8.37+1.87\times10^4/T+0.30\ \ell n\,T$	Saturation	e† (calculated)
4	$GaCl_3+2Ga \rightarrow 3GaCl_{(g)}$	$4.87-4.66\times10^3/T$	Saturation	b† (experimental)
5	$\frac{1}{2}H_2+\frac{1}{2}Cl_2 \rightarrow HCl_{(g)}$	$2.79+4.56\times10^3/T-0.31\ \ell n\,T$	Saturation	a† (calculated)
6	$GaCl_3+H_2 \rightarrow GaCl+2HCl$	$13.95-9.58\times10^3/T-0.92\ \ell n\,T$	Saturation	calc. from reactions 3&5
7	$As_{4(g)} \rightarrow 2As_{2(g)}$	$11.6-1.36\times10^4/T-0.43\ \ell n\,T$	Reaction	b,d† (calculated)
8	$\frac{1}{4}As_4+\frac{3}{2}H_2 \rightarrow AsH_{3(g)}$	$3.65-7.52\times10^3/T-1.0\ \ell n\,T$ $+0.6\times10^{-3}\,T$	Reaction	a,b,d† (calculated)
9	$\frac{1}{4}As_4+\frac{3}{3}Cl_2 \rightarrow AsCl_3$	$-6.18+1.76\times10^4/T+0.37\ \ell n\,T$	Reaction	a,b,d† (calculated)
10	$Ga(\ell)+\frac{1}{4}As_4 \rightarrow GaAs_{(s)}$	$-4.62+6.15\times10^3/T+0.35\times10^{-3}\,T$	Deposition	a,b,f† (calculated)
11	$2GaCl+\frac{1}{2}As_4 \rightarrow 2GaAs_{(s)}+Cl_2$	$-21.64+4.86\times10^3/T+1.1\ \ell n\,T$	Deposition	a† (calculated)

Table I. (continued)

Reaction number	Reaction	$\log_{10}K_1$ (atm units)	Zone	Reference
12	$3GaCl+\frac{1}{2}As_4 \rightarrow 2GaAs_{(s)}+GaCl_3$	$-30.1+2.36\times10^4/T+1.4 \ln T +0.7\times10^{-3}T$	Deposition	g† (experimental)
13	$GaCl+\frac{1}{4}As_4+\frac{1}{2}H_2 \rightarrow GaAs+HCl$	$-8.04+6.99\times10^3/T+0.22 \ln T +0.35\times10^{-3}T$	Deposition	h† (experimental)
14	$P_4 \rightarrow 2P_2$	$11.5-1.21\times10^4/T-0.5 \ln T$	Reaction	b,i† (calculated)
15	$\frac{1}{4}P_4+\frac{3}{2}H_2 \rightarrow PH_3$	$4.88+1.47\times10^3/T-1.2 \ln T$	Reaction	b,i† (calculated)
16	$\frac{1}{4}P_4+\frac{3}{2}Cl_2 \rightarrow PCl_3$	$-6.21+1.79\times10^4/T+0.25 \ln T$	Reaction	b,f,i† (calculated)
17	$Ga+\frac{1}{2}P_2 \rightarrow GaP$	$-5.36+9.41\times10^3/T$	Deposition	i† (experimental)
18	$Ga+\frac{1}{4}P_4 \rightarrow GaP$	$-2.46+6.38\times10^3/T-0.13 \ln T$	Deposition	Calculated from reactions 14 &17
19	$2GaCl+\frac{1}{2}P_4 \rightarrow 2GaP+Cl_2$	$-18.00+5.39\times10^3/T+0.68 \ln T$	Deposition	Calculated from reactions 18 &12
20	$3GaCl+\frac{1}{2}P_4 \rightarrow 2GaP+GaCl_3$	$-26.46+2.41\times10^4/T+0.98 \ln T$	Deposition	Calculated from reactions 19 &16
21	$GaCl+\frac{1}{4}P_4+\frac{1}{2}H_2 \rightarrow GaP+HCl$	$-6.08+7.255\times10^3/T+0.03 \ln T$	Deposition	Calculated from reactions 18,14

Table I. (continued)

Reaction number	Reaction	$\log_{10}K_i$ (atm units)	Zone	Reference
22	$As_2 + P_2 \rightarrow As_2P_2$	not determined	Reaction	---
23	$As_2P_2 \rightarrow 2AsP$	not determined	Reaction	---
24	$2As_2P_2 \rightarrow As_3P + AsP_3$	not determined	Reaction	---
25	$Ga(\ell) + HCl \rightarrow GaCl + \frac{1}{2}H_2$	$K_{25} = K_1/K_5$	Saturation	Calculated from reactions 1&5
26	$GaCl + 2HCl \rightarrow GaCl_3 + H_2$	$K_{26} = K_3/K_5^2$	Saturation	Calculated from reactions 3&5

† a Furgusson and Gabor (1964)
b Kelley (1960)
c Quill (1950)
d Stull and Sinke (1956)
e Bleicher (1972)
f Perry (1963)
g Kirwan (1970)
h Zengel (1965)
i Rossini (1952)

There is currently insufficient data to determine the equilibria with polymers of arsenic and phosphorous. However Ban (1971) reported that the polymers AsP, As_2P_2, As_3P, AsP_3 are present. The total concentration of these polymers is about 10-20% of the total of arsenic and phosphorous combined, and should become significant at high temperatures. These polymers are excluded in the present analysis, since in the deposition zone the total component partial pressures of arsenic and phosphorous present do not change significantly during the deposition process.

The calculation of phase equilibria required in the Ga-As-P-H-Cl system requires knowledge of important reacting species, appropriate reaction constants, and conditions for conservation of mass. A measure of the number of system constraints required for equilibrium is the Gibbs phase rule which relates the number of degrees of freedom of a multicomponent, multiphase equilibrium, v, to the number of restrictions r, and the variance n

$$v = n + 2 - r \qquad (1)$$

The variance is the number of variables whose values must be assigned in order to specify completely the state of the system. Thus, for the five components Ga, As, P, H and Cl, and two phases (gallium liquid and vapor, or $GaAs_{1-x}P_x$ solid and vapor), v = 5. If temperature and pressure are two of the variables held constant, then three additional variables must be constant for equilibrium. If equilibrium in the gas phase alone is considered, v = 6, and four constraints are needed in addition to T and P. System properties can then be defined as a function of T, P and the constraints, q_1. Then for any system property we have,

$$\text{system property} = f(P,T,q_1,\cdots q_{v-2}). \qquad (2)$$

The constraints can be deduced by requiring conservation of mass for each of the component elements. If m_i denotes the moles of component i while n_j denotes the moles of species j, then for I components and J species the conservation conditions are

$$m_i = \sum_{j=1}^{J} \alpha_{ij} n_j, \quad i = 1,2\cdots I \tag{3}$$

where α_{ij} is the stoichiometric number of components i in species j. Additional constraints are supplied by the reaction equilibria. These are expressed in terms of partial pressures of species i, P_i, or in terms of numbers of moles, by

$$P_j = n_j P \left(\sum_{j=1}^{J} n_j \right)^{-1} \tag{4}$$

and, therefore,

$$K = f(P_j) \text{ or } K = f(n_j) \tag{5}$$

Finally, the system constraints can be defined on the basis of a fixed total moles by the ratios,

$$q_i = m_i \left(\sum_{i=1}^{J} m_i \right)^{-1} \quad i = 1,2,\cdots v-2 \tag{6}$$

In systems where one component, n_I, is in excess, an alternate definition can be made

$$q_i = \frac{n_i}{n_I} \tag{7}$$

The definition of q_i in terms of a species molar ratio has been used in equilibria involving III-V compounds where H_2 is in excess.

To convert to a partial pressure basis, Eqs. (3) and (4) can be combined to give

$$m_i P\left(\sum_{j=1}^{J} n_j\right)^{-1} = \sum_{J=1}^{J} \alpha_{ij} P_j \qquad (3')$$

The total system moles, $\sum_{j=1}^{J} n_j$, can be specified by fixing the total system volume V, or alternately for an open system, the total volumetric flow rate, and assuming the ideal gas law as the equation of state for the gas phase. Therefore

$$\sum_{j=1}^{J} n_j = \frac{PV}{RT} \qquad (8)$$

The following composition parameters can then be introduced:

$$q_{Cl} = \frac{p_{HCl} + p_{GaCl} + 3p_{GaCl_3}}{P} = \frac{p^{\circ}_{HCl}}{P} \qquad (9)$$

$$q_{As} = \frac{4p_{As_4} + p_{As_2} + \cdots\cdots}{P} = \frac{p^{\circ}_{AsH_3}}{P} \qquad (10)$$

$$q_P = \frac{4p_{P_4} + 2p_{P_2} + \cdots\cdots}{P} = \frac{p^{\circ}_{PH_3}}{P} \qquad (11)$$

It will be seen later that these quantities are conserved throughout the gallium saturation and reaction zones. However a more useful parameter, which is independent of the deposition reaction can be deduced from the above three expressions

$$q_{GaAsP} = q_{Ga} - q_{As} - q_{P} \tag{12}$$

This parameter is very useful in determining the equilibria in the deposition zone as this is satisfied by the material balance of species Ga, As and P in the formation of $GaAs_{1-x}P_x$.

A general solution to an equilibrium problem in terms of Eqs. (3), (4), and (5), utilizes the following procedure:

1. After eliminating the species which are not present in any great extent relative to majority species, the system's five degrees of freedom can be completely specified by fixing temperature, pressure and flow rates (composition parameters) of AsH_3, PH_3 and HCl relative to that of H_2.
2. The system of equations for the equilibrium can be solved by assuming reactions 1, 5 in the gallium saturator zone, reactions 7, 8, 14, 15 in the reaction zone, reactions 3, 7, 13, 14, 21 in the deposition zone (besides the reactions for combination of GaAs and GaP).

Gallium Saturation Equilibria

In the saturation zone Ga(ℓ) reacts with HCl and H_2 gas to form volatile gallium compounds, principally GaCl and $GaCl_3$. The species present in this zone are Ga, Cl and H, and for Ga(ℓ) — vapor phase equilibrium the Gibbs phase rule requires three constraints for equilibrium e.g., T, P and q_{Cl}. A typical value for the input q_{Cl}, denoted by q°_{Cl} is 0.01 corresponding to an HCl partial pressure in the range of 10^{-2}-10^{-3} atm in H_2. The majority species present at equilibrium in this zone are GaCl, $GaCl_3$, HCl and H_2. Therefore, in addition

to q_{Cl}, reactions 1, 2, and 5 in Table I and the total pressure constraint (here P=1 atm) are sufficient to specify the equilibrium. The resulting system of equations for equilibrium are then

$$q_{Cl} = P_{HCl} + P_{GaCl} + 3P_{GaCl_3} = q^{\circ}_{Cl} = P^{\circ}_{HCl} \tag{13}$$

$$1 = P_{GaCl} + P_{GaCl_3} + P_{HCl} + P_{H_2} \tag{14}$$

$$Ga(\ell) + HCl = GaCl + \frac{1}{2} H_2, \qquad \frac{K_1}{K_5} = \frac{P_{GaCl} P_{H_2}^{1/2}}{P_{HCl}} \tag{15}$$

$$Ga(\ell) + 3HCl = GaCl_3 + \frac{3}{2} H_2, \qquad \frac{K_2}{K_5^3} = \frac{P_{GaCl_3} P_{H_2}^{3/2}}{P_{HCl}^3} \tag{16}$$

A very good approximation is to assume that the partial pressure of hydrogen is 1 atm. This is a very sound assumption in the region of interest since $p^{\circ}_{HCl} \sim 10^{-2}$-$10^{-3}$ atm. The simplified expressions for equilibrium become,

$$P_{HCl} = \frac{K_5}{K_1} \; P_{GaCl} \tag{17}$$

$$P_{GaCl_3} = \frac{K_2}{K_5^3} \cdot P_{HCl}^3 = \frac{K_2}{K_1^3} \; P_{GaCl}^3 \tag{18}$$

and

$$q^{\circ}_{Cl} = \frac{K_5}{K_1} \cdot P_{GaCl} + 1\, P_{GaCl} + 3 \frac{K_2}{K_1^3} \cdot P_{GaCl}^3 \tag{19}$$

$$= \left(1 + \frac{K_5}{K_1}\right) \cdot P_{GaCl} + 3 \frac{K_2}{K_1^3} \cdot P_{GaCl}^3$$

These three equations can be combined to give a single equation in the variable p_{GaCl}

$$p_{GaCl}^3 + C_1\, p_{GaCl} + C_2 \cdot q_{Cl}^{\circ} = 0 \tag{20}$$

On solving this equation by iteration, one finds at 850°C the following magnitudes for p_{GaCl}, p_{GaCl_3} and p_{HCl} in equilibrium for $p_{HCl}^{\circ} = 0.01$ atm,

$$p_{GaCl} = 0.995\ p_{HCl}^{\circ} \cong 10^{-2}\ \text{atm}$$

$$p_{HCl} = 0.005\ p_{HCl}^{\circ} = 5 \times 10^{-5}\ \text{atm} \tag{21}$$

$$p_{GaCl_3} = 10^{-6} \times p_{HCl}^{\circ} = 10^{-8}\ \text{atm}$$

and therefore

$$p_{H_2} = 0.99\ \text{atm.}$$

These sample calculations show that virtually all of the HCl fed into this zone is converted to GaCl and that $GaCl_3$ is only present at many orders of magnitude less than $GaCl_1$. This is a strong proof that GaCl is the primary gallium compound reacting in the deposition process.

Another conclusion which can be drawn here is that the HCl conversion at equilibrium is essentially 100%; thus, with a properly designed saturator, all the HCl can be utilized for growth in the form of GaCl. Excess HCl can be introduced, however, by designing a saturator with fractional efficiency, or introduced separately beyond the saturator.

Another great advantage of designing the saturator to produce equilibrium is that the conversion of HCl to GaCl is independent of temperature in the range of 750-900°C. Therefore the saturator temperature does not affect the conversion efficiency to any great extent and the temperature of gallium boat need not be regulated to any great precision. This fact is very important for a large gallium saturator since it is difficult to maintain a uniform temperature over a long distance without costly furnace design.

Reaction Zone Equilibria

In the reaction zone the output from the saturator is mixed with an input PH_3, AsH_3, H_2 mixture, and three events take place:

1. Heating of the arsine-phosphine-hydrogen stream and the gallium saturator output stream to the reaction temperature,
2. decomposition of arsine and phosphine
3. mixing of the decomposition products by turbulent flow through orifices.

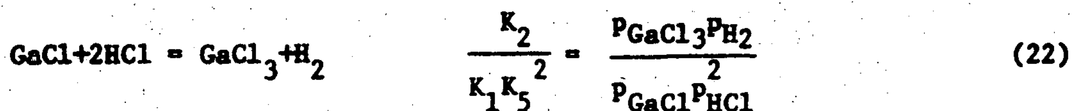
The temperature in this zone is higher than that of the saturation zone so that the equilibrium for products of the gallium saturator will change only slightly. Earlier studies by Zengel (1965) have indicated that no reaction takes place between GaCl and arsenic or phosphorous in this region possibly due to the absence of any nucleating surface. Therefore, the only reactions taking place in the reaction zone are reactions 7, 8, 14 and 15 in Table I.

The gaseous species existing in this zone are GaCl, $GaCl_3$, AsH_3, H_2, HCl, PH_3, P_2, P_4, As_2, As_4 and for gas phase equilibria the Gibbs phase rule

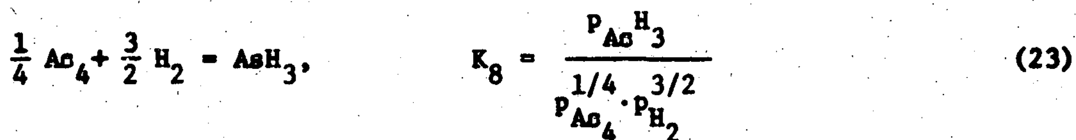
requires that four composition variables, one for each of the gas phase species, be specified in addition to T and P.

The polymer species AsP , As_3P, AsP_3 and As_2P_2 should also be taken into account, but the lack of sufficient thermodynamic data prevents this. However, it can be estimated that the combined entropies of reaction for reactions 22, 23 and 24 in Table I are near zero since the number of bonds broken on one side of each reaction equation equals the number of bonds formed on the other, and since the vibrational and rotational mode energies for the tetramers is only slightly less than that of the dimers. The polymers reaction equilibria should therefore change slowly with temperature in the gas phase. This contention is supported by the similar reactions $2P_2 \rightleftharpoons P_4$ and $2As_2 = As_4$ whose reaction constants (K_{14} and K_7 respectively in Table I) change slowly with temperature.

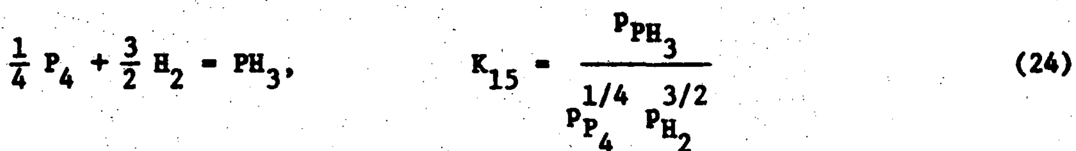
The significant gaseous species, neglecting As-P polymers, are HCl, AsH_3, PH_3, P_4, P_2, As_4, As_2, H_2, GaCl and $GaCl_3$. For ten unknowns, we require ten equations. These are obtained from reactions 7, 8, 14, 15 in Table I, from the composition constraints, q_{As}, q_P, q_{Ga}, and q_{Cl}, and the total pressure constraints. The solving equations are then,



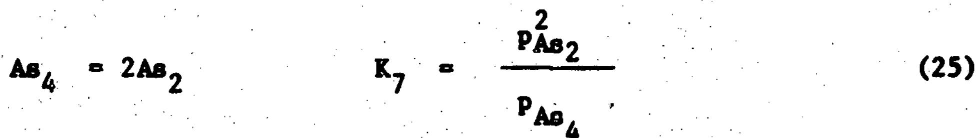
$$GaCl+2HCl = GaCl_3+H_2 \qquad \frac{K_2}{K_1K_5^2} = \frac{p_{GaCl_3}p_{H_2}}{p_{GaCl}p_{HCl}^2} \tag{22}$$



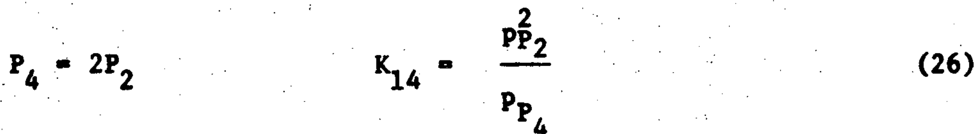
$$\frac{1}{4}As_4+\frac{3}{2}H_2 = AsH_3, \qquad K_8 = \frac{p_{AsH_3}}{p_{As_4}^{1/4}\cdot p_{H_2}^{3/2}} \tag{23}$$



$$\frac{1}{4}P_4+\frac{3}{2}H_2 = PH_3, \qquad K_{15} = \frac{p_{PH_3}}{p_{P_4}^{1/4}\ p_{H_2}^{3/2}} \tag{24}$$



$$As_4 = 2As_2 \qquad K_7 = \frac{p_{As_2}^2}{p_{As_4}} \tag{25}$$



$$P_4 = 2P_2 \qquad K_{14} = \frac{p_{P_2}^2}{p_{P_4}} \tag{26}$$

$$q_{As} = p^{\circ}_{AsH_3} = p_{AsH_3} + 4p_{As_4} + 2p_{As_2} \tag{27}$$

$$q_P = p^{\circ}_{PH_3} = p_{PH_3} + 4p_{P_4} + 2p_{P_2} \tag{28}$$

$$q_{Ga} = 0.995\ p^{\circ}_{HCl} = p_{GaCl} + p_{GaCl_3} \tag{29}$$

$$q_{Cl} = p^{\circ}_{HCl} = p_{HCl} + p_{GaCl} + 2p_{GaCl_3} \tag{30}$$

and

$$1 = p_{AsH_3}+p_{PH_3}+p_{P_4}+p_{P_2}+p_{As_4}+p_{As_2}+p_{GaCl}+p_{GaCl_3}+p_{HCl}+p_{H_2}. \tag{31}$$

It can be shown from these equations that arsenic and phosphorous equilibria are totally independent of each other and hence separately solvable.

Arsenic equilibria, can be calculated from Eqs. 23, 25 and 27. Upon combining these equations, and simplifying, we obtain

$$p_{As_4} + \frac{K_7^{1/2}}{2} p_{As_4}^{1/2} + \frac{K_8}{4} p_{As_4}^{1/4} - \frac{1}{4} q_{As} = 0 \qquad (32)$$

from which it follows that, at 900°C,

$$p_{As_4} \cong \frac{1}{4} q_{As}$$

$$p_{As_2} \cong \frac{1}{2} q_{As} \times 10^{-3} \qquad (33)$$

$$p_{AsH_3} \cong q_{As} \times 10^{-7}.$$

From this calculation, it is apparent that most of the arsine is converted to As_4, the tetramer rather than the dimer.

Phosphorous equilibria is calculable from Eqs. 29, 26, 28. The equations are combined in a similar manner to that for arsenic to solve for a single partial pressure unknown. At 900°C, the partial pressures of phosphorous polymers are,

$$p_{P_4} = \frac{1}{4} q_p \times 0.99$$

$$p_{P_2} = \frac{1}{2} q_p \times 10^{-2}$$

$$p_{PH_3} = q_p \times 10^{-4}$$

Again the tetramer is the majority phosphorous component. Although the magnitude of P_2 and PH_3 are higher than those of As_2 and AsH_3 they are safely negligible at this temperature.

In conclusion, virtually all of arsine is converted to As_4 in the reaction zone and all phosphine converted to P_4. The unassessed partial pressure of As_2P_2 should be similar, be large compared to that of AsP. Therefore, in spite of the large number of group V polymers, only the tetramers enter the deposition zone making the solution of gas phase equilibria in that zone easier. These majority gas species leaving the reaction zone are then H_2, GaCl, As_4, P_4, and probably As_2P_2.

Deposition Zone Equilibria

This is by far the most important phase equilibrium in the reactor, and also the most difficult to calculate. The analysis of equilibria in the gallium saturation zone and the reactor zone show that only certain gaseous species enter this zone. Once in contact with solid $GaAs_{1-x}P_x$, however, other species can appear in quantities which can affect the rate of deposition of solid, as will be shown in Chapter IV. The analysis of equilibria at the solid-gas interface will enable us to predict the driving forces for deposition, the composition of the alloy solid and the effects of various parameters on the growth rates, e.g. temperature and flow rates of input gases.

As shown earlier, the gases entering this zone are principally H_2, GaCl, As_4, P_4 and traces of other species. But once the gases come into contact with the solid substrate, the gas phase composition changes by selective evaporation of the solid, or condensation. It will be shown that the possible gaseous species which exist in this region are be H_2, HCl, GaCl, $GaCl_3$, As_4, As_2, P_4, P_2, besides the polymers of arsenic and phosphorous, neglected here.

The Gibbs phase rule for species Ga, As, P, Cl and H, and for vapor and solid phases gives a variance of five, requiring that T, P, and three composition functions be held constant for equilibrium. The eight unknowns, however, require eight equations to solve the equilibrium problem. An additional unknown is x in the compound $GaAs_{1-x}P_x$, requiring a ninth equation. The required equations are given by reactions 7, 14, 13, 21, 3 in Table I, the composition parameters q_{Cl} and q_{GaAsP}, the

ratio of phosphorus to arsenic in the gas phase, $q_{P_{P+As}}$ and an independent expression for x deduced from the activities of the group V elements in the solid, a_{GaAs} and a_{GaP}. The required set of equations are then,

$$P_4 = 2P_2, \qquad K_{14} = p_P^2 \cdot p_{P_4}^{-1} \tag{35}$$

$$As_4 = 2As_2, \qquad K_7 = p_{As_2}^2 \, p_{As_4}^{-1} \tag{36}$$

$$GaCl+2HCl = GaCl_3+H_2 \qquad K_3/K_5^{\,2} = p_{GaCl_3}p_{H_2}\, p_{GaCl}^{-1}p_{HCl}^{-2} \tag{37}$$

$$GaCl+\frac{1}{4}As_4+\frac{1}{2}H_2 = GaAs_{(s)}+HCl \qquad K_{13} = p_{HCl}p_{GaCl}^{-1}p_{As_4}^{-1/4}p_{H_2}^{-1/2} \tag{38}$$

$$GaCl+\frac{1}{4}P_4+\frac{1}{2}H_2 = GaP_{(s)}+HCl \qquad K_{21} = p_{HCl}p_{GaCl}^{-1}p_{P_4}^{-1/4}p_{H_2}^{-1/2} \tag{39}$$

$$q_{Cl} = p^{\circ}_{HCl} = p_{GaCl} + 3p_{GaCl_3} + p_{HCl} \tag{40}$$

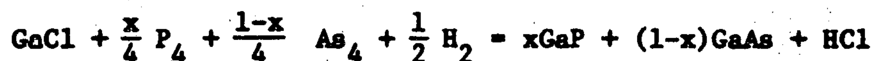
$$q_{GaAsP} = 0.995\ p^{\circ}_{HCl} - p^{\circ}_{AsH_3} - p^{\circ}_{PH_3} \tag{41}$$

$$= p_{GaCl}+p_{GaCl_3}-4p_{P_4}-4p_{As_4}-2p_{P_2}-2p_{As_2}$$

$$q_{AsP} = \frac{p^{\circ}_{PH_3}}{p^{\circ}_{PH_3}+p_{AsH_3}} = \frac{4p_{P_4}+2p_{P_2}+p_P^s}{4(p_{P_4}+p_{As_4})+2(p_{P_2}+p_{As_2})+p_P^s+p_{As}^s} \tag{42}$$

where p_P^s and p_{As}^s are defined as the partial pressures of phosphorous and arsenic equivalent to the amount of these components in the solid $GaAs_{1-x}P_x$. The expression for x can be deduced from reactions 13 and 21 in Table I, and the activities a_{GaAs} and a_{GaP}. If the fraction

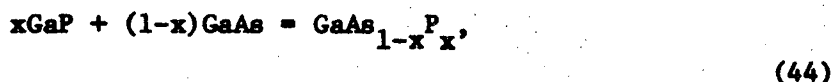
x of reaction 21 is added to the fraction (1-x) of reaction 13, the following reqction equation results:



$$GaCl + \frac{x}{4} P_4 + \frac{1-x}{4} As_4 + \frac{1}{2} H_2 = xGaP + (1-x)GaAs + HCl$$

$$\Delta F = x\Delta F_{21} + (1-x)\Delta F_{13} , \quad (43)$$

where $\Delta F_i = -RT \ln K_i$ the free energy change for the reaction. To this equation must be added the free energy of mixing of the alloy



$$xGaP + (1-x)GaAs = GaAs_{1-x}P_x ,$$

$$\Delta F = RT[x \ln a_{GaP} + (1-x) \ln a_{GaAs}] \quad (44)$$

Since the alloys of III-V compounds are known to be regular, the activities can be expressed in terms of x by a regular solution model:

$$a_{GaP} = x \exp[\alpha(1-x)^2/RT]$$

$$a_{GaAs} = (1-x) \exp[\alpha x^2/RT]. \quad (45)$$

The heat of mixing coefficient α has been reported by Bleicher (1972) to be 1 kcal/mole, and consequently the ratio $\alpha/RT << 1$, for temperatures near 700°C. The equilibrium constant for the sum of reactions given in Eqs. 43 and 44 is

$$K_{21}^{x} K_{13}^{(1-x)} = \frac{a_{GaP}^{x} a_{GaAs}^{1-x} p_{HCl}}{p_{GaCl} p_{P_4}^{x/4} p_{As_4}^{(1-x)/4} p_{H_2}^{1/2}} . \quad (46)$$

And finally, the implicit expression for x is

$$x = \frac{\ln\left[K_{13}^{-1} a_{GaAs} p_{HCl} p_{GaCl} p_{As_2}^{-1/4} p_{H_2}^{-1/2}\right]}{\ln\left[\left(\frac{K_{12}}{K_{13}}\right)\left(\frac{a_{GaAs}}{a_{GaP}}\right)\left(\frac{p_{P_4}}{p_{As_4}}\right)^{1/4}\right]} \quad (47)$$

A very good assumption for initial estimates is to neglect the gaseous species $GaCl_3$ altogether and set $P_{GaCl_3} = 0$. The pressure of $GaCl_3$ does not exceed 10^{-6} atm at typical conditions whereas the pressures of GaCl and arsenic, etc. are on the order of 10^{-2} atm. By substituting $p_{GaCl_3} = 0$ and eliminating p_{As_2}, p_{P_4}, p_{P_2} from Eqs. in Eq. 41 , the following equation is obtained:

$$q_{GaAsP} = p_{GaCl} - 4\left[1 + \left(\frac{K_{13}}{K_{21}}\right)^4\right] p_{As_4} - 2\left[K_7^{1/2} + K_{14}^{1/2}\left(\frac{K_{13}}{K_{21}}\right)^2\right] p_{As_4}^{1/2} \tag{48}$$

Alternately this equation can be written as

$$q_{GaAsP} = p_{GaCl} - A\, p_{As_4} - B\, p_{As_4}^{1/2} \tag{49}$$

where

$$A = 4\left[1 + \left(\frac{K_{13}}{K_{21}}\right)^4\right]$$

$$B = 2\left[K_7^{1/2} + K_{14}^{1/2}\left(\frac{K_{13}}{K_{21}}\right)^2\right] .$$

Then solving Eq. 49 for $p_{As_4}^{1/2}$, we obtain

$$p_{As_4}^{1/2} = \frac{1}{2A}\left\{\sqrt{B^2 - 4\,Aq_{GaAsP} + 4Ap_{GaCl}} - B\right\} . \tag{50}$$

A simple equation in P_{GaCl} is finally obtained by substituting Eq. 50 in Eq. 38 and simplifying with the help of Eq. 40 :

$$f = p_{GaCl}\left[\pm\sqrt{B^2-4A\,q_{GaAsP}+4A\,p_{GaCl}}\;-B\right]^{1/2} + \frac{\sqrt{2A}}{K_{13}}\left(p_{GaCl}-q_{Cl}\right) \qquad (51)$$

Equation 51 can now be solved iteratively for p_{GaCl}.

A and D are functions of temperature which is held constant, as are only q_{Cl} and q_{GaAsP}, which are determined by the initial conditions of gas flow to the reactor.

The equilibria of gases as well as value of x can now be determined from p_{GaCl} by substitution. This approach allows a direct solution which is easier to calculate than a simultaneous set of non-linear equations, yet the accuracy of the calculation is maintained. One parameter can be varied at a time with the others kept constant to examine its effects on the equilibrium.

Results

The reaction model presented above was explored in numerical simulation studies to deduce optimal design and operation conditions for industrial $GaAs_{1-x}P_x$ reactors. In addition, experimental studies were performed to test the predicted conditions for controlled deposition of desired alloy compositions. Because only thermodynamic equilibria were considered in the numerical studies, the kinetic limitations that occur at low temperatures are neglected in the results.

Figures 3 to 7 summarize the results of the computational method outlined above in which Eq. 15 is solved by iteration with constant substrate temperature and input flow rates. In Figs. 7a, 3b and 3c the gas phase equilibrium partial pressures are shown plotted versus substrate temperature for fixed alloy compositions, and for the value composition parameter q_{GaAsP} equal to -0.01, 0 and +0.01, respectively. It can be seen from these figures that the partial pressures of P_2 and P_4 are more than an order of magnitude lower than those of As_2 and As_4 for $x = 0.4$, indicating that phosphorus has a much lower activity in the $GaAs_{1-x}P_x$ alloy than does arsenic. Also, the equilibrium partial pressure of As_4 becomes greater than the input value at temperatures in excess of 850°C, indicating that etching of the substrate occurs in that temperature range.

Figure 4 shows the dependence of the alloy composition of the deposited layer on substrate temperature under steady state conditions. This figure shows that the temperature of the substrate should greatly

influence the composition of the deposited layer for fixed flow rates to the reactor. A change in x from 0.35 to 0.45 is possible for a substrate temperature change from 750°C to 800°C. Therefore, in order to grow an epitaxial layer of fixed composition the maintenance of very strict temperature control is required.

The effect of varying the phosphorus fraction in the reactor gas phase is shown in Figs. 5a, 5b and 5c in which the alloy compositon x is plotted as a function of the ratio of input PH_3 to the total input of PH_3 and AsH_3, for q_{GaAsP} equal to -0.01, 0 and +0.01 respectively. Because of the approximations utilized in the computations these figures are accurate only over the limited range of $0.2 < x < 0.8$, and are in agreement with the results of Manabe (1972).

Figures 6a, 6b and 6c show the effect of changing the input flow rates of HCl to the gallium saturator on the equilibrium partial pressures at the substrate. The equilibrium partial pressures of the arsenic and phosphorus species are found to decrease to a minimum at a critical value for the HCl flow rate. These figures show that the lowest partial pressures over the substrate, and thus the greatest deposition efficiency are obtained at this minimum, corresponding to a value of q_{GaAsP} somewhat less than zero. Also, the greatest utilization of the group V compounds is achieved at this value of q_{GaAsP} , corresponding to a value of q_{Cl} denoted by $q_{Cl(max)}$. Figure 7 shows the dependence of $q_{Cl(max)}$ on substrate temperature as derived from Eq. 6. Therefore, Figs. 6 and 7 provide

a means for estimating the inlet flow rates of HCl needed for maximum deposition efficiency as well as for maximum utilization of the group V reactants in the design of industrial $GaAs_{1-x}P_x$ reactors.

Experimental studies were conducted to explore the predicted gas-solid phase equilibria. The experimental reactor was a vertical, three-zone reactor with independent temperature control of the gallium saturator and GaAs substrates. In individual experiments the substrates were first exposed to 1% HCl in H_2 to clean the surface by gas phase etching. The input gas composition required for deposition of GaAs was then established for a fifteen minute period. The flow rate of PH_3 was then slowly increased at a constant rate to the value predicted from the theory for deposition of $GaAs_{0.6}P_{0.4}$, then held constant for deposition of a homogeneous epitaxial alloy layer. The substrates were then slowly cooled in pure hydrogen and examined for epitaxial growth characteristics. The composition of the $GaAs_{1-x}P_x$ alloy layer was determined from the peak in the photoluminescence spectrum.

The results of experimental studies directed toward deposition of the alloy $GaAs_{0.6}P_{0.4}$ are summarized in Table I. The growth rate of the epitaxial layer tends to increase with increasing temperature in the temperature range from 760 to 780°C because of surface kinetic limitations at low temperatures, and to decrease at higher temperatures where the group V component partial pressures become large. The composition parameter q_{GaAsP} was varied through

Table I

Substrate Temperature (°C)	Composition Parameter q_{GaAsP}	Alloy Composition x	Relative Deposition Rate
760	-0.005	0.408	moderate
762	0.0	0.410	moderate
770	-0.005	0.405	high
780	-0.005	0.402	high
780	-0.006	0.395	high
790	-0.005	0.395	moderate
792	0.0	0.385	very low
800	-0.004	0.393	very low
802	-0.006	0.389	very low
825	-0.0065	0.375	very low
825	-0.005	0.383	(slow etching)
850	-0.006	0.387	(slow etching)
850	-0.004	0.379	(moderate etching)

small, negative values from 0 to −0.0065. More negative values of q_{GaAsP} caused a decrease in the composition of the epitaxial layer, whereas positive values of q_{GaAsP} caused a decrease in growth rate, and promoted the growth of surface defects.

Discussion

The conditions for phase equilibria and methods of calculation outlined above permit an assessment of equilibrium partial pressures of the gas phase species throughout the $GaAs_{1-x}P_x$ reactor utilizing arsine, phosphine and liquid gallium as source chemicals. When H_2 carrier gas is the majority species, the halide reactant HCl is almost completely converted to GaCl in the gallium saturator. Therefore, unless additional HCl gas is added after the saturator, the reaction zone will contain principally H_2 , GaCl and the arsine and phosphine decomposition products As_4 and P_4 , and in addition the minor species HCl , P_2 , As_2 , $GaCl_3$ and other group V compounds. By far, the most complex equilibrium is the gas-solid equilibrium in the deposition zone, and the deposition rate and efficiency will depend strongly on this equilibrium in relation to the simpler reaction zone equilibrium.

The numerical study provides several important criteria for successful reactor operation. Figure 5 shows that the alloy composition x varies linearly with the phosphorus fraction of the group V component partial pressures for a fixed substrate temperature and that the proportionality constant increases as the substrate temperature is increased. From Fig. 4 it can be concluded that greatest control of the epitaxial alloy layer composition is obtainable when the substrate temperature is less than 800°C, and whereas x is most sensitive to the ratio of PH_3° to $(AsH_3^\circ + PH_3^\circ)$ in the temperature range above 800°C. The greatest control of x is thus

achieved for q_{GaAsP} parameters slightly less than 0.0. At temperatures below 750°C there is very little change in x with gas phase composition, but slow growth kinetics prevent successful operation of the deposition reaction in this range.

The experimental study confirms the variation in epitaxial layer composition on substrate temperature. Although a change in x from 0.48 to 0.32 was calculated for a change from 750°C to 800°C in substrate temperature the experimentally measured change was from 0.410 to 0.375 for the same temperature interval. In actual reactor operation, therefore, the temperature stability required to guarantee uniformity in the alloy composition is less than predicted by the theoretical study.

The requirement of precise temperature control can be circumvented for low values of the alloy composition x. Consider the dependence of x on the parameter q_{AsP} as shown in Figs. 5a, b, c. These figures strengthen the conclusion that a very rapid change in the alloy composition takes place with a slight change in temperature or in the ratio of arsine to phosphine only for high values of x. However the change with arsine to phosphine ratio is not large for $x < 0.2$, and particularly for temperatures between 800 and 850°C. This is a very important conclusion as one alloy composition important in device applications is $x = 0.19$. For this particular composition, slight changes in flow rates of incoming gases or temperature of the substrate do not significantly affect the composition of the alloy.

The simulation study shows that the As_4 equilibrium partial pressure over $GaAs_{1-x}P_x$ increases rapidly with temperature in the

temperature range studied. Thus, at temperatures above 850°C the equilibrium partial pressure exceeds the ambient partial pressure for an AsH_3 input flow rate of 1% which implies that etching of the substrate will occur instead of epitaxial growth, and that the alloy will tend to become depleted slightly in arsenic. This result is varified by the experimental study for which the input flow rate of AsH_3 was held in the range of 1%.

The prediction of an optimum HCl flow rate to the reactor saturator is highly important to successful industrial reactor operation. The experimental results of Table I support this prediction in that an increase in the HCl flow rate at 790°C caused a decrease in the observed growth rate. The predicted optimal HCl flow rate tends to increase as the substrate temperature is raised, and this variation is also consistant with the experimental results. Part of the observed growth or etching rate dependence on q_{GaAsP} could have been caused by incomplete conversion of HCl to GaCl in the saturator but the general results support the desired objective of operating the reactor at maximum deposition efficiency.

Conclusions

In summary, the following conclusions can be made for the phase equilibrium properties of the $GaAs_{1-x}P_x$ reactor:

1. Temperature variations of the substrate, and changes in flow rates of the gases will greatly affect the composition of the alloy deposited, with the greatest effect occurring when the composition variable $x >> 0.2$, and with limited effect for $x \approx 0.2$.

2. The HCl flow to the gallium saturator should be set to a critical value in order to achieve maximum chemical vapor deposition efficiency. The exact value can be estimated from the theoretical study but varies greatly with the temperature of the substrate.
3. Temperatures above 850°C will result in the growth of nearly pure GaP due to the high value of $P^{eq}_{As_4}$ above that temperature, and causes etching of GaAs for 1% HCl input partial pressures to the gallium saturator.
4. Arsine should always be in excess of the arsenide fraction desired by a proportionality factor which increases with the substrate temperature.
5. The presence of the minority species (i.e., $GsCl_3$, Cl , Cl_2) do not appear to significantly affect the equilibrium calculations of phase equilibria.

Nomenclature

I number of components in the gas phase

J number of species in the gas phase

K_i equilibrium constant for reaction i

T_s substrate temperature (°C)

V molar volume of the vapor phase

a_i activity of component i in solid $GaAs_{1-x}P_x$

m_i moles of component i

n variance in the Gibbs phase rule

n_j moles of species j

p total pressure of the vapor phase (atm)

p_i partial pressure of species i in the vapor phase (atm)

p_i^o reactor input partial pressure of species i in the vapor phase (atm)

q_i ratio of moles of component i to moles of component I

r number of restrictions in the Gibbs phase rule

x mole fraction of GaP in the alloy $GaAs_{1-x}P_x$

v number of degrees of freedom in the Gibbs phase rule

α heat of mixing coefficient

α_{ij} stoichiometric number of components i in species j

Acknowledgment

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Figure Captions

Fig. 1. Dependence of reaction equilibrium constants in the Ga-As-P-Cl-H system on temperature.

Fig. 2. Schematic of the $GaAs_{1-x}P_x$ reactor utilizing arsine, phosphine and gallium source chemicals with HCl/H_2 transport. Major gaseous species are shown in each zone.

Fig. 3. Partial pressures of gaseous species in equilibrium with $GaAs_{1-x}P_x$ as a function of temperature.

a) $q_{Cl} = 0.01$, $q_{GaAsP} = 0.002$, $q_p^\circ/p{+}As = 0.250$

b) $q_{Cl} = 0.01$, q_{GaAsP} = zero, $q_p^\circ/P{+}As = 0.200$

c) $q_{Cl} = 0.01$, $q_{GaAsP} = -0.002$, $q_p^\circ/P{+}As = 0.167$

Fig. 4. Dependence of x in $GaAs_{1-x}P_x$ on temperature.

Fig. 5. Dependence of x in $GaAs_{1-x}P_x$ on $p^\circ_{PH_3}/p^\circ_{PH_3} + p^\circ_{AsH_3}$, for fixed temperature and a) $q_{Cl} = 0.01$, $q_{GaAsP} = 0.002$,

b) $q_{Cl} = 0.01$, $q_{GaAsP} = 0$ c) $q_{Cl} = 0.01$, $q_{GaAsP} = -0.002$.

Fig. 6. Partial pressures of gaseous species in equilibrium with $GaAs_{1-x}P_x$ as a function of the input HCl partial pressure at $q_p^\circ/P{+}As = 0.20$ a) T = 750° b) T = 800°C c) T = 850°C.

Fig. 7. Dependence of the input partial pressures of HCl corresponding to maximum efficiency of group V elements deposition on temperature.

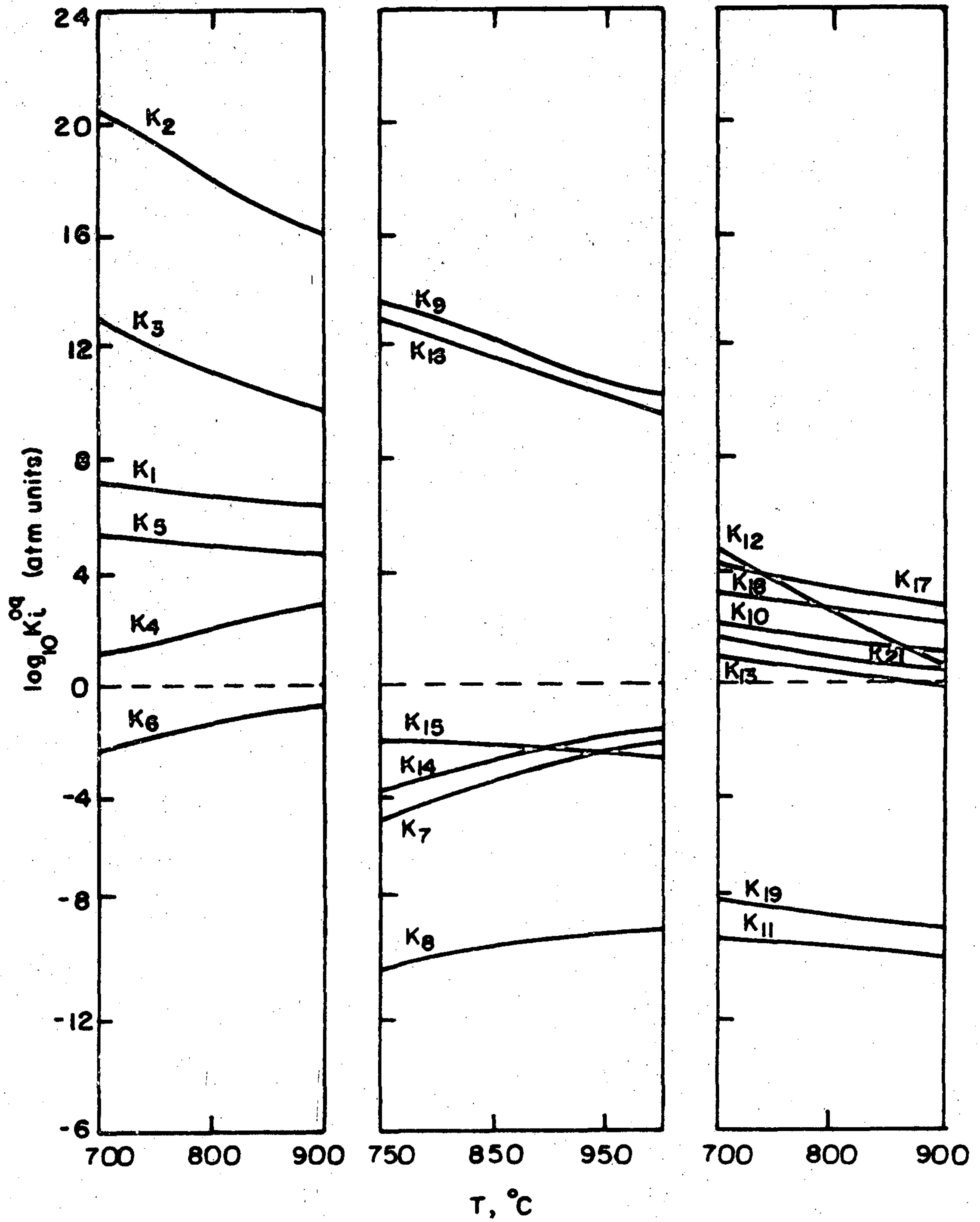


Fig. 1

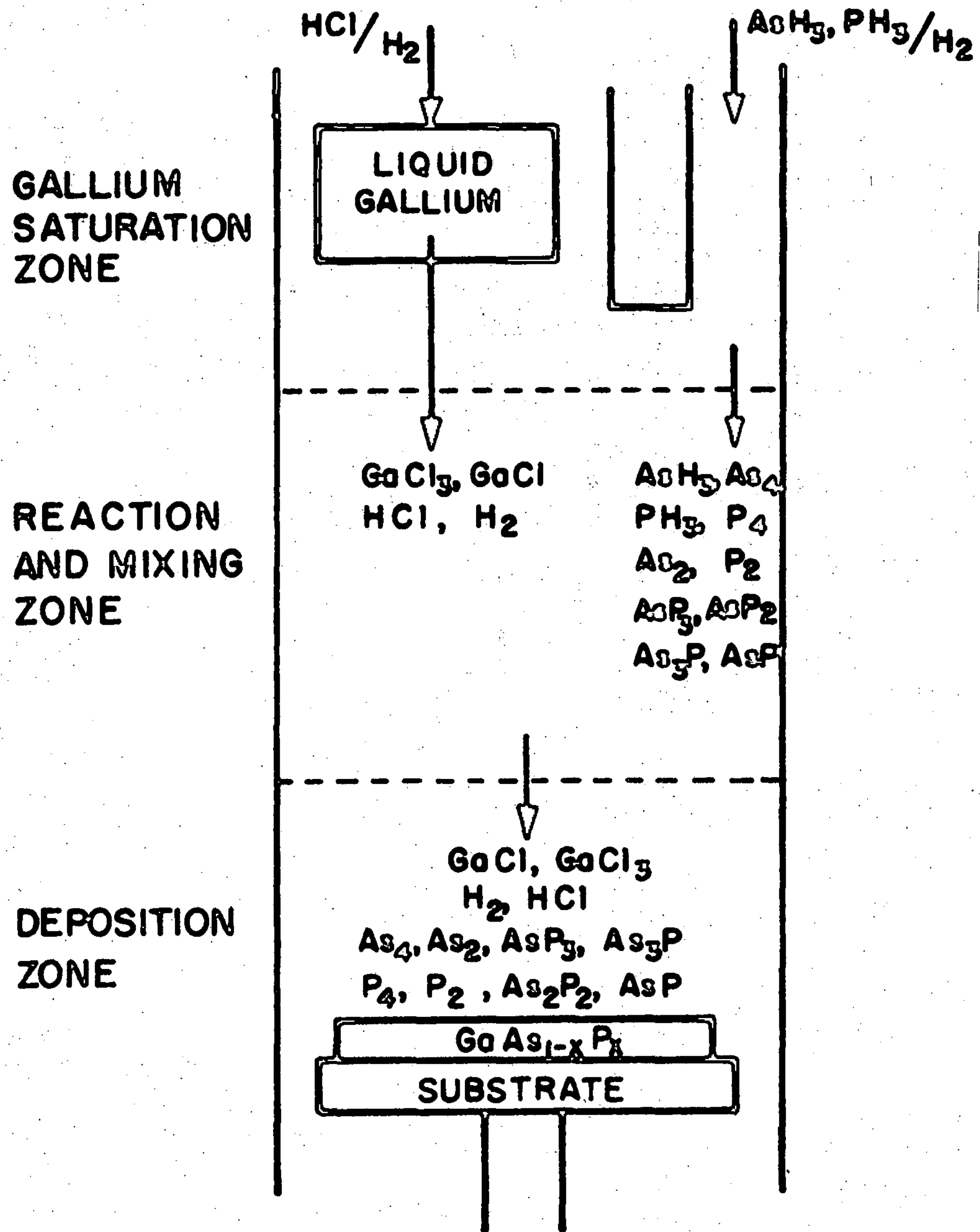
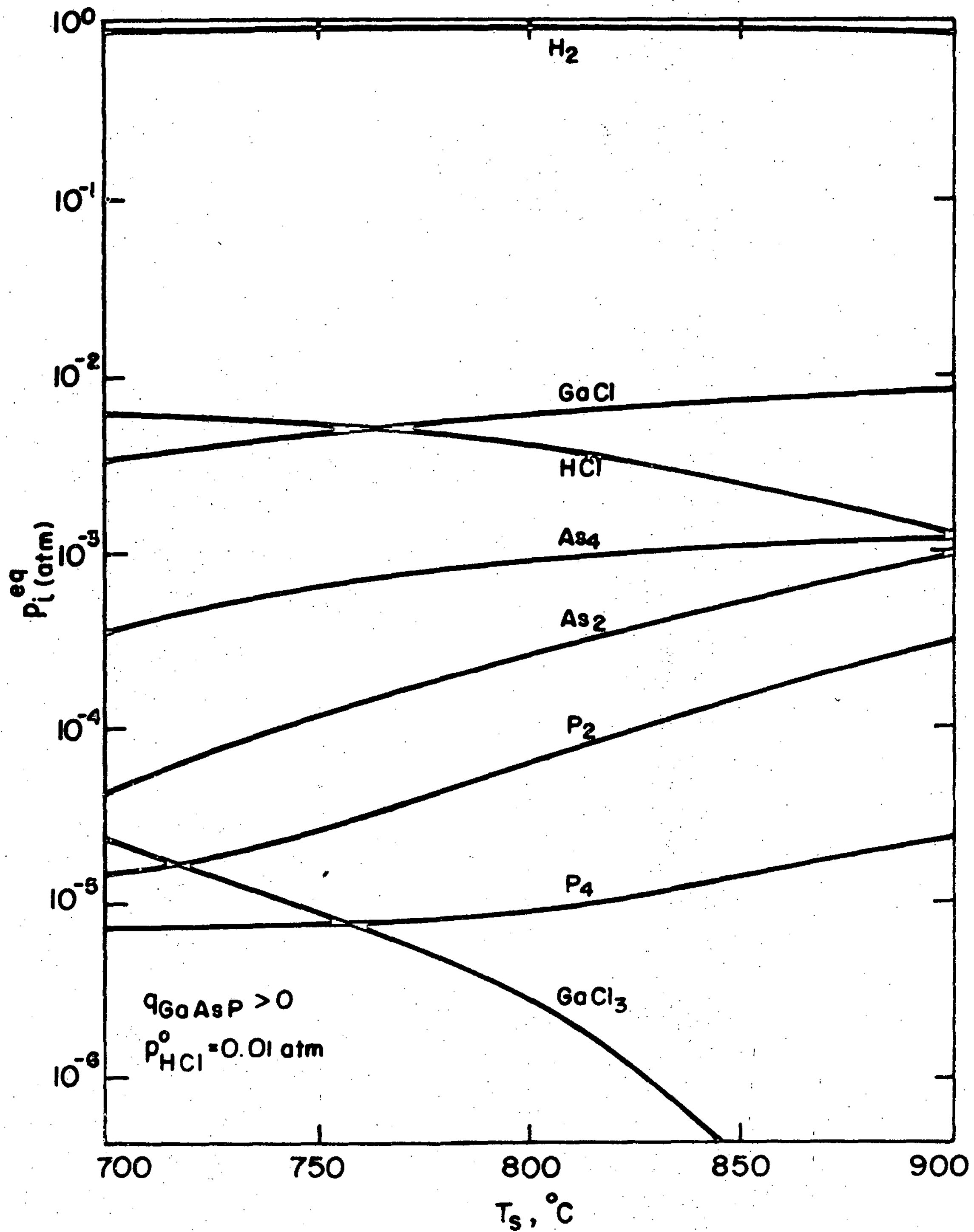


Fig. 2



XBL 729-6987

Fig. 3a

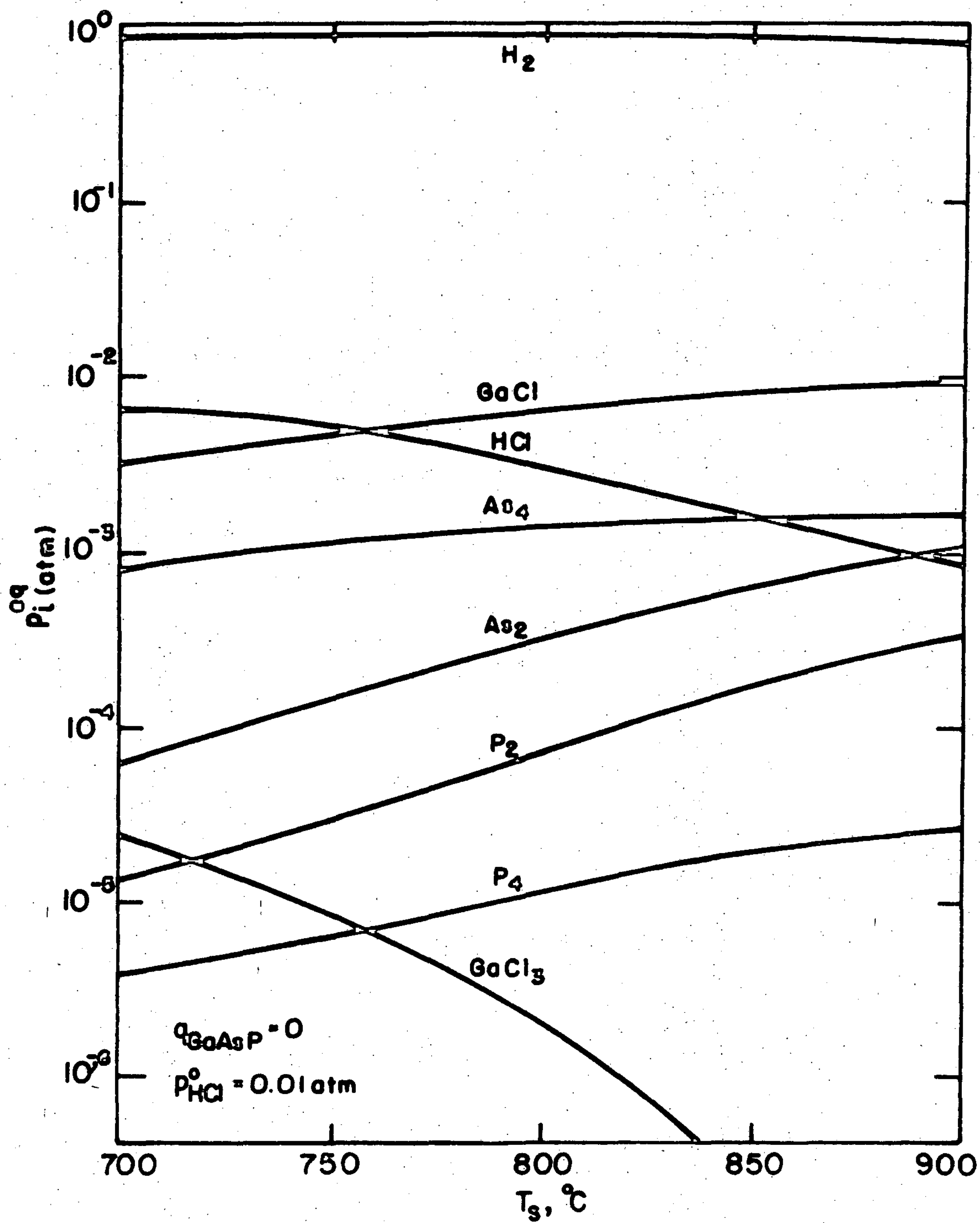


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Fig. 3b

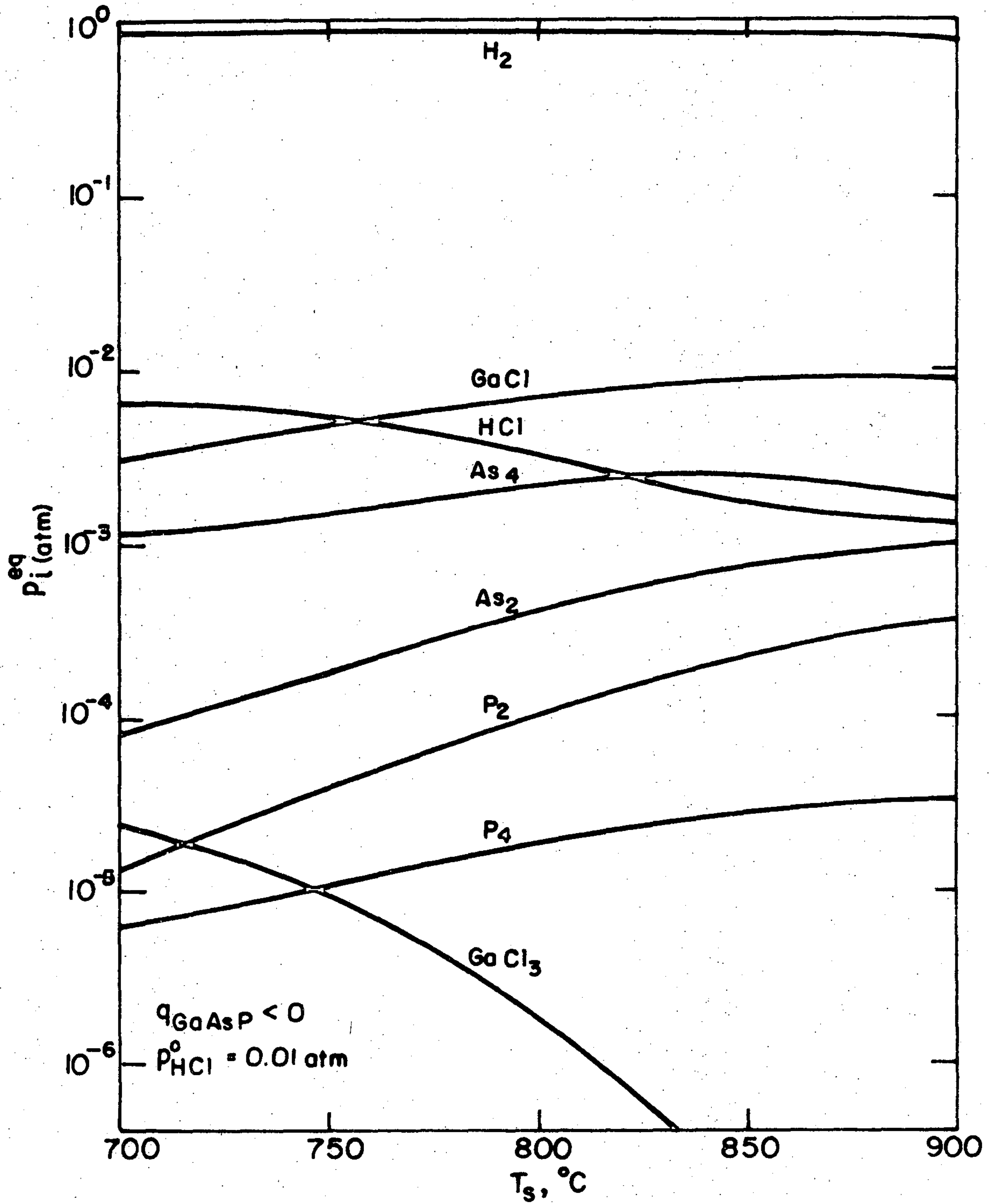

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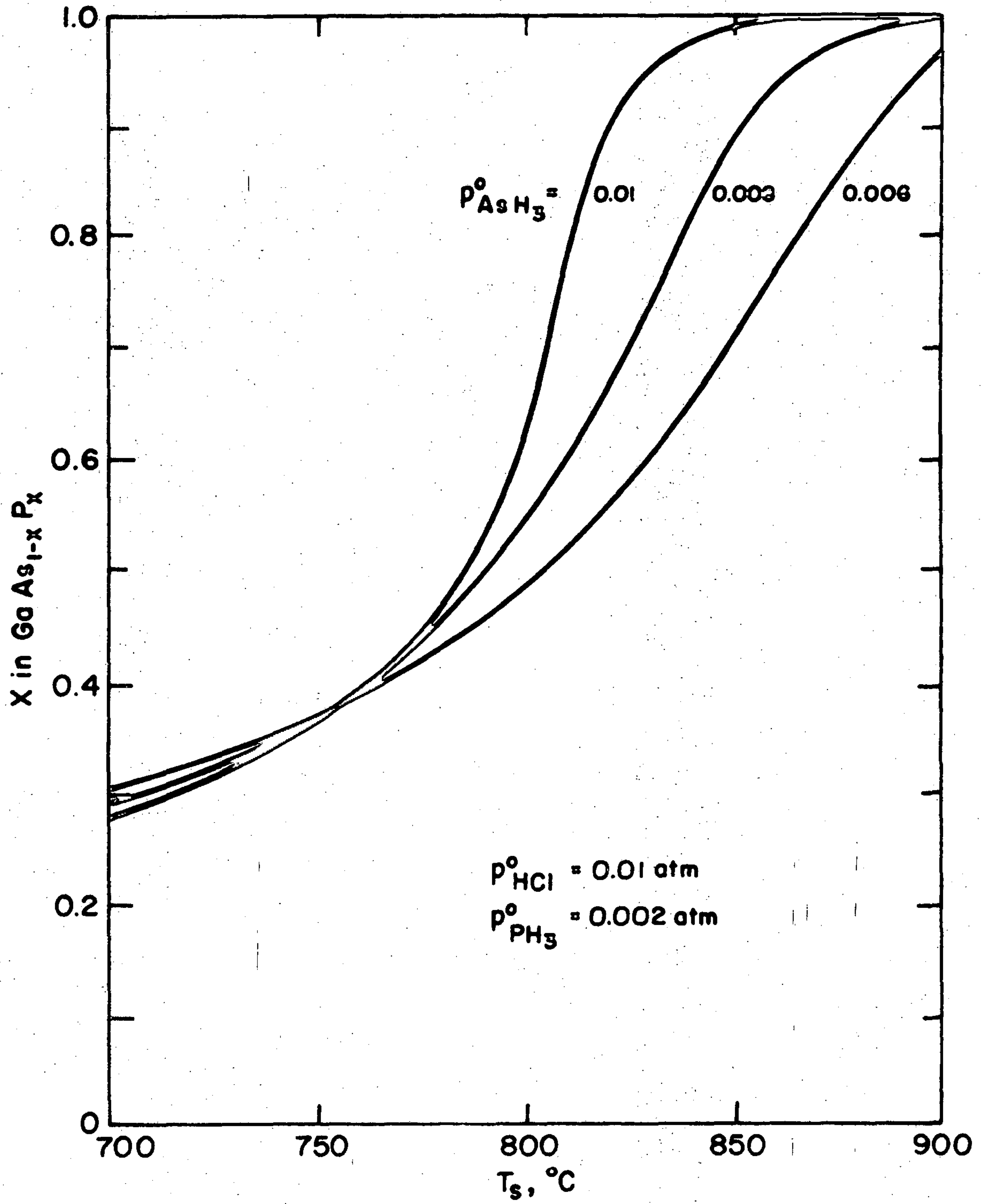
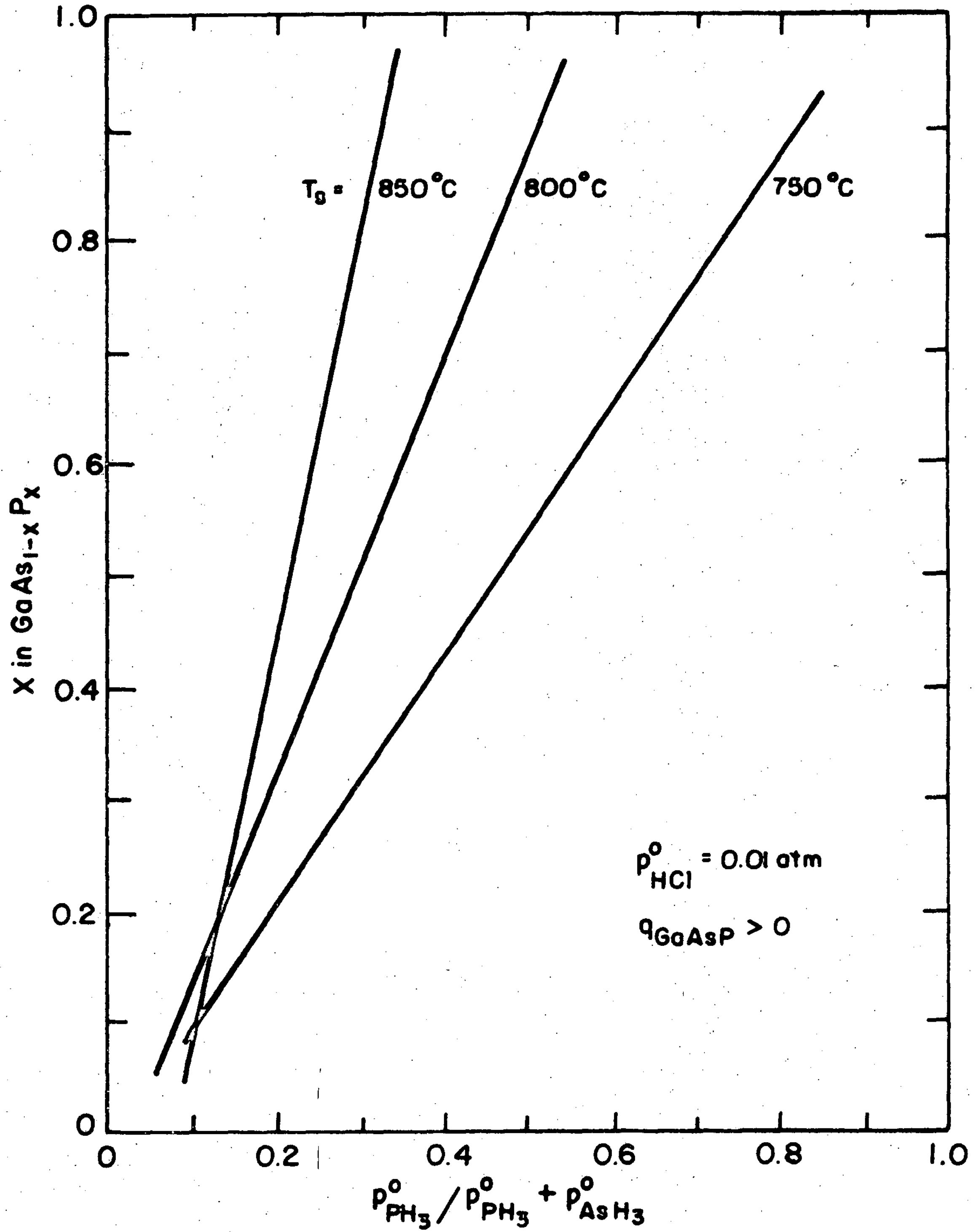
Fig. 3c



XBL 729-6990

Fig. 4



XBL 729-6991

Fig. 5a

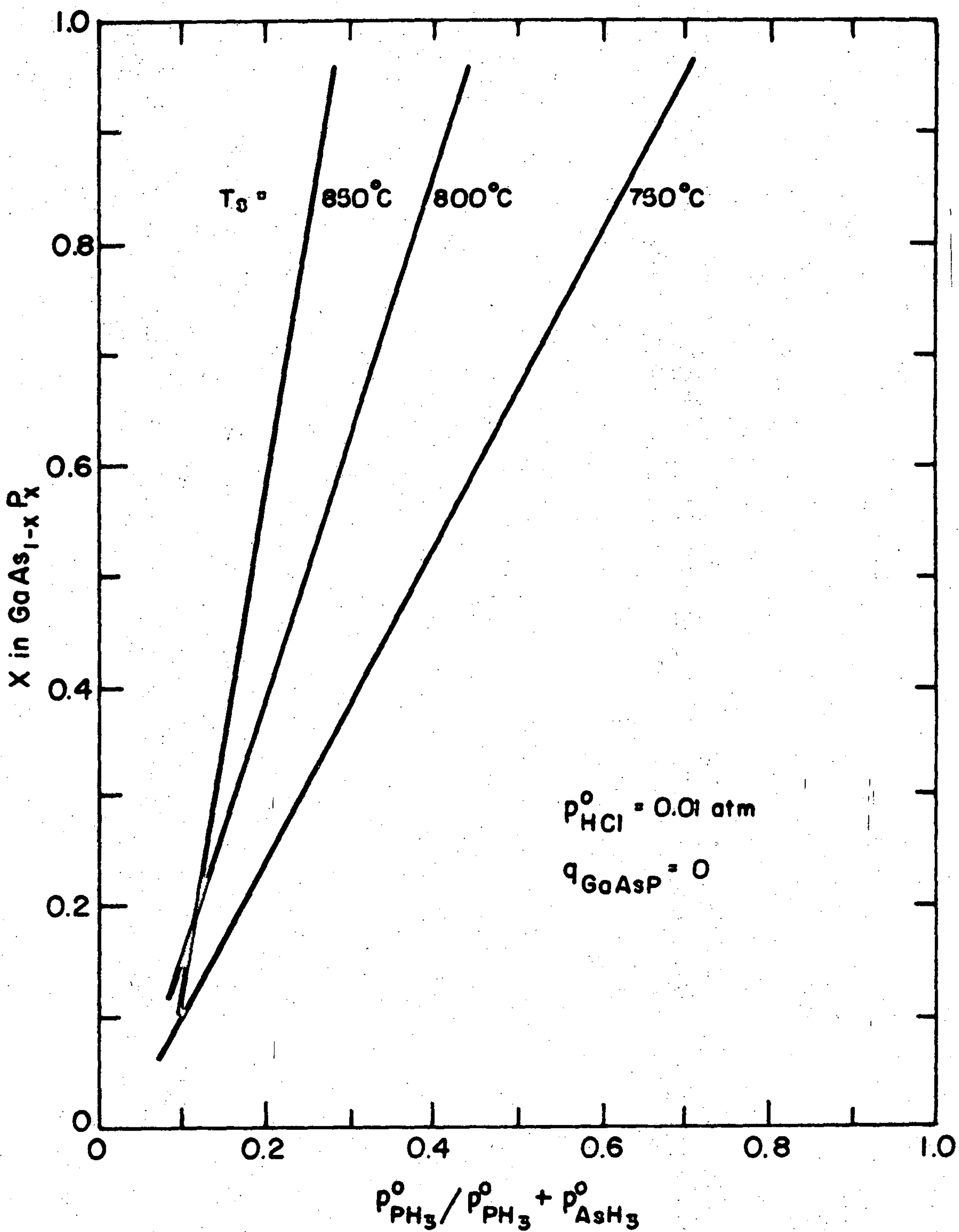


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Fig. 5b

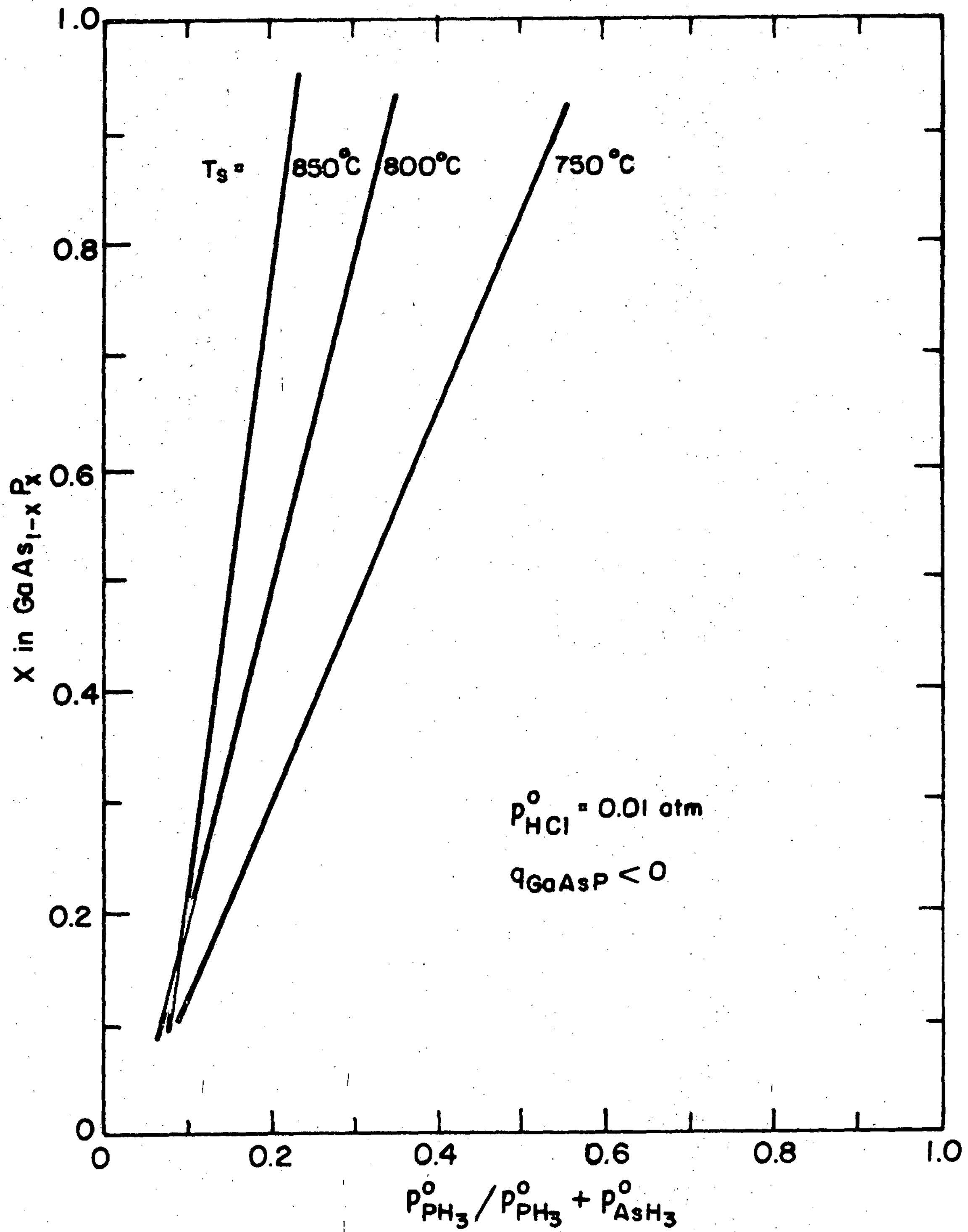

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Fig. 5c

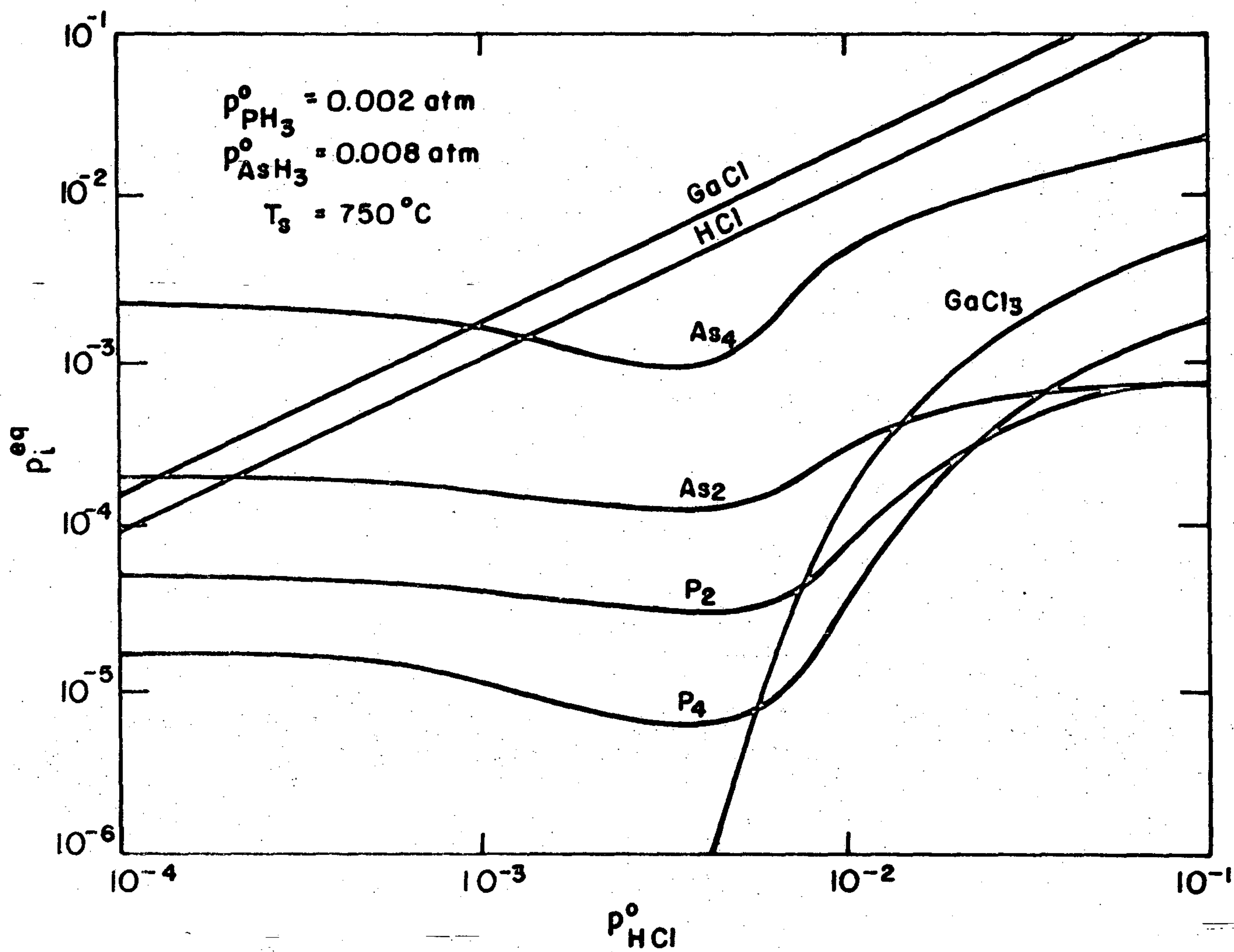

Fig. 6 a

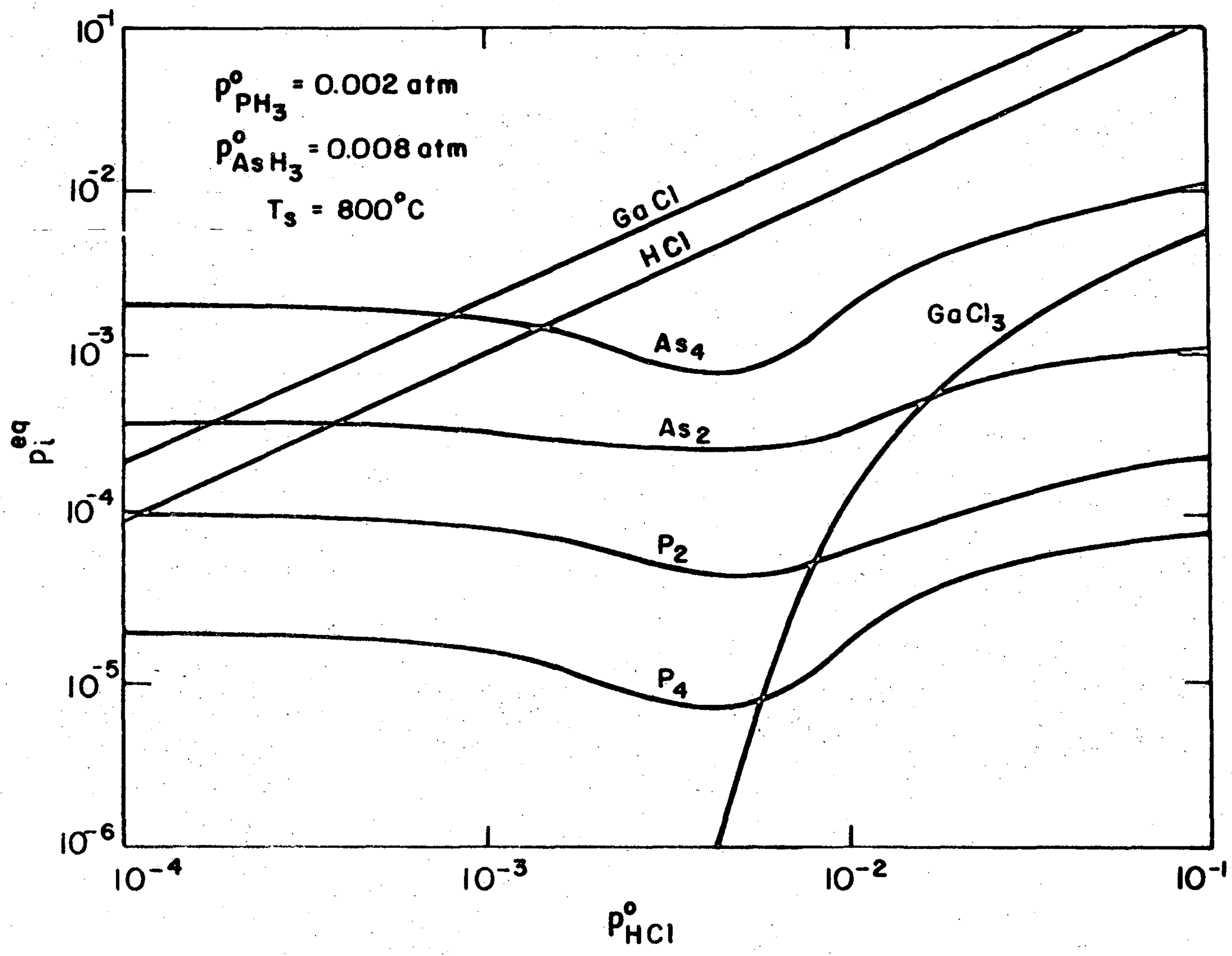

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Fig. 6b

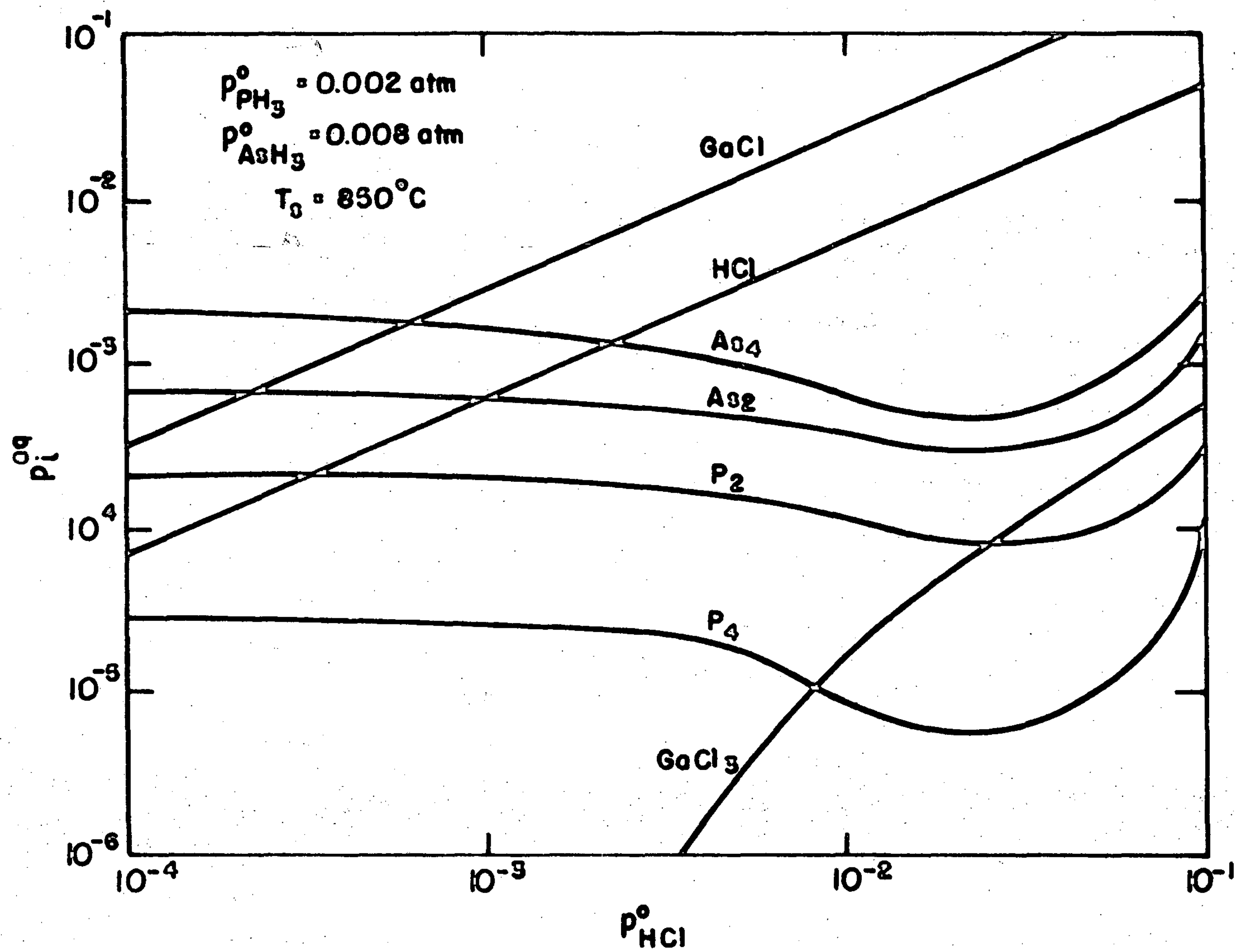

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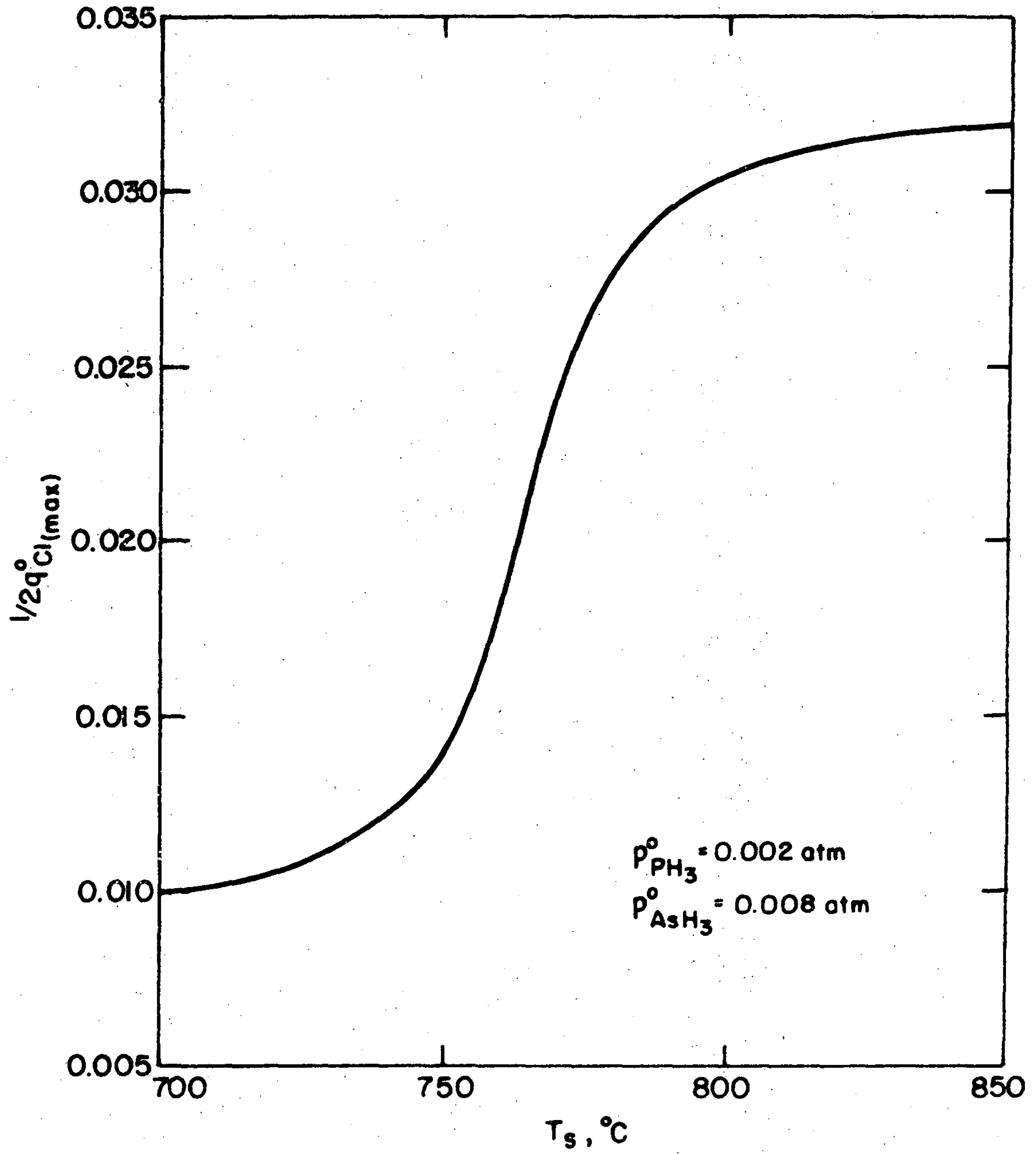
Fig. 6c



XBL 729-6997

Fig. 7

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