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Growth of InP Based Films Using the  
Hydride Growth Technique

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## ABSTRACT

A hydride growth system has been constructed that is capable of growing InGaAsP films or any ternary or binary combination. The system was designed to keep the background carrier density to a minimum as there are a number of device applications for low carrier concentration films. This was done by building a system that is leak tight down to  $10^{-6}$ - $\text{cm}^{-3}$  and constructing a forechamber from which the substrate can be magnetically loaded through a gate valve. Therefore, the growth zone is never opened to the atmosphere during a growth run.

Thus far only InP films have been grown, but we plan to soon grow InGaAs films. The first films that were grown contained many hillocks, but their density was reduced in the later films by reducing the input HCl concentration. The HCl concentration in the deposition zone was increased by introducing HCl downstream from the liquid indium. This was done to try to reduce the silicon contamination. However, we found that this greatly reduced the growth rate, and in some instances the substrate was actually etched. This also occurred when the input HCl was not forced to come into intimate contact with the liquid indium. We, therefore, concluded that there was too much HCl in the deposition zone which impeded the deposition process.

Theoretical thermodynamic calculations were made on the effects of varying the deposition temperature, input HCl and  $\text{PH}_3$  partial pressures, and downstream HCl partial pressure, as well as the dependence of the

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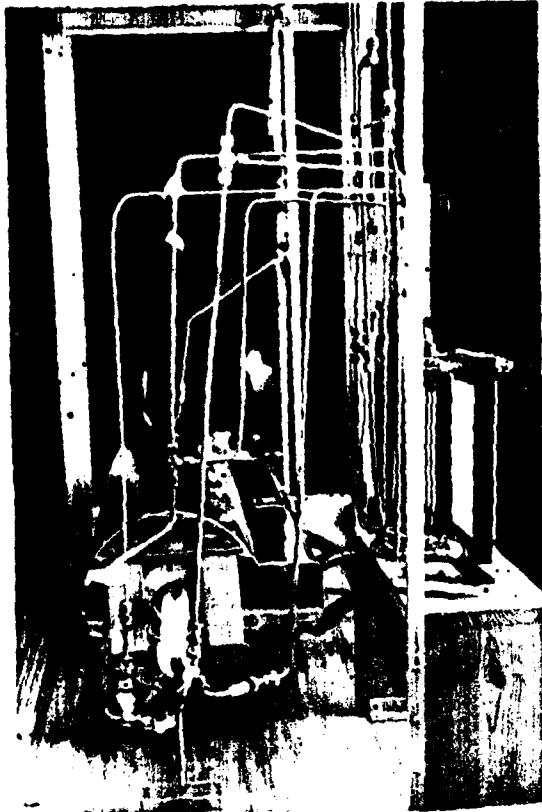
silicon activity on the HCl concentration and temperature. It was found that the most effective way to increase the deposition zone HCl concentration is to increase the input partial pressure since the HCl-In reaction is 99% efficient over a large range of temperatures and pressures. Increasing the deposition zone HCl concentration by introducing HCl downstream is not an effective method due to the fact that this impedes the deposition process. Increasing the  $\text{PH}_3$  concentration is not as effective since it does not have as large an effect on the free energy change of the deposition reaction as does the HCl concentration. It is also shown that the silicon activity can be substantially reduced by increasing the deposition zone HCl concentration and lowering the deposition temperature.

## I. GROWTH SYSTEM

### A. Initial Design

The first step in this project was to design and build a hydride growth system. Photographs of the system, which is a hybrid of the systems designed by Olsen<sup>(1)</sup> and by Johnston and Strege,<sup>(2)</sup> are shown in Figure 1 and a schematic of the system is shown in Figure 2. The toxic gases are contained in a vented enclosure, and the gases flow from the tanks through two stage regulators and one quarter or one eighth inch stainless steel tubing to rotameters where their calibrated flow rate is controlled by a needle valve. Rotameters were used both because they are much cheaper than mass flow controllers, and they do not need to be recalibrated constantly. The shut off valves used are Nupro bellows seal valves and the hydrogen gas used is purified using a Matheson hydrogen purifier.

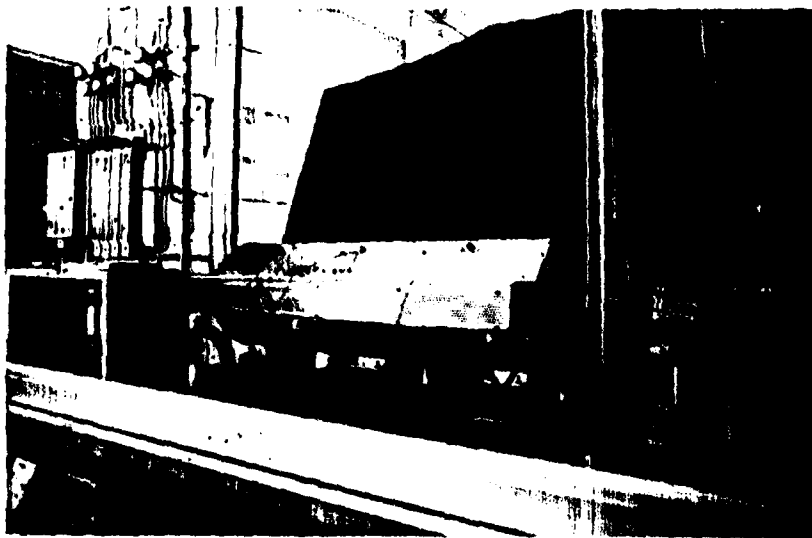
The growth chamber shown in Figure 3 contains five zones - the forechamber, the predeposition, deposition, mixing, and source zones. A forechamber is used so that the substrate can be injected into the growth zone without fear of introducing outside contaminants. It is connected to the growth zone by a gate valve. The specimen is placed on the holder, the forechamber is closed, the gate valve is closed, the forechamber is evacuated, and then it is backfilled with hydrogen. After the furnace has reached the steady state profile, the specimen is moved into the predeposition position where it is bathed in  $\text{PH}_3$ . It is next placed in the growth position, and then it is retracted into the forechamber after the deposition process has been completed where it is allowed to cool.



(a)



(c)



(b)

Fig. 1. Photographs of the growth system (a) end view of the furnace, (b) side view of the furnace, and (c) vented enclosure containing some of the gases.

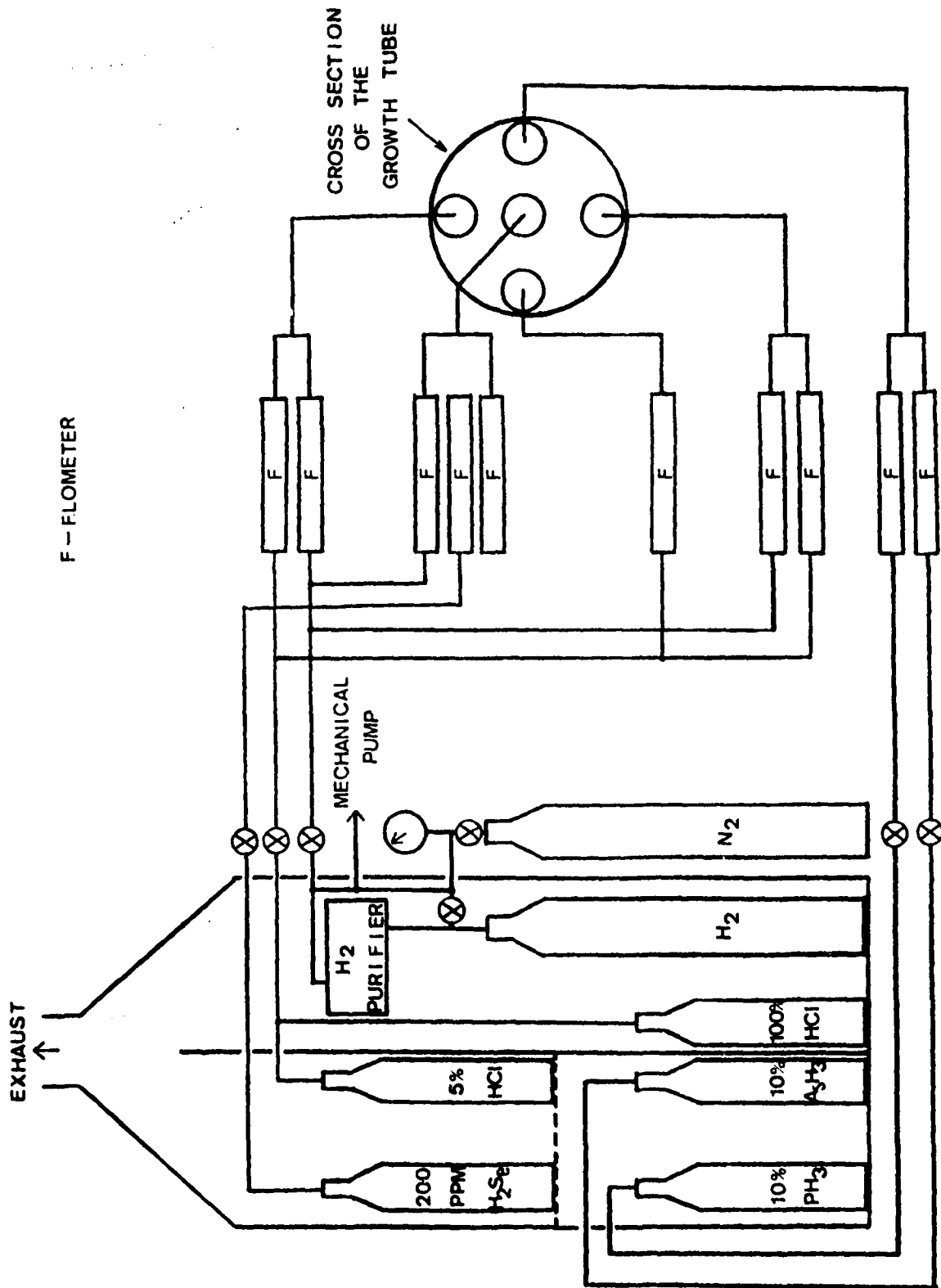


Fig. 2. Schematic diagram of the gas handling system.

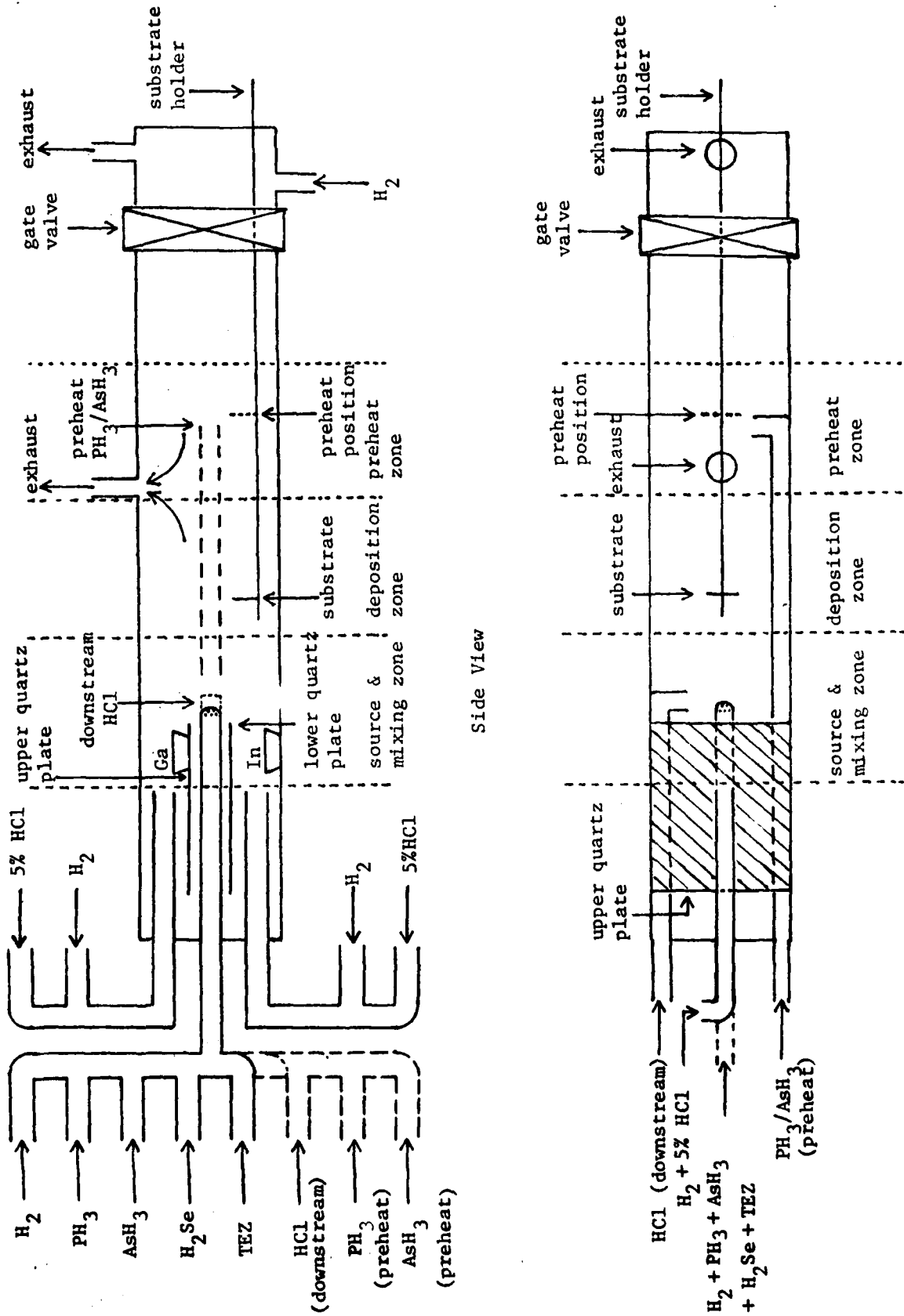


Fig. 3. A schematic of the growth tube.

The growth tube was designed for the growth of the quaternary, InGaAsP, and any ternary or binary combinations thereof. The cation compartments are separated so there is no mixing in the vicinity of the metal containing boats. The anion hydrides are injected downstream through a closed tube containing many small holes to facilitate the mixing process. Additionally, the system is designed so that HCl can be injected downstream in addition to flowing over the metal melts. The downstream HCl can be used to etch the substrate prior to deposition as well as impede the deposition on the walls of the growth tube. The boats are designed so that the HCl comes in intimate contact with the liquid metals to insure that the metal chloride reaction is driven to completion.

The gases in the cylinders in the vented enclosure shown in Figure 2 are 10%  $\text{PH}_3$  in  $\text{H}_2$ , 10%  $\text{AsH}_3$  in  $\text{H}_2$ , 200 ppm  $\text{H}_2\text{Se}$  in  $\text{H}_2$ , and 100% HCl (used to clean the system). The liquid diethyl zinc (DEZ) through which hydrogen is bubbled and the 5% HCl in  $\text{H}_2$  used in the growth process are contained in cylinders inside of the growth vented enclosure. The exhaust gases are bubbled through silicone oil, burned, and then exhausted to the roof.

#### B. Design Changes

It has been found that it is difficult to completely retract the specimen into the forechamber because material is deposited from the vapor on to the push rod. Further, there is some concern about a small amount of leakage through the ultratorr fitting when it is loosened in order to move the push rod. Also, the pushrod might have impurities such as water adsorbed onto the rod. Therefore, the forechamber has been increased in size to make retraction of the push rod easier and

a magnetic loader has been built to eliminate the problem associated with the ultratorr fitting. A schematic of this loader is shown in Figure 4.

We also found that the exhaust tube would become clogged with precipitates from the vapor. Therefore, a mercury manometer was attached to the growth zone to monitor any pressure build ups, and the exhaust tube was moved to the cooler end beyond the region where most of the wall deposition occurred.

There is some concern that the purity of the HCl gas is not as pure as the  $\text{PCl}_3$  vapor used in the chloride process.<sup>(3-5)</sup> In order to eliminate this variable, we are in the process of constructing a  $\text{PCl}_3$  cracking furnace, which is shown in Figure 5. The  $\text{PCl}_3$  is heated in hydrogen to such a temperature and pressure that the  $\text{PCl}_3$  decomposes into HCl and primarily  $\text{P}_2$  and  $\text{P}_4$  although some  $\text{PH}_3$  will be present. The outlet gas is passed through an ice water cold trap to precipitate out as much of the phosphorous containing compounds as possible.

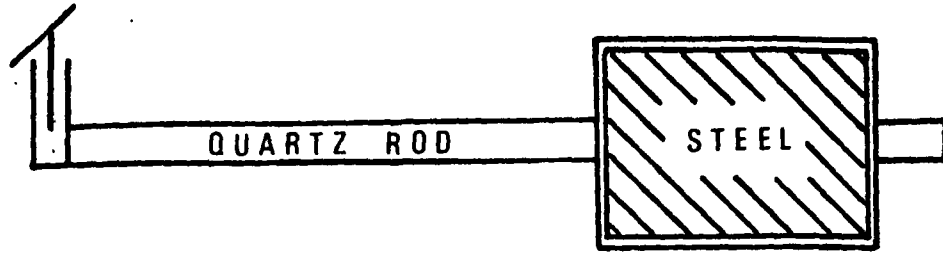
The  $\text{PCl}_3$  can bypass the cracking furnace so that films can be grown using the chloride method. Thus a useful comparison between the hydride and chloride<sup>(6-10)</sup> methods can be made.

The system will also be constructed with an  $\text{AsH}_3$  bubbler so that  $\text{AsH}_3$  can be used instead of  $\text{PH}_3$ .

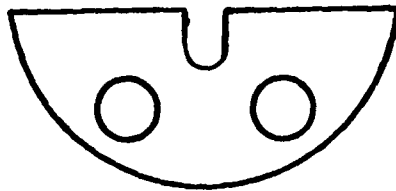
#### C. Film Growth

Homoepitaxial InP films were grown in the following manner. The furnace was turned on and allowed one hour to reach its steady state. The indium boat was in a thermal plateau of  $800^\circ\text{C}$  and the growth position for the substrate was at the end of a  $650^\circ\text{C}$  plateau. The gradient between these two constant temperature regions was about  $6^\circ\text{C}$  per cm.

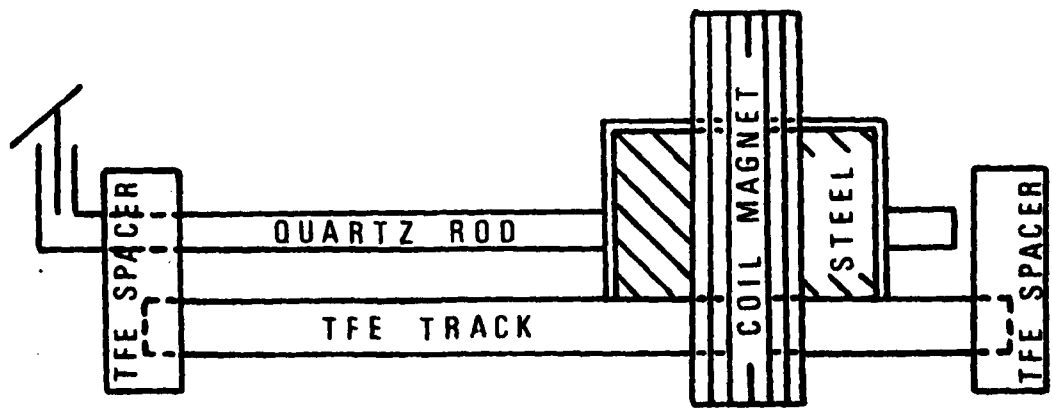
(See Figure 6).



The magnetically driven substrate pushing rod.



The teflon spacer.



The magnetically driven substrate moving system.

Figure 4. Schematic of the magnetic loader.

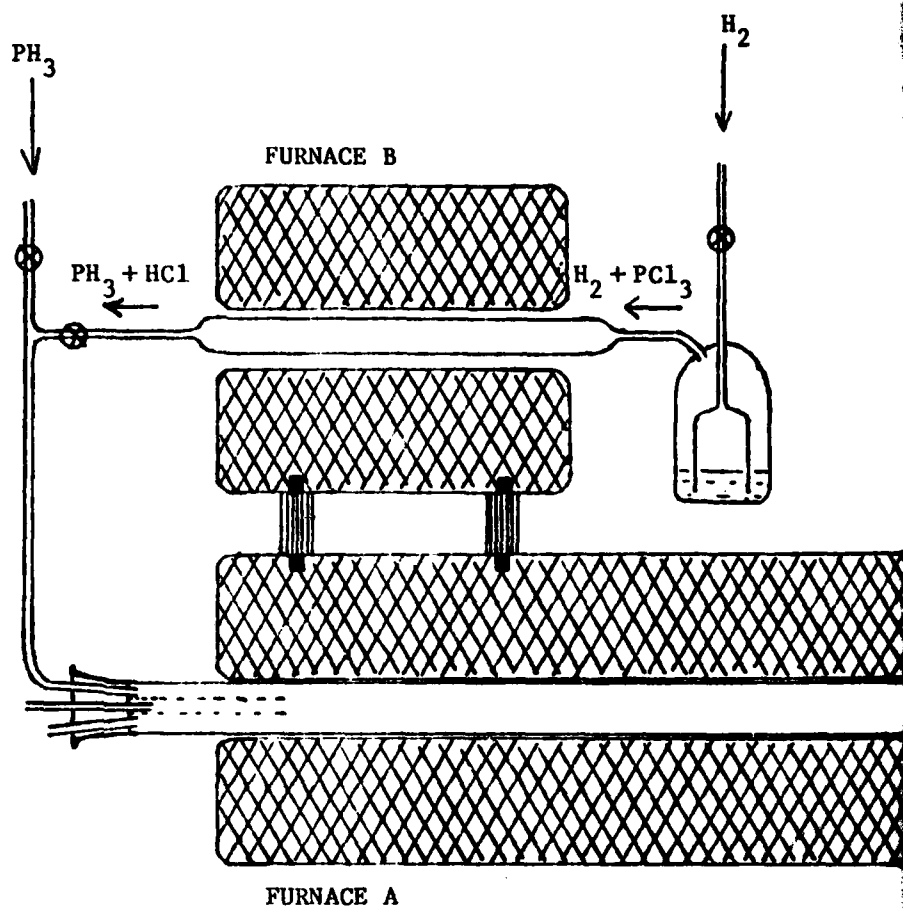
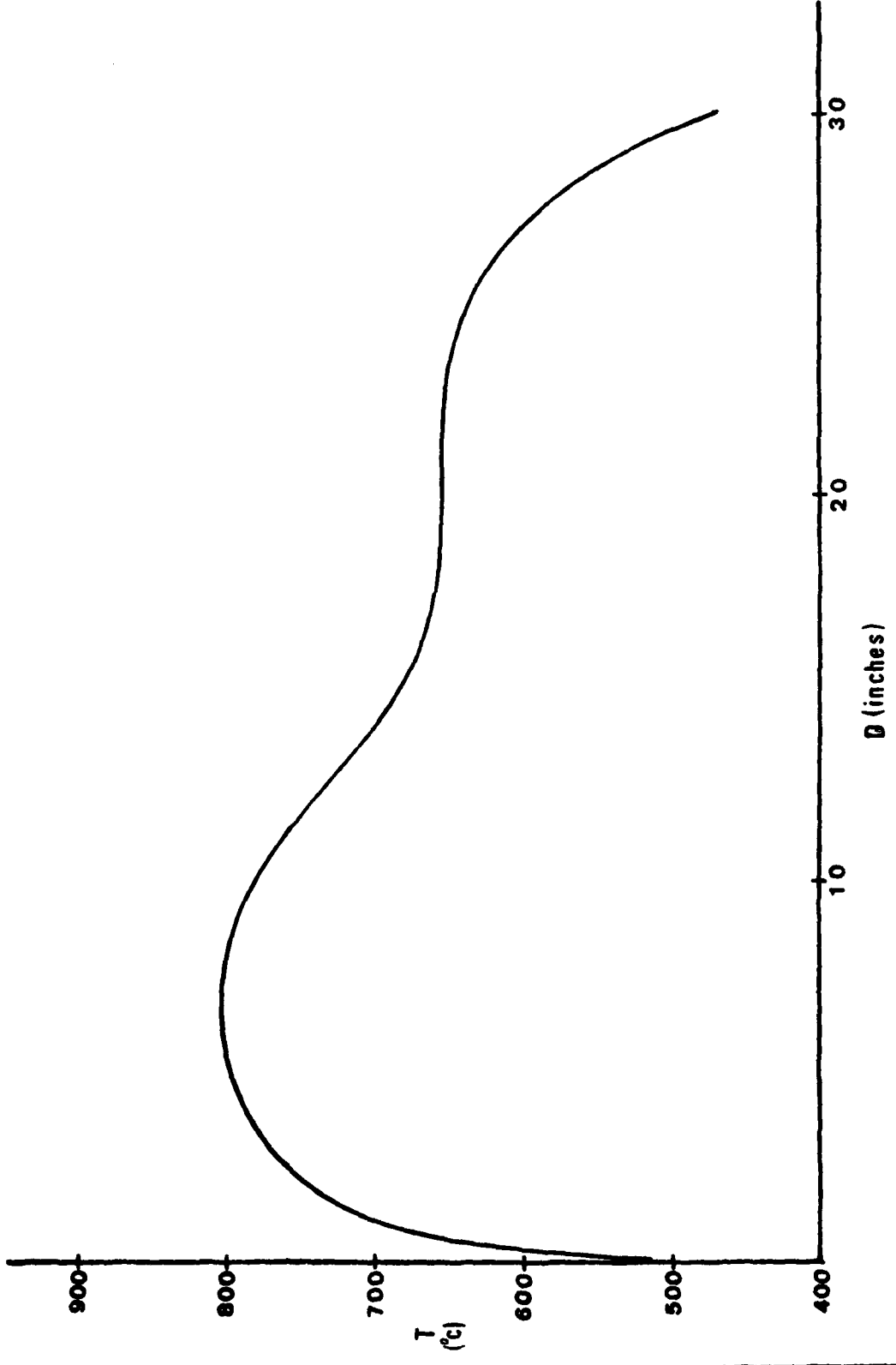


Figure 5. Schematic of the cracking furnace for the anion chlorides.



Before the (001) insulating substrate oriented  $3^\circ$  toward the [110] direction (Crystal Comm) was placed in the substrate holder, it was polished in a manner similar to that described by Clawson et al.<sup>(11)</sup> This included a chemical-mechanical polish in a 1% bromine-methanol solution and a thorough wash in deionized water. Immediately before the substrate was mounted, it was soaked in concentrated KOH solution to remove the surface oxide, and was then rinsed in a 1% Br-Me solution. The substrate was placed in the forechamber, the forechamber was evacuated, and then it was back filled with hydrogen. Next, the gate valve was opened and the substrate was inserted into the predeposition position which was at the same temperature as the growth position -  $650^\circ\text{C}$ . It was held there for ten minutes being bathed in a 10%  $\text{PH}_3$  in  $\text{H}_2$  gas mixture flowing at 50-75 ccm, and then it was placed in the growth position. The predeposition  $\text{PH}_3$  was turned off and the substrate was inserted into the growth position. The flow rate for the 10%  $\text{PH}_3$  in  $\text{H}_2$  was 50-75 ccm, the flow rate for the 5%  $\text{HCl}$  in  $\text{H}_2$  was 100-150 ccm, and there was an additional flow of  $\text{H}_2$  mixed in with the  $\text{HCl}$  gas mixture for a total flow rate of 500 ccm. These flow rates translate into the input partial pressures,  $P_{\text{HCl}}^0 = 10^{-2} - 1.5 \times 10^{-2}$  atm. and  $P_{\text{PH}_3}^0 = 10^{-2} - 1.5 \times 10^{-2}$  atm., which are similar to those used by Zinkiewicz et al.<sup>(2)</sup> The source and deposition temperatures are also similar. The film was deposited for a period of 30 minutes and then it was retracted to a position near the gate valve. It could not be retracted all the way into the forechamber because the substrate rod became coated with materials from the gas phase.

The primary focus was to examine how the input  $\text{HCl}$ ,  $\text{HCl}^0$ , and input,  $\text{PH}_3$ ,  $\text{PH}_3^0$ , flow rates affect the morphology. Our goal was to find the maximum

$\text{HCl}^{\circ}/\text{PH}_3^{\circ}$  ratio for which a smooth film could be grown. We want to maximize this ratio because Zinkiewicz et al.<sup>(12)</sup> found that this minimizes the degree of compensation. Our preliminary results support this finding.

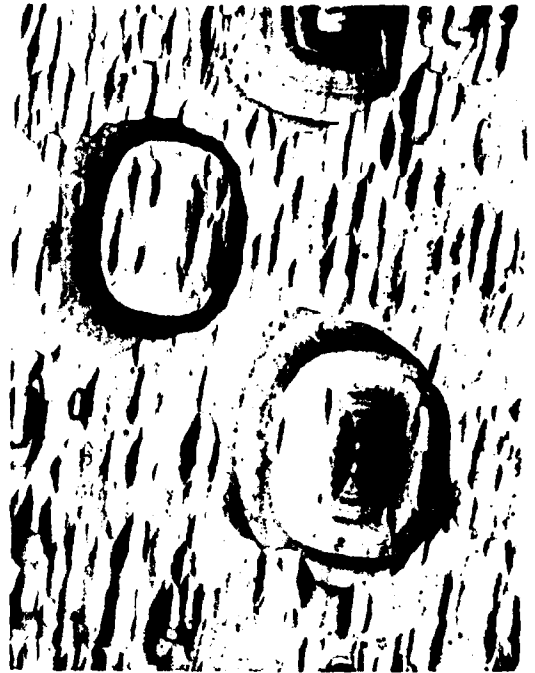
The photograph of the morphology shown in figure 7a is typical of a film grown with an  $\text{HCl}^{\circ}$  partial pressure of  $1.5 \times 10^{-2}$  atm. and a  $\text{PH}_3^{\circ}$  partial pressure of  $1.0 \times 10^{-2}$  atm. There it is seen that there are hillocks on top of the hillocks. The photograph in figure 1b is a typical morphology when equal partial pressures of  $1.5 \times 10^{-2}$  atm. were employed. The facets are more distinct and the surface is smoother, but it is still unacceptably rough. The morphology in figure 1c is for equal partial pressures of  $1.0 \times 10^{-2}$  atm. The hillocks are still present but their density is much reduced. These preliminary results suggest that the morphology depends on the magnitudes of the two partial pressures as well as their ratios.<sup>(12,13)</sup> At these partial pressures the total  $\text{H}_2$  flow rate no doubt also affects the morphology. We will examine this effect in a later report.

A possible explanation of these observations is that hillocks form by growth around indium droplets which form when the indium is not given sufficient time to diffuse to its equilibrium position.<sup>(4)</sup> Thus, the morphology of the film grown with the  $\text{HCl}^{\circ}$  and  $\text{PH}_3^{\circ}$  pressures of .01 atm. is better than that grown with the  $\text{HCl}^{\circ}$  and  $\text{PH}_3^{\circ}$  pressures of .015 atm. because the rate of arrival of the indium atoms is less. This allows the surface indium atoms more time to diffuse to their equilibrium position before the next 'layer' of indium atoms arrive.

A possible explanation of the observation that there is less compensation in the films containing more hillocks is that more of the excess indium is tied up in the electrically inactive droplets. This assumes, of course, that some of the compensation is due to the excess indium.



7a



7b



7c

Figure 7. Micrographs of the hillocks formed on films for which the  $\text{HCl}^{\circ}$  and  $\text{PH}_3^{\circ}$  partial pressures were a) .01 and .015 atm., b) .015 and .015 atm., and c) .01 and .01 atm.

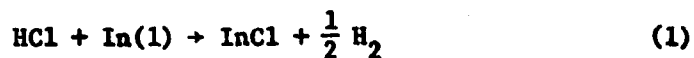
We also attempted to increase the deposition zone HCl concentration by introducing HCl downstream.<sup>(15)</sup> We found that doing this greatly impeded growth, and when the downstream HCl concentration was too high, etching of the substrate occurred. We observed similar behavior when the input HCl was not brought into intimate contact with the liquid indium in the source zone. Our conclusion, therefore, is that an increased deposition zone HCl concentration, whether the HCl comes from unreacted HCl in the source zone or HCl injected downstream, greatly inhibits the deposition process.

## II. THEORETICAL STUDIES

While the furnace was being built and tested, theoretical studies of the growth processes were undertaken to better understand what the important growth parameters are. The studies continued after we had begun to grow films in order to better understand our results. These studies focused on the thermodynamic properties, and they include the concentration of HCl and InCl in the source zone in equilibrium with the liquid indium, the equilibrium concentration of  $\text{PCl}_3$  under normal growth conditions, the effect of varying the deposition temperature, the effect of varying the input HCl and  $\text{PH}_3$  pressures, and the effect of introducing HCl downstream. The silicon activity in the growth zone was also calculated as a function of the equilibrium HCl concentration.

### A. Equilibrium Pressures of HCl and InCl in the Source Zone

In the source zone HCl reacts with the liquid indium according to the equation



The equilibrium constant for the reaction is given by

$$\ln K_1 = \ln \left( \frac{P_{\text{InCl}} P_{\text{H}_2}^{1/2}}{P_{\text{HCl}}} \right) = - \frac{\Delta G_1}{RT} \quad (2)$$

The input HCl pressure is  $\text{HCl}^0$ , so that the equilibrium InCl pressure is

$$P_{\text{InCl}} = \text{HCl}^0 - P_{\text{HCl}} \quad (3)$$

Because the total pressure is 1 atm.

$$P_{\text{H}_2} = 1 - P_{\text{HCl}} - P_{\text{InCl}} = 1 - P_{\text{HCl}^0} \quad (4)$$

Substituting (3) and (4) into (2) yields

$$P_{\text{HCl}} = \frac{P_{\text{HCl}^0} (1 - P_{\text{HCl}^0})^{1/2}}{\exp(-\Delta G_1/RT) + (1 - P_{\text{HCl}^0})^{1/2}} \quad (5)$$

$\Delta G_1$  can be found from the equations

$$\Delta G_1 = \Delta G_0 \frac{T}{T_0} + \Delta H_I - aT \ln T - \frac{1}{2} \Delta b T^2 - \frac{1}{2} \Delta c/T - IT \quad (6)$$

where

$$\Delta H_I = \Delta H_0 - \Delta a T_0 - \frac{1}{2} \Delta b T_0^2 + \Delta c/T_0 \quad (7)$$

and

$$I = \frac{\Delta H_I}{T_0} - \Delta a \ln T_0 - \frac{1}{2} \Delta b T_0 - \frac{1}{2} \Delta c/T_0^2 \quad (8)$$

Using the thermodynamic values listed in Table 1,

$$\Delta G_1 = 4122 + 1.06 T \ln T + .5075 T^2 \times 10^{-3} + 1.19 \times 10^5/T - 20.795T \quad (9)$$

Table 1. The standard enthalpies and entropies and the heat capacity coefficients for the phosphorous and indium compounds involved in the transport process (from Shaw<sup>(16)</sup>).

Specie (gaseous unless designated)	$\Delta H_f^{\circ}$ (kcal $\text{mol}^{-1}$ )	$S_{298}^{\circ}$ (e.u.)	$C_p^{\circ} = a + b T + c T^{-2}$ (e.u.)		
			a	b x $10^3$	c x $10^{-5}$
P <sub>2</sub>	42.68	52.11	8.46	0.41	-0.84
P <sub>4</sub>	30.77	66.89	19.31	0.42	-3.04
PH <sub>3</sub>	5.47	50.24	8.56	6.85	-1.68
PCl <sub>3</sub>	-61.03	74.42	19.54	0.25	-2.15
InCl	-16.7	59.3	8.93	--	-2.09
InCl <sub>3</sub>	-90.0	82.3	18.00	1.70	--
In(l)	0.8	15.53	7.10	--	--
In	57.0	41.51	4.55	1.77	-0.16
InP(s)	-14.6	14.28	12.27	--	-1.14
HCl	-22.06	44.64	6.18	1.34	.35
H <sub>2</sub>	0	31.21	6.58	.65	.12
Cl <sub>2</sub>	0	53.29	8.76	.26	-.65

In Table 2 the HCl, InCl, and H<sub>2</sub> concentrations, as well as the fraction of the input HCl(HCl<sup>0</sup>) converted to InCl (FC) and the molar free energy change, GO, for the reaction (1) are tabulated as a function of source temperature, T<sub>g</sub>, and input HCl pressure. It is clear from this table that >98.7% of the HCl is converted to InCl at all temperatures considered. Thus, from a thermodynamic point of view, as opposed to a kinetic point of view, there is no need for the source temperature to be high. This could be an important point because the silicon activity is greater at higher temperatures.<sup>(17)</sup>

Table 2. The reaction temperature,  $T_s$ , molar free energy change,  $G_0$ , equilibrium HCl, InCl, and  $H_2$  partial pressures, fraction of input HCl converted to InCl,  $^2FC$ , for different input HCl pressures,  $HCl^0$ .

T	$G_0$	$HCl^0$	HCL	INCL	H2	FC
700.	-8412.	.100E-02	.127E-04	.987E-03	.9990	.9873
		.178E-02	.226E-04	.176E-02	.9982	.9873
		.316E-02	.402E-04	.312E-02	.9968	.9873
		.562E-02	.714E-04	.555E-02	.9944	.9873
		.100E-01	.127E-03	.987E-02	.9900	.9873
		.178E-01	.224E-03	.176E-01	.9822	.9874
		.316E-01	.396E-03	.312E-01	.9684	.9875
		.562E-01	.696E-03	.555E-01	.9438	.9876
		.100E+00	.121E-02	.988E-01	.9000	.9875
		750.	-8989.	.100E-02	.119E-04	.988E-03
.178E-02	.211E-04			.176E-02	.9982	.9881
.316E-02	.375E-04			.312E-02	.9968	.9881
.562E-02	.666E-04			.556E-02	.9944	.9882
.100E-01	.118E-03			.988E-02	.9900	.9882
.178E-01	.209E-03			.176E-01	.9822	.9882
.316E-01	.370E-03			.313E-01	.9684	.9883
.562E-01	.649E-03			.556E-01	.9438	.9885
.100E+00	.113E-02			.989E-01	.9000	.9887
800.	-9559.			.100E-02	.112E-04	.989E-03
		.178E-02	.199E-04	.176E-02	.9982	.9888
		.316E-02	.353E-04	.313E-02	.9968	.9888
		.562E-02	.627E-04	.556E-02	.9944	.9889
		.100E-01	.111E-03	.989E-02	.9900	.9889
		.178E-01	.197E-03	.176E-01	.9822	.9889
		.316E-01	.348E-03	.313E-01	.9684	.9890
		.562E-01	.611E-03	.556E-01	.9438	.9891
		.100E+00	.106E-02	.989E-01	.9000	.9894
		850.	-10124.	.100E-02	.106E-04	.989E-03
.178E-02	.188E-04			.176E-02	.9982	.9894
.316E-02	.335E-04			.313E-02	.9968	.9894
.562E-02	.594E-04			.556E-02	.9944	.9894
.100E-01	.105E-03			.989E-02	.9900	.9895
.178E-01	.187E-03			.176E-01	.9822	.9895
.316E-01	.330E-03			.313E-01	.9684	.9896
.562E-01	.579E-03			.557E-01	.9438	.9897
.100E+00	.101E-02			.990E-01	.9000	.9899

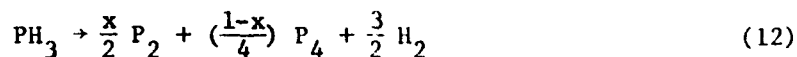
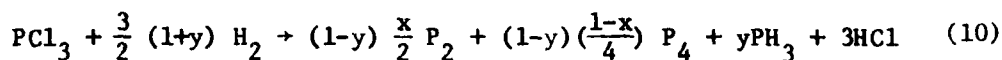
Table 2 - Continued.

900.	-10683.	.100E-02	.171E-04	.890E-03	.9990	.9899
		.178E-02	.180E-04	.176E-02	.9982	.9899
		.316E-02	.319E-04	.313E-02	.9968	.9899
		.562E-02	.567E-04	.557E-02	.9944	.9899
		.100E-01	.101E-03	.990E-02	.9900	.9899
		.178E-01	.178E-03	.176E-01	.9822	.9900
		.316E-01	.315E-03	.313E-01	.9684	.9900
		.562E-01	.553E-03	.557E-01	.9438	.9902
		.100E+00	.960E-03	.990E-01	.9000	.9904
950.	-11238.	.100E-02	.921E-05	.890E-03	.9990	.9903
		.178E-02	.173E-04		.9982	.9903
		.316E-02	.317E-04		.9968	.9903
		.562E-02	.564E-04		.9944	.9903
		.100E-01	.567E-04		.9900	.9903
		.178E-01	.178E-04		.9822	.9903
		.316E-01	.300E-03		.9684	.9903
		.562E-01	.553E-03		.9438	.9906
		.100E+00	.920E-03		.9000	.9903
1000.	-11787.	.100E-02	.938E-05	.890E-03	.9990	.9903
		.178E-02	.168E-04		.9982	.9903
		.316E-02	.290E-04		.9968	.9903
		.562E-02	.526E-04		.9944	.9906
		.100E-01	.934E-04		.9900	.9903
		.178E-01	.160E-03		.9822	.9907
		.316E-01	.292E-03		.9684	.9907
		.562E-01	.513E-03		.9438	.9907
		.100E+00	.890E-03		.9000	.9911

### B. Equilibrium $\text{PCl}_3$ Concentration

In a number of computations such as those by Shaw,<sup>(16)</sup> it is assumed that the primary constituents are  $\text{H}_2$ ,  $\text{InCl}$ ,  $\text{HCl}$ ,  $\text{P}_4$ ,  $\text{P}_2$  and  $\text{PH}_3$ . We wanted to verify that the equilibrium  $\text{PCl}_3$  concentration is substantially less than those of the other gases both because it could affect the calculations for the other gases and we will later want to make a comparison between the hydride and chloride techniques.

For the reactions



one can calculate the free energy change,  $\Delta G$ , and the equilibrium constant,  $K$ , for these reactions using the thermochemical data compiled by Shaw<sup>(16)</sup> and listed in Table 1. First a value of  $P_{\text{P}_4}$  is assumed and is used to compute  $P_{\text{P}_2}$  with the equation

$$P_{\text{P}_2} = P_{\text{P}_4}^{1/2} / K_3 \quad (13)$$

For the conservation of phosphorous

$$P_{\text{PCl}_3^0} - P_{\text{PCl}_3} = 2P_{\text{P}_2} + 4P_{\text{P}_4} + P_{\text{PH}_3} \quad (14a)$$

where  $P_{\text{PCl}_3^0}$  is the input  $\text{PCl}_3$  partial pressure.

Assuming  $P_{\text{PCl}_3}$  is negligible

$$P_{\text{PH}_3} = P_{\text{PCl}_3^0} - 2P_{\text{P}_2} - 4P_{\text{P}_4} \quad (14b)$$

From the conservation of chlorine

$$P_{\text{HCl}} = 3(P_{\text{PCl}_3^0} - P_{\text{PCl}_3}) = 3P_{\text{PCl}_3} \quad (15)$$

and the fact that the total pressure is 1 atm.

$$P_{\text{H}_2} = 1 - P_{\text{P}_2} - P_{\text{P}_4} - P_{\text{HCl}} - P_{\text{PH}_3} \quad (16)$$

Now, knowing that

$$x = \frac{P_{\text{P}_2}}{P_{\text{P}_2} + 2P_{\text{P}_4}} \quad (17)$$

the equilibrium constant

$$K_4 = \frac{P_{\text{P}_2}^{x/2} P_{\text{P}_4}^{1-x/4} P_{\text{H}_2}^{3/2}}{P_{\text{PH}_3}} \quad (18)$$

can be computed and compared with the value of  $K_4$  determined from  $\Delta G_{12}$ .

A new guess is made for the value of  $P_{\text{P}_4}$  and the process is repeated until the two computed values of  $K_4$  are the same. The value of  $y$  is

Eq. (10) is given by

$$y = \frac{P_{\text{PH}_3}}{xP_{\text{P}_2} + (1-x)P_{\text{P}_4} + P_{\text{PH}_3}} \quad (19)$$

and is used to calculate the thermodynamic parameters in the set of equations, 6-8.

Finally,

$$P_{\text{PCl}_3} = \frac{P_{\text{P}_2}^{(1-y)x/2} P_{\text{P}_4}^{(1-y)(1-x)/4} P_{\text{PH}_3}^y P_{\text{HCl}}^3}{K_2 P_{\text{H}_2}^{3/2} (1+y)} \quad (20)$$

As can be seen in Table 3, the assumption that  $P_{\text{PCl}_3}$  is negligible compared to the partial pressures of the other constituents, is a good assumption so that these other partial pressures do not need to be further modified. For  $P_{\text{PCl}_3^0}$  values of  $10^{-3}$  -  $10^{-1}$  atm. and temperature values of 700-1000°C, the equilibrium  $P_{\text{PCl}_3}$  partial pressures range from a maximum of  $6 \times 10^{-8}$  atm. for  $P_{\text{PCl}_3^0} = .1$  atm. and  $T = 700^\circ\text{C}$  to a minimum of  $4 \times 10^{-15}$  for  $P_{\text{PCl}_3^0} = .001$  atm. and  $T = 1000^\circ\text{C}$ . Note further that  $P_{\text{PCl}_3}$  for these temperature and pressure ranges is more sensitive to the pressure changes.

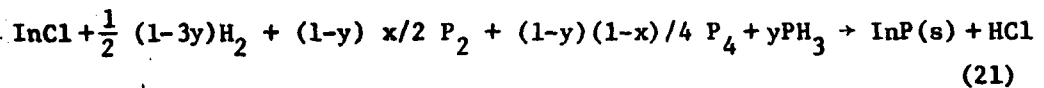
Table 3. The equilibrium  $\text{PCl}_3$ ,  $\text{HCl}$ ,  $\text{PH}_3$ ,  $\text{P}_4$ ,  $\text{P}_2$ , and  $\text{H}_2$  partial pressures for  $\text{PCl}_3$ - $\text{H}_2$  mixtures at different temperatures and with different initial  $\text{PCl}_3$  partial pressures, PCL30.

PCL30	T(°C)	PCL3	HCL	PH3	P4	P2	H2
.100E-02	700.	.846E-14	.300E-02	.164E-03	.162E-03	.944E-04	.9966
	800.	.763E-14	.300E-02	.117E-03	.920E-04	.258E-03	.9965
	900.	.592E-14	.300E-02	.719E-04	.276E-04	.409E-03	.9965
	1000.	.424E-14	.300E-02	.365E-04	.610E-05	.470E-03	.9965
.316E-02	700.	.414E-12	.949E-02	.229E-03	.639E-03	.188E-03	.9895
	800.	.386E-12	.949E-02	.172E-03	.459E-03	.576E-03	.9893
	900.	.323E-12	.949E-02	.118E-03	.205E-03	.111E-02	.9891
	1000.	.241E-12	.949E-02	.753E-04	.566E-04	.143E-02	.9890
.100E-01	700.	.193E-10	.300E-01	.300E-03	.225E-02	.352E-03	.9671
	800.	.185E-10	.300E-01	.233E-03	.186E-02	.116E-02	.9667
	900.	.166E-10	.300E-01	.172E-03	.114E-02	.263E-02	.9661
	1000.	.134E-10	.300E-01	.122E-03	.451E-03	.404E-02	.9654
.316E-01	700.	.941E-09	.949E-01	.359E-03	.749E-02	.643E-03	.8966
	800.	.916E-09	.949E-01	.283E-03	.673E-02	.220E-02	.8959
	900.	.864E-09	.949E-01	.217E-03	.508E-02	.555E-02	.8943
	1000.	.761E-09	.949E-01	.170E-03	.282E-02	.101E-01	.8921
.100E+00	700.	.618E-07	.300E+00	.283E-03	.243E-01	.116E-02	.6742
	800.	.609E-07	.300E+00	.225E-03	.229E-01	.407E-02	.6728
	900.	.594E-07	.300E+00	.175E-03	.195E-01	.109E-01	.6694
	1000.	.560E-07	.300E+00	.135E-03	.138E-01	.223E-01	.6637

C. Effect of Varying  $T_D$ 

In order to calculate the equilibrium constituent partial pressures in the growth zone, one must know the input partial pressures. These include the HCl and InCl pressures from the source zone,  $P_{\text{HCl}}^1$  and  $P_{\text{InCl}}^1$ , the downstream HCl pressure,  $P_{\text{HCl}}^2$ , and the  $\text{PH}_3$  pressure  $P_{\text{PH}_3}^0$ . These species are illustrated in Figure 8.

The deposition reaction is



where  $x$  is given by (17) and  $y$  is

$$y = \frac{P_{\text{PH}_3}}{P_{\text{PH}_3} + xP_{P_2} + (1-x)P_{P_4}} \quad (22)$$

For every mole of InCl consumed, one mole of new HCl must be formed so that

$$P_{\text{InCl}} = P_{\text{InCl}}^1 - (P_{\text{HCl}} - P_{\text{HCl}}^1 - P_{\text{HCl}}^2) = R - P_{\text{HCl}} \quad (23)$$

$P_{\text{PH}_3}$  can be found from (12) where

$$\ln K_{12} = \ln \frac{P_{P_2}^{x/2} P_{P_4}^{(1-x)/4} P_{\text{H}_2}^{3/2}}{P_{\text{PH}_3}} = - \frac{\Delta G_{12}}{RT} \quad (24)$$

The total pressure is 1 atm. so

$$\begin{aligned} P_{\text{H}_2} &= 1 - P_{\text{InCl}} - P_{\text{PH}_3} - P_{P_2} - P_{P_4} - P_{\text{HCl}} \\ &= 1 - P_{\text{InCl}}^1 - 2P_{\text{HCl}}^1 - 2P_{\text{HCl}}^2 - P_{\text{PH}_3}^0 + P_{P_2} + 3P_{P_4} + P_{\text{HCl}} \\ &= S + \text{HCl} \end{aligned} \quad (25)$$

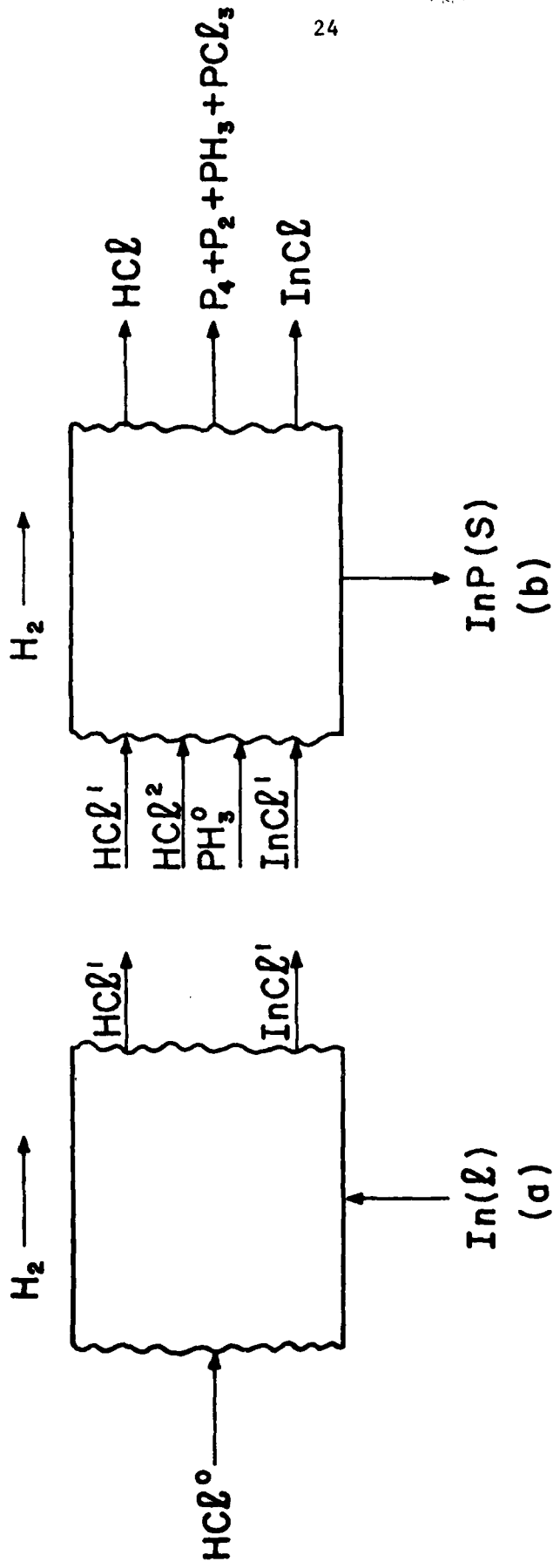


Fig. 8. The nomenclature used to describe the gases flowing into and out of (a) the source zone and (b) the deposition zone.

From (21)

$$\begin{aligned}
 K_{21} &= P_{\text{HCl}} / (P_{\text{InCl}} P_{\text{H}_2}^{(1-3y)/2} P_{\text{P}_2}^{(1-y)x/2} P_{\text{P}_4}^{(1-y)(1-x)/4} P_{\text{PH}_3}^y) \\
 &= P_{\text{HCl}} / \{ (R - P_{\text{HCl}}) (S + P_{\text{HCl}})^{(1-3y)/2} P_{\text{P}_2}^{(1-y)x/2} P_{\text{P}_4}^{(1-y)(1-x)/4} P_{\text{PH}_3}^y \} \\
 &= \exp(-\Delta G_{21}/RT) \quad . \quad (26)
 \end{aligned}$$

After a value of  $P_{\text{P}_4}$  has been assumed,  $P_{\text{P}_2}$  is determined from (13),  $P_{\text{PH}_3}$  is found from (24),  $P_{\text{HCl}}$  is computed from (26) by realizing that  $S \gg P_{\text{HCl}}$ ,  $P_{\text{H}_2}$  is calculated using (25), and  $P_{\text{InCl}}$  is found from (23).  $P_{\text{PH}_3}$  can also be computed from the phosphorous balance. For every mole of InP formed one mole of new HCl is formed and one mole of  $\text{PH}_3$  is consumed. Thus,

$$P_{\text{PH}_3} = P_{\text{PH}_3^0} - 2P_{\text{P}_2} - 4P_{\text{P}_4} - (P_{\text{HCl}} - P_{\text{HCl}^1} - P_{\text{HCl}^2}) \quad . \quad (27)$$

The two values of  $P_{\text{PH}_3}$  are compared, and then a new value of  $P_{\text{P}_4}$  is assumed. This process continues until the two values are equal.

In Tables 4 and Figure 9, the InCl, HCl,  $\text{PH}_3$ ,  $\text{P}_4$ ,  $\text{P}_2$  and  $\text{H}_2$  concentrations in equilibrium with InP are computed as a function of the deposition temperature,  $T_D$ , for a source temperature,  $T_S$ , of 850°C, an initial source HCl pressure (HCL0) of  $10^{-2}$  atm., an initial  $\text{PH}_3$  (PH30) concentration of  $10^{-2}$  atm., and downstream initial HCl pressures (HCL2) of 0 and  $10^{-4}$  atm. There it is seen that the InCl concentration increases, or, conversely, the amount of InP being deposited decreases, as  $T_D$  increases until a temperature is reached where no InP is deposited. For HCL<sup>2</sup> = 0 this temperature is 822°C and for HCL2 =  $10^{-4}$  atm. it is 766°C. As the HCL2 concentration increases, the maximum

Table 4. The equilibrium  $\text{InCl}$ ,  $\text{HCl}$ ,  $\text{PH}_3$ ,  $\text{P}_4$ ,  $\text{P}_2$  and  $\text{H}_2$  partial pressures calculated for different deposition temperatures,  $T_D$ , when  $T_S = 850^\circ\text{C}$ ,  $\text{HCl}^0 = .01 \text{ atm.}$ , and  $\text{HCl}^2 = \text{a.) } 0$ , and  $\text{b.) } 10^{-4} \text{ atm.}$

TS	HCLO	INCL1	HCL1	HCL2	PH30	P/IN
T	INCL	HCL	PH3	P4	P2	H2
850.	.100E-01	.989E-02	.105E-03	0.	.100E-01	1.0107
650.	.905E-02	.952E-03	.347E-03	.212E-02	.162E-03	.9874
654.	.910E-02	.902E-03	.344E-03	.213E-02	.172E-03	.9874
658.	.915E-02	.854E-03	.341E-03	.214E-02	.184E-03	.9873
662.	.919E-02	.809E-03	.338E-03	.214E-02	.196E-03	.9873
666.	.923E-02	.766E-03	.336E-03	.215E-02	.208E-03	.9873
670.	.927E-02	.725E-03	.333E-03	.215E-02	.222E-03	.9873
674.	.931E-02	.687E-03	.330E-03	.215E-02	.236E-03	.9873
678.	.935E-02	.651E-03	.326E-03	.216E-02	.250E-03	.9873
682.	.938E-02	.617E-03	.323E-03	.216E-02	.266E-03	.9873
686.	.941E-02	.585E-03	.320E-03	.216E-02	.282E-03	.9872
690.	.945E-02	.555E-03	.318E-03	.216E-02	.299E-03	.9872
694.	.947E-02	.526E-03	.315E-03	.216E-02	.317E-03	.9872
698.	.950E-02	.499E-03	.312E-03	.216E-02	.335E-03	.9872
702.	.953E-02	.474E-03	.309E-03	.215E-02	.354E-03	.9872
706.	.955E-02	.449E-03	.307E-03	.215E-02	.375E-03	.9872
710.	.957E-02	.427E-03	.303E-03	.215E-02	.396E-03	.9872
714.	.959E-02	.405E-03	.300E-03	.214E-02	.418E-03	.9871
718.	.962E-02	.385E-03	.298E-03	.214E-02	.441E-03	.9871
722.	.963E-02	.365E-03	.295E-03	.213E-02	.465E-03	.9871
726.	.965E-02	.347E-03	.292E-03	.212E-02	.490E-03	.9871
730.	.967E-02	.330E-03	.290E-03	.211E-02	.516E-03	.9871
734.	.969E-02	.314E-03	.287E-03	.210E-02	.543E-03	.9871
738.	.970E-02	.298E-03	.285E-03	.209E-02	.571E-03	.9870
742.	.972E-02	.283E-03	.282E-03	.208E-02	.600E-03	.9870
746.	.973E-02	.270E-03	.279E-03	.207E-02	.631E-03	.9870
750.	.974E-02	.257E-03	.276E-03	.206E-02	.662E-03	.9870
754.	.976E-02	.244E-03	.274E-03	.205E-02	.695E-03	.9870
758.	.977E-02	.232E-03	.272E-03	.204E-02	.729E-03	.9870
762.	.978E-02	.221E-03	.269E-03	.202E-02	.764E-03	.9869
766.	.979E-02	.211E-03	.266E-03	.201E-02	.800E-03	.9869
770.	.980E-02	.201E-03	.264E-03	.199E-02	.837E-03	.9869
774.	.981E-02	.191E-03	.261E-03	.198E-02	.876E-03	.9869
778.	.982E-02	.182E-03	.258E-03	.196E-02	.915E-03	.9869
782.	.983E-02	.174E-03	.256E-03	.194E-02	.956E-03	.9868
786.	.983E-02	.166E-03	.253E-03	.192E-02	.999E-03	.9868
790.	.984E-02	.158E-03	.251E-03	.190E-02	.104E-02	.9868
794.	.985E-02	.151E-03	.248E-03	.188E-02	.109E-02	.9868
798.	.986E-02	.144E-03	.246E-03	.186E-02	.113E-02	.9868
802.	.986E-02	.137E-03	.243E-03	.184E-02	.118E-02	.9867
806.	.987E-02	.131E-03	.240E-03	.182E-02	.123E-02	.9867
810.	.988E-02	.125E-03	.238E-03	.180E-02	.128E-02	.9867
814.	.988E-02	.119E-03	.236E-03	.177E-02	.133E-02	.9867
818.	.989E-02	.114E-03	.234E-03	.175E-02	.138E-02	.9866
822.	.989E-02	.109E-03	.232E-03	.172E-02	.143E-02	.9866

(a)

TS	HCL0	INCL1	HCL1	HCL2	PH30	P/IN
850.	.100E-01	.989E-02	.105E-03	.100E-03	.100E-01	1.0107
T	INCL	HCL	PH3	P4	P2	H2
650.	.914E-02	.964E-03	.348E-03	.214E-02	.162E-03	.9872
654.	.919E-02	.913E-03	.345E-03	.215E-02	.173E-03	.9872
658.	.924E-02	.864E-03	.342E-03	.216E-02	.185E-03	.9872
662.	.928E-02	.818E-03	.339E-03	.216E-02	.197E-03	.9872
666.	.932E-02	.775E-03	.336E-03	.217E-02	.210E-03	.9872
670.	.937E-02	.734E-03	.333E-03	.217E-02	.223E-03	.9872
674.	.940E-02	.696E-03	.330E-03	.218E-02	.237E-03	.9872
678.	.944E-02	.659E-03	.328E-03	.218E-02	.252E-03	.9871
682.	.948E-02	.625E-03	.324E-03	.218E-02	.267E-03	.9871
686.	.951E-02	.593E-03	.321E-03	.218E-02	.283E-03	.9871
690.	.954E-02	.562E-03	.319E-03	.218E-02	.300E-03	.9871
694.	.957E-02	.533E-03	.315E-03	.218E-02	.318E-03	.9871
698.	.959E-02	.505E-03	.312E-03	.218E-02	.337E-03	.9871
702.	.962E-02	.479E-03	.310E-03	.218E-02	.356E-03	.9871
706.	.964E-02	.455E-03	.307E-03	.217E-02	.377E-03	.9870
710.	.967E-02	.432E-03	.305E-03	.217E-02	.398E-03	.9870
714.	.969E-02	.410E-03	.301E-03	.216E-02	.420E-03	.9870
718.	.971E-02	.389E-03	.298E-03	.216E-02	.443E-03	.9870
722.	.973E-02	.370E-03	.296E-03	.215E-02	.467E-03	.9870
726.	.975E-02	.352E-03	.293E-03	.214E-02	.493E-03	.9870
730.	.977E-02	.334E-03	.291E-03	.214E-02	.519E-03	.9870
734.	.978E-02	.318E-03	.288E-03	.213E-02	.546E-03	.9869
738.	.980E-02	.302E-03	.285E-03	.212E-02	.574E-03	.9869
742.	.981E-02	.287E-03	.282E-03	.211E-02	.604E-03	.9869
746.	.983E-02	.273E-03	.280E-03	.210E-02	.634E-03	.9869
750.	.984E-02	.260E-03	.277E-03	.208E-02	.666E-03	.9869
754.	.985E-02	.247E-03	.275E-03	.207E-02	.699E-03	.9869
758.	.986E-02	.235E-03	.272E-03	.206E-02	.733E-03	.9868
762.	.988E-02	.224E-03	.270E-03	.204E-02	.768E-03	.9868
766.	.989E-02	.213E-03	.267E-03	.203E-02	.804E-03	.9868

(b)

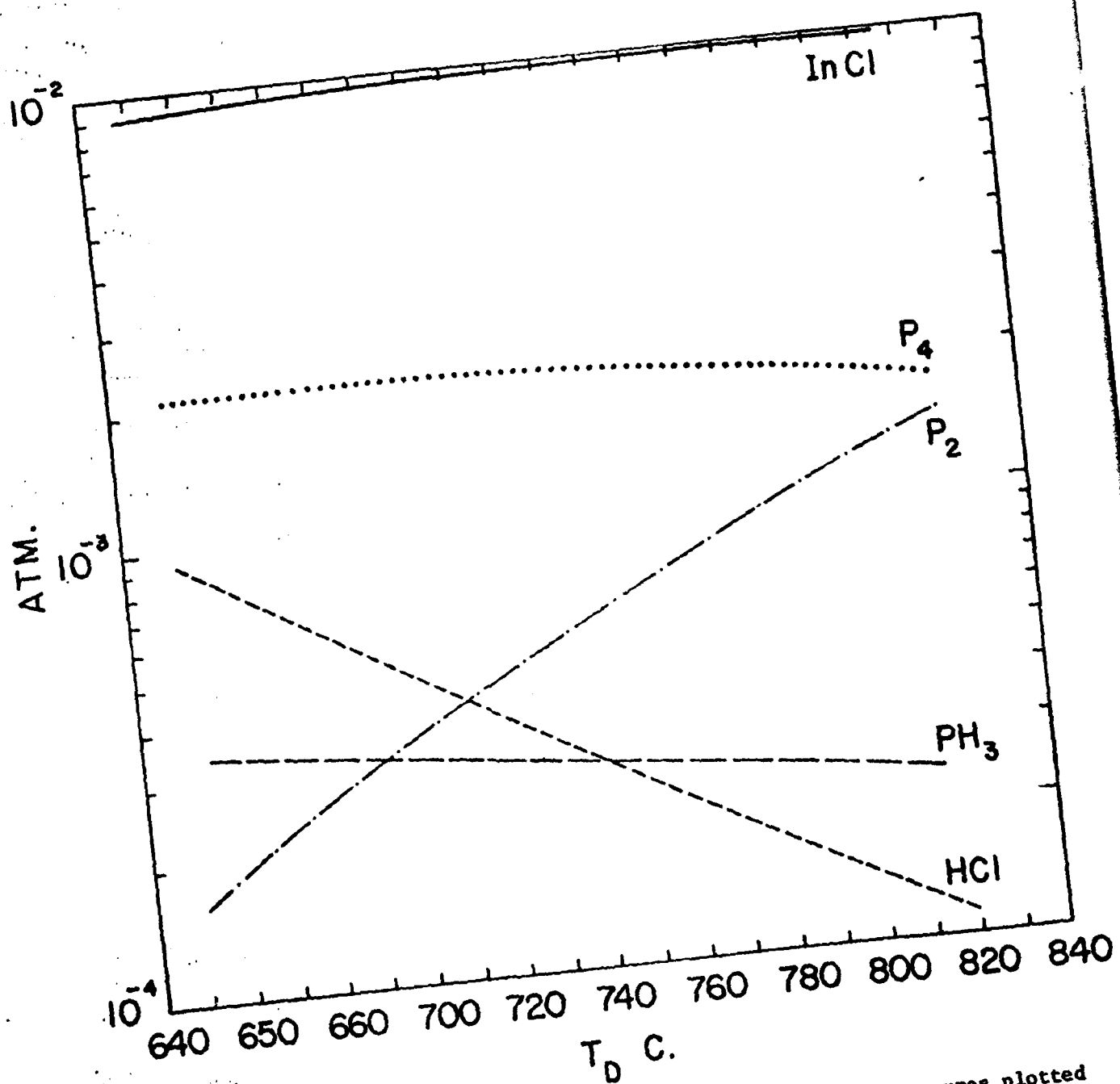


Fig. 9. The InCl, HCl, PH<sub>3</sub>, P<sub>4</sub>, and P<sub>2</sub> equilibrium partial pressures plotted as a function of the deposition temperature,  $T_D$ , when  $T_S = 850^\circ\text{C}$ ,  $\text{HCl}^0 = .01 \text{ atm.}$ ,  $\text{HCl}^2 = 0$ , and  $\text{PH}_3^0 = .01 \text{ atm.}$

deposition temperature decreases due to the fact that HCl is generated by the InP deposition process (Eq. (21)). Clearly, if the HCl2 concentration is too high at a given deposition temperature, the InP will evaporate instead of deposit.

The other trends with increasing deposition temperature are  $P_{\text{HCl}}$  decreases,  $P_{\text{P}_2}$  increases, and  $P_{\text{P}_4}$  and  $P_{\text{PH}_3}$  do not change much.  $P_{\text{HCl}}$  decreases due to the fact that there is less InP deposition. Because there is less InP deposited, there is more phosphorous in the vapor phase, and most of the extra phosphorous is taken up by  $\text{P}_2$  since  $\text{P}_4$  and  $\text{PH}_3$  have a greater tendency to dissociate as the temperature is increased.

The fraction of the indium that is deposited under equilibrium conditions,  $f_{\text{In}}$ , is determined rather than the equilibrium growth rate because more insight into the thermodynamics can be obtained. For example, the growth rate does not distinguish between changes produced by altering the flow rates and those produced by altering the free energy. Also, the deposition rate can be obtained from  $f_{\text{In}}$  by multiplying it by the number of atoms per unit volume in the gas phase, the input HCl input pressure and flow rate, and the fraction ( $\sim 0.99$ ) of the  $\text{HCl}^0$  converted to InCl in the source zone,  $\text{InCl}^1$ , and dividing the product by the number of atoms of indium per unit volume in InP. The equation for  $f_{\text{In}}$  is simply

$$f_{\text{In}} = \frac{P_{\text{InCl}}^1 - P_{\text{InCl}}}{P_{\text{InCl}}^1} \quad (28)$$

where  $P_{\text{InCl}}$  is the equilibrium InCl partial pressure in the deposition zone. The values of  $P_{\text{InCl}}$  and  $P_{\text{InCl}}^1$  are those which were computed

for the standard conditions which are:  $T_s = 850^\circ\text{C}$ ,  $T_D = 700^\circ\text{C}$ ,

$P_{\text{HCl}^0} = .01 \text{ atm.}$ ,  $P_{\text{PH}_3^0} = .01 \text{ atm.}$ , and  $P_{\text{HCl}^2}$  is either 0 or  $10^{-4} \text{ atm.}$

Increasing the deposition temperature also causes  $f_{\text{In}}$  to decrease because it drives the deposition reaction to the left. It is shown in Figure 10 and Table 5 that at  $650^\circ\text{C}$   $f_{\text{In}} = .0856$  and it decreases to 0 at  $T = 825^\circ\text{C}$  when no  $\text{HCl}^2$  is present, but these values are reduced when  $P_{\text{HCl}^2} = 10^{-4} \text{ atm.}$  At  $650^\circ\text{C}$   $f_{\text{In}} = .0766$  and the temperature for which it is zero is  $768^\circ\text{C}$ .

#### D. The Effect of Varying $\text{HCl}^0$

The equations used in this section are the same as those used in the previous section. The only difference is that  $P_{\text{HCl}^0}$  is varied instead of  $T_D$ . In Figure 11 and Tables 6a and b the input HCl pressure is varied from .001 to .1, and again the equilibrium  $\text{InCl}$ ,  $\text{HCl}$ ,  $\text{PH}_3$ ,  $P_4$ ,  $P_2$  and  $\text{H}_2$  pressures are determined for  $T_s = 850^\circ\text{C}$ ,  $T_D = 700^\circ\text{C}$ ,  $P_{\text{PH}_3^0} = .01 \text{ atm.}$ , and  $P_{\text{HCl}^2} = 0 \text{ or } 10^{-4} \text{ atm.}$

The plot and Table 6a show that  $P_{\text{InCl}}$  and  $P_{\text{HCl}}$  increase almost linearly whereas the pressures of the phosphorus containing compounds decrease slightly.  $P_{\text{InCl}}$  increases almost linearly since the source reaction is ~99% efficient over a wide range of temperatures and pressures. For the same reason  $P_{\text{HCl}}$  increases almost linearly. There is a small additional increase in  $P_{\text{HCl}}$  due to the fact that a greater percent of the indium is deposited as  $\text{InP}$ . That a bit more  $\text{InP}$  is deposited also accounts for the slight decreases in the pressures of the phosphorous containing compounds.

In Table 6b it is seen that adding HCl downstream increases  $P_{\text{HCl}}$  only slightly. This is due to the fact that the added HCl drives the deposition reaction (21) to the left. The effect of the HCl is so great

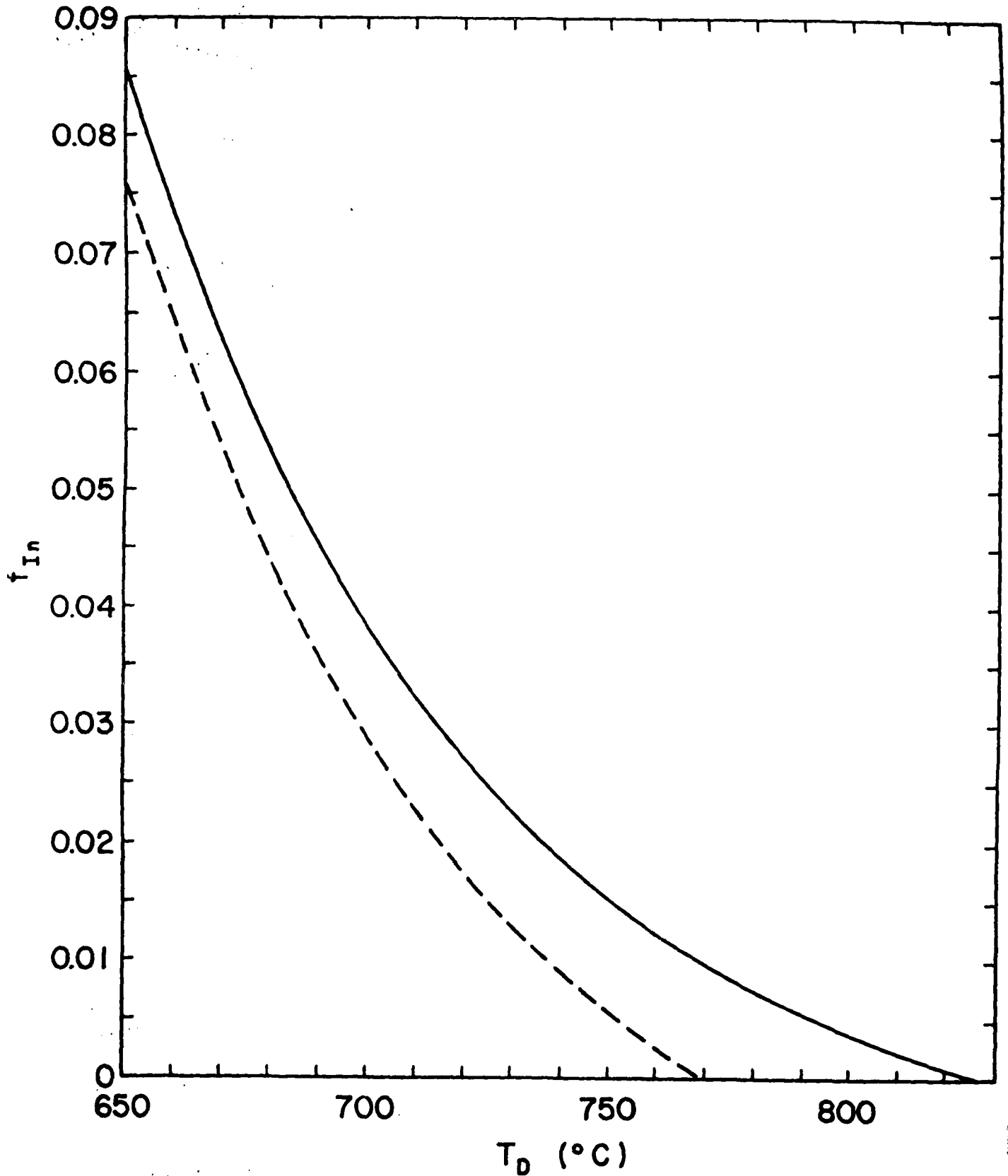


Fig. 10. The fraction of indium deposited,  $f_{In}$ , plotted as a function of the deposition temperature,  $T_D$ , when the downstream HCl concentration is 0 (—) and  $10^{-4}$  atm. (-----).

Table 5. The equilibrium InCl partial pressure in the source (INCL1) and deposition (INCL) zones and the fraction of indium deposited,  $f_{In}$ , for different deposition temperatures,  $T_D$ , when the downstream HCl concentrations are 0 and  $10^{-4}$  atm.

TS	PH30	HCL2	HCL0	HCL2	
850.	0.	0.0000	.01	.0001	
TD	INCL1	INCL	$f_{In}$	INCL	$f_{In}$
650.	.9895E-02	.9048E-02	.0856	.9136E-02	.0766
654.	.9895E-02	.9098E-02	.0805	.9187E-02	.0715
658.	.9895E-02	.9146E-02	.0756	.9236E-02	.0666
662.	.9895E-02	.9191E-02	.0711	.9282E-02	.0620
666.	.9895E-02	.9234E-02	.0667	.9325E-02	.0576
670.	.9895E-02	.9275E-02	.0627	.9366E-02	.0535
674.	.9895E-02	.9313E-02	.0588	.9404E-02	.0496
678.	.9895E-02	.9349E-02	.0552	.9441E-02	.0459
682.	.9895E-02	.9383E-02	.0517	.9475E-02	.0424
686.	.9895E-02	.9415E-02	.0485	.9507E-02	.0391
690.	.9895E-02	.9445E-02	.0454	.9538E-02	.0360
694.	.9895E-02	.9474E-02	.0425	.9567E-02	.0331
698.	.9895E-02	.9501E-02	.0398	.9595E-02	.0303
702.	.9895E-02	.9526E-02	.0372	.9621E-02	.0277
706.	.9895E-02	.9551E-02	.0348	.9645E-02	.0252
710.	.9895E-02	.9573E-02	.0325	.9668E-02	.0229
714.	.9895E-02	.9595E-02	.0303	.9690E-02	.0207
718.	.9895E-02	.9615E-02	.0282	.9711E-02	.0186
722.	.9895E-02	.9635E-02	.0263	.9730E-02	.0166
726.	.9895E-02	.9653E-02	.0244	.9748E-02	.0148
730.	.9895E-02	.9670E-02	.0227	.9766E-02	.0130
734.	.9895E-02	.9686E-02	.0210	.9782E-02	.0113
738.	.9895E-02	.9702E-02	.0195	.9798E-02	.0097
742.	.9895E-02	.9717E-02	.0180	.9813E-02	.0083
746.	.9895E-02	.9730E-02	.0166	.9827E-02	.0068
750.	.9895E-02	.9743E-02	.0153	.9840E-02	.0055
754.	.9895E-02	.9756E-02	.0140	.9853E-02	.0042
758.	.9895E-02	.9768E-02	.0128	.9865E-02	.0030
762.	.9895E-02	.9779E-02	.0117	.9876E-02	.0019
766.	.9895E-02	.9789E-02	.0106	.9887E-02	.0008
770.	.9895E-02	.9799E-02	.0096		
774.	.9895E-02	.9809E-02	.0087		
778.	.9895E-02	.9818E-02	.0078		
782.	.9895E-02	.9826E-02	.0069		
786.	.9895E-02	.9834E-02	.0061		
790.	.9895E-02	.9842E-02	.0053		
794.	.9895E-02	.9849E-02	.0046		
798.	.9895E-02	.9856E-02	.0039		
802.	.9895E-02	.9863E-02	.0032		
806.	.9895E-02	.9869E-02	.0026		
810.	.9895E-02	.9875E-02	.0020		
814.	.9895E-02	.9881E-02	.0014		
818.	.9895E-02	.9886E-02	.0009		
822.	.9895E-02	.9891E-02	.0.		

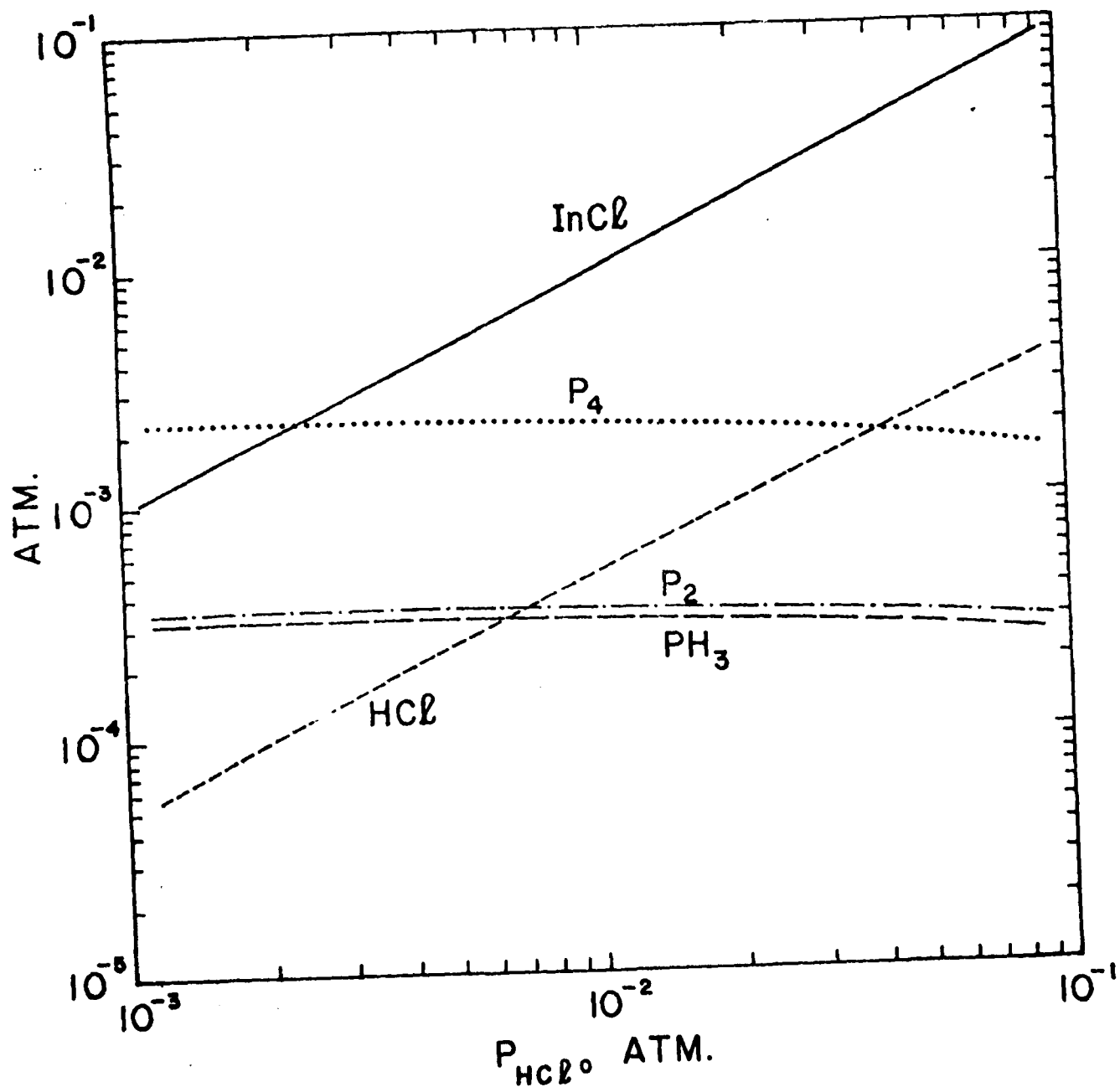


Fig. 11. The InCl, HCl,  $PH_3$ ,  $P_4$ , and  $P_2$  equilibrium partial pressures plotted as a function of the source input HCl concentration,  $HCl^0$  when  $T_S = 850^\circ C$ ,  $T_D = 700^\circ C$ ,  $PH_3^0 = .01$  atm., and  $HCl^2 = 0$ .

Table 6. The equilibrium  $\text{InCl}$ ,  $\text{HCl}$ ,  $\text{PH}_3$ ,  $\text{P}_4$ ,  $\text{P}_2$  and  $\text{H}_2$  partial pressures calculated for different source input  $\text{HCl}$  concentrations,  $\text{HCl}^0$ , when  $T_S = 850^\circ\text{C}$ ,  $T_D = 700^\circ\text{C}$ ,  $\text{PH}_3^0 = .01 \text{ atm}$ . and  $\text{HCl}^2 = \text{a.) } 0$  and  $\text{b.) } 10^{-4} \text{ atm}$ .

TS	TD	HCL2	PH3				H2
850.	700. 0.	HCL	.100E-01	P4	P2		
HCL0	INCL		PH3				
.100E+00	.959E-01	.407E-02	.248E-03	.153E-02	.290E-03	.8979	
.912E-01	.875E-01	.372E-02	.249E-03	.148E-02	.286E-03	.9068	
.832E-01	.797E-01	.345E-02	.254E-03	.153E-02	.291E-03	.9147	
.759E-01	.727E-01	.319E-02	.260E-03	.159E-02	.296E-03	.9220	
.692E-01	.662E-01	.295E-02	.265E-03	.163E-02	.300E-03	.9288	
.631E-01	.604E-01	.273E-02	.269E-03	.168E-02	.304E-03	.9347	
.575E-01	.550E-01	.252E-02	.273E-03	.172E-02	.308E-03	.9402	
.525E-01	.502E-01	.232E-02	.276E-03	.176E-02	.312E-03	.9452	
.479E-01	.457E-01	.214E-02	.280E-03	.180E-02	.315E-03	.9497	
.437E-01	.417E-01	.197E-02	.284E-03	.184E-02	.318E-03	.9539	
.398E-01	.380E-01	.181E-02	.286E-03	.187E-02	.321E-03	.9577	
.363E-01	.346E-01	.166E-02	.289E-03	.190E-02	.323E-03	.9612	
.331E-01	.316E-01	.152E-02	.292E-03	.193E-02	.326E-03	.9643	
.302E-01	.286E-01	.140E-02	.294E-03	.195E-02	.328E-03	.9672	
.275E-01	.263E-01	.128E-02	.296E-03	.198E-02	.330E-03	.9699	
.251E-01	.239E-01	.118E-02	.298E-03	.200E-02	.332E-03	.9723	
.229E-01	.218E-01	.108E-02	.300E-03	.202E-02	.334E-03	.9744	
.209E-01	.199E-01	.986E-03	.301E-03	.204E-02	.335E-03	.9764	
.191E-01	.182E-01	.903E-03	.303E-03	.206E-02	.337E-03	.9783	
.174E-01	.166E-01	.826E-03	.304E-03	.207E-02	.338E-03	.9799	
.158E-01	.151E-01	.756E-03	.305E-03	.209E-02	.339E-03	.9814	
.145E-01	.138E-01	.691E-03	.306E-03	.210E-02	.340E-03	.9828	
.132E-01	.126E-01	.632E-03	.308E-03	.211E-02	.341E-03	.9841	
.120E-01	.114E-01	.578E-03	.308E-03	.212E-02	.342E-03	.9852	
.110E-01	.104E-01	.528E-03	.309E-03	.213E-02	.343E-03	.9862	
.100E-01	.952E-02	.483E-03	.311E-03	.214E-02	.344E-03	.9872	
.912E-02	.868E-02	.441E-03	.311E-03	.215E-02	.344E-03	.9881	
.832E-02	.791E-02	.403E-03	.312E-03	.216E-02	.345E-03	.9889	
.759E-02	.722E-02	.368E-03	.312E-03	.217E-02	.346E-03	.9896	
.692E-02	.658E-02	.336E-03	.313E-03	.217E-02	.346E-03	.9902	
.631E-02	.600E-02	.307E-03	.313E-03	.218E-02	.347E-03	.9909	
.575E-02	.547E-02	.280E-03	.314E-03	.219E-02	.347E-03	.9914	
.525E-02	.497E-02	.256E-03	.314E-03	.219E-02	.348E-03	.9919	
.479E-02	.455E-02	.234E-03	.314E-03	.220E-02	.348E-03	.9924	
.437E-02	.415E-02	.213E-03	.314E-03	.220E-02	.348E-03	.9928	
.398E-02	.379E-02	.195E-03	.315E-03	.220E-02	.349E-03	.9932	
.363E-02	.345E-02	.178E-03	.315E-03	.221E-02	.349E-03	.9935	
.331E-02	.315E-02	.162E-03	.315E-03	.221E-02	.349E-03	.9938	
.302E-02	.287E-02	.148E-03	.315E-03	.221E-02	.349E-03	.9941	
.275E-02	.262E-02	.135E-03	.317E-03	.222E-02	.349E-03	.9944	
.251E-02	.239E-02	.123E-03	.317E-03	.222E-02	.350E-03	.9946	
.229E-02	.218E-02	.112E-03	.317E-03	.222E-02	.350E-03	.9948	
.209E-02	.199E-02	.102E-03	.316E-03	.222E-02	.350E-03	.9950	
.191E-02	.181E-02	.935E-04	.317E-03	.222E-02	.350E-03	.9952	
.174E-02	.165E-02	.853E-04	.317E-03	.223E-02	.350E-03	.9954	
.158E-02	.151E-02	.778E-04	.318E-03	.223E-02	.350E-03	.9955	
.145E-02	.137E-02	.710E-04	.318E-03	.223E-02	.351E-03	.9957	
.132E-02	.125E-02	.648E-04	.318E-03	.223E-02	.351E-03	.9958	
.120E-02	.114E-02	.591E-04	.316E-03	.223E-02	.351E-03	.9959	
.110E-02	.104E-02	.539E-04	.317E-03	.223E-02	.351E-03	.9960	

(a)

TS 850. HCLO	TB 700. INCL	HCL2 .100E-03 HCL	PH30 .100E-01 PH3	P4	P2	H2
.100E+00	.961E-01	.402E-02	.244E-03	.144E-02	.282E-03	.8979
.912E-01	.876E-01	.373E-02	.250E-03	.150E-02	.288E-03	.9067
.832E-01	.798E-01	.346E-02	.256E-03	.155E-02	.293E-03	.9146
.759E-01	.728E-01	.321E-02	.260E-03	.161E-02	.298E-03	.9219
.692E-01	.663E-01	.297E-02	.265E-03	.165E-02	.302E-03	.9285
.631E-01	.605E-01	.274E-02	.270E-03	.170E-02	.306E-03	.9345
.575E-01	.551E-01	.253E-02	.274E-03	.174E-02	.310E-03	.9400
.525E-01	.503E-01	.233E-02	.278E-03	.178E-02	.314E-03	.9450
.479E-01	.458E-01	.215E-02	.281E-03	.183E-02	.317E-03	.9496
.437E-01	.418E-01	.197E-02	.284E-03	.188E-02	.320E-03	.9538
.398E-01	.381E-01	.182E-02	.287E-03	.189E-02	.323E-03	.9576
.363E-01	.347E-01	.167E-02	.290E-03	.192E-02	.325E-03	.9611
.331E-01	.317E-01	.153E-02	.293E-03	.195E-02	.328E-03	.9642
.302E-01	.289E-01	.141E-02	.294E-03	.197E-02	.330E-03	.9671
.275E-01	.264E-01	.129E-02	.297E-03	.200E-02	.332E-03	.9697
.251E-01	.240E-01	.118E-02	.299E-03	.202E-02	.334E-03	.9721
.229E-01	.219E-01	.108E-02	.301E-03	.204E-02	.335E-03	.9743
.209E-01	.200E-01	.993E-03	.302E-03	.206E-02	.337E-03	.9763
.191E-01	.182E-01	.910E-03	.303E-03	.208E-02	.338E-03	.9781
.174E-01	.166E-01	.833E-03	.305E-03	.209E-02	.340E-03	.9798
.158E-01	.152E-01	.762E-03	.306E-03	.211E-02	.341E-03	.9813
.145E-01	.139E-01	.698E-03	.307E-03	.212E-02	.342E-03	.9827
.132E-01	.126E-01	.638E-03	.308E-03	.213E-02	.343E-03	.9839
.120E-01	.115E-01	.584E-03	.309E-03	.215E-02	.344E-03	.9851
.110E-01	.105E-01	.534E-03	.310E-03	.216E-02	.345E-03	.9861
.100E-01	.961E-02	.489E-03	.311E-03	.217E-02	.345E-03	.9871
.912E-02	.877E-02	.447E-03	.312E-03	.217E-02	.346E-03	.9879
.832E-02	.801E-02	.409E-03	.313E-03	.218E-02	.347E-03	.9887
.759E-02	.731E-02	.374E-03	.312E-03	.219E-02	.347E-03	.9895
.692E-02	.668E-02	.342E-03	.314E-03	.220E-02	.348E-03	.9901
.631E-02	.610E-02	.312E-03	.314E-03	.220E-02	.348E-03	.9907
.575E-02	.557E-02	.286E-03	.315E-03	.221E-02	.349E-03	.9913
.525E-02	.509E-02	.261E-03	.315E-03	.221E-02	.349E-03	.9918
.479E-02	.465E-02	.239E-03	.315E-03	.222E-02	.350E-03	.9922
.437E-02	.425E-02	.219E-03	.316E-03	.222E-02	.350E-03	.9926
.398E-02	.388E-02	.200E-03	.316E-03	.223E-02	.350E-03	.9930
.363E-02	.355E-02	.183E-03	.316E-03	.223E-02	.351E-03	.9934
.331E-02	.324E-02	.167E-03	.317E-03	.223E-02	.351E-03	.9937
.302E-02	.297E-02	.153E-03	.317E-03	.224E-02	.351E-03	.9940
.275E-02	.271E-02	.140E-03	.317E-03	.224E-02	.351E-03	.9942
.251E-02	.248E-02	.128E-03	.317E-03	.224E-02	.351E-03	.9945
.229E-02	.227E-02	.118E-03	.317E-03	.224E-02	.352E-03	.9947

(b)

that for every HCl molecule added downstream, almost one less InP 'molecule' is deposited and therefore one less HCl molecule is created.

The effect of the downstream HCl is so strong that small amounts of it can completely stop the deposition. In Table 5b it is seen that this condition is reached when  $P_{\text{HCl}^0} = 2.3 \times 10^{-3}$  atm. if  $P_{\text{HCl}^2} = 10^{-4}$  atm.

In Figure 12 and Table 7 one sees that  $f_{\text{In}}$  changes very little as the input HCl pressure is varied from .001 to .1 atm and  $P_{\text{HCl}^2} = 0$ . This can be explained by the fact that the deposition input  $\text{HCl}$ ,  $\text{HCl}^1$ , and  $\text{InCl}^1$  concentrations increase at about the same rate since ~99% of the  $\text{HCl}^0$  is converted into  $\text{InCl}$  for all values of  $P_{\text{HCl}^0}$ . The increased  $\text{InCl}$  concentration in the deposition zone drives the deposition reaction to the right whereas the increased HCl concentration drives the reaction to the left. These effects essentially cancel each other. This is not the case for small  $P_{\text{HCl}^0}$  values when  $P_{\text{HCl}^2} = 10^{-4}$  atm. because now the HCl from both sources -  $\text{HCl}^1$  and  $\text{HCl}^2$  - have comparable values when  $P_{\text{HCl}^0} = .01$  atm., and  $P_{\text{HCl}^2} > P_{\text{HCl}^1}$  for smaller  $P_{\text{HCl}^0}$  values. As a result the effects of the  $\text{HCl}^2$  dominate at the smaller  $\text{HCl}^0$  pressures and drive  $f_{\text{In}}$  to zero for  $P_{\text{HCl}^0} \leq 2.4 \times 10^{-3}$  atm.

#### E. The Effects of Varying $\text{PH}_3^0$

The effects of varying the input  $\text{PH}_3$  pressure are illustrated in Figures 13 and 14 and in Tables 8 and 9. In Figure 13 the constituent partial pressures are plotted as a function of  $\text{PH}_3^0$  and there it is seen that  $P_{\text{InCl}}$  dips ever so slightly,  $P_{\text{HCl}}$  increases slowly, and the partial pressures of the phosphorous containing compounds increase with the increase in  $P_{\text{P}_4}$  being the most rapid.  $P_{\text{InCl}}$  dips slightly due to the fact that more  $\text{InP}$  is deposited as  $\text{PH}_3^0$  increases. For the same

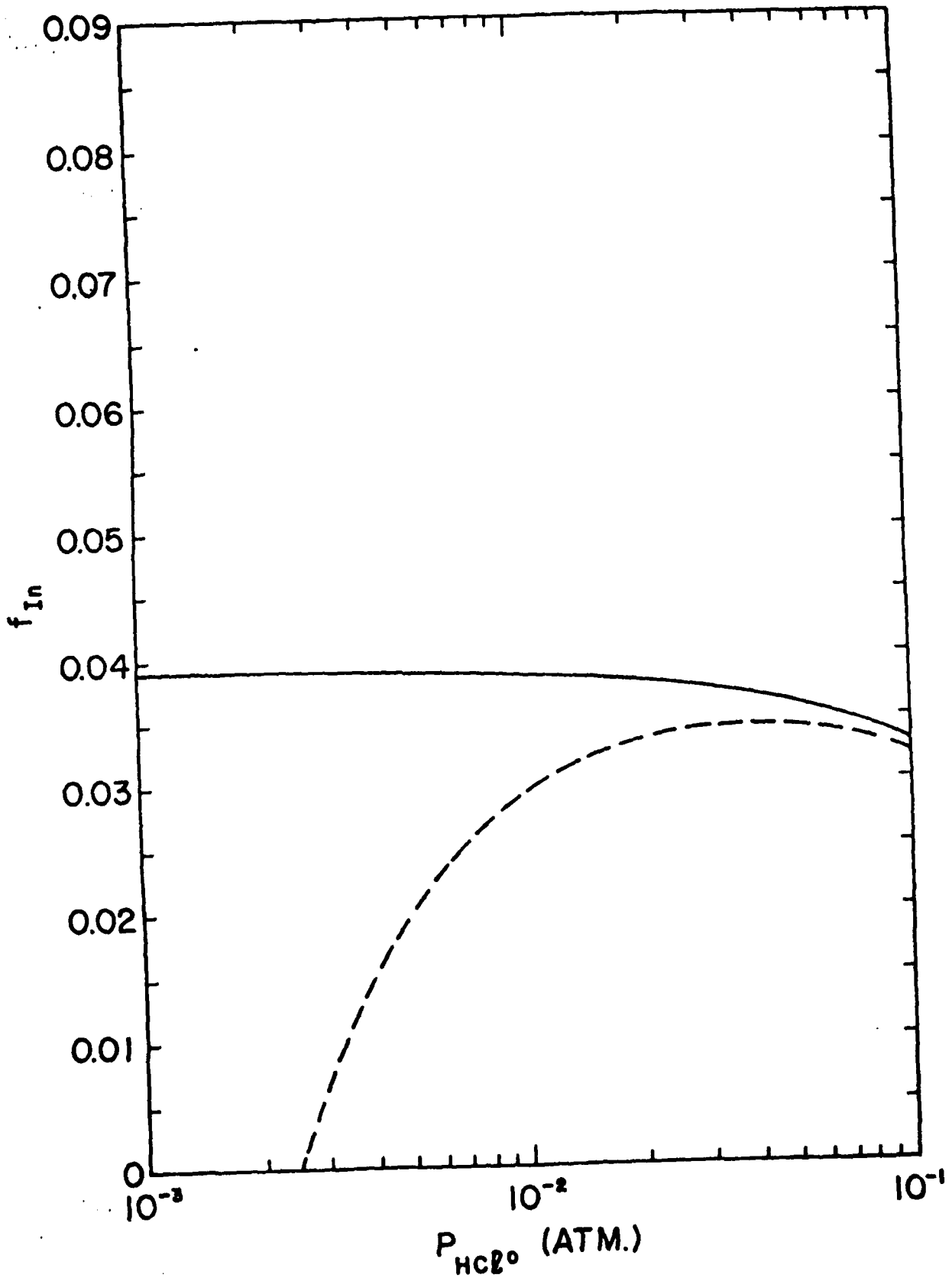


Fig. 12. The fraction of indium deposited,  $f_{In}$ , plotted as a function of the input HCl concentration,  $P_{HCl^0}$ , when the downstream HCl pressure is 0 (—) and  $10^{-4}$  atm. (-----).

Table 7. The equilibrium InCl partial pressures in the source (INCL1) and deposition (INCL) zones and the fraction of indium deposited,  $f_{In}$ , for different input HCl partial pressures, HCL0, when the downstream HCl concentrations are 0 and  $10^{-4}$  atm.

TS 850. HCL0	TD 700. INCL1	HCL2 0.0000 INCL	PN30 .01 $f_{In}$	HCL2 .0001 INCL	$f_{In}$
.100E+00	.9899E-01	.9575E-01	.0328	.9583E-01	.0320
.912E-01	.9028E-01	.8727E-01	.0333	.8735E-01	.0324
.832E-01	.8233E-01	.7955E-01	.0338	.7963E-01	.0328
.759E-01	.7508E-01	.7251E-01	.0343	.7260E-01	.0331
.692E-01	.6848E-01	.6610E-01	.0347	.6619E-01	.0334
.631E-01	.6245E-01	.6026E-01	.0351	.6035E-01	.0337
.575E-01	.5695E-01	.5494E-01	.0354	.5502E-01	.0339
.525E-01	.5194E-01	.5008E-01	.0357	.5017E-01	.0340
.479E-01	.4737E-01	.4566E-01	.0360	.4575E-01	.0341
.437E-01	.4320E-01	.4163E-01	.0363	.4172E-01	.0342
.398E-01	.3940E-01	.3796E-01	.0365	.3805E-01	.0342
.363E-01	.3593E-01	.3461E-01	.0368	.3470E-01	.0342
.331E-01	.3277E-01	.3156E-01	.0370	.3165E-01	.0342
.302E-01	.2988E-01	.2877E-01	.0372	.2887E-01	.0341
.275E-01	.2725E-01	.2624E-01	.0373	.2633E-01	.0340
.251E-01	.2486E-01	.2392E-01	.0375	.2401E-01	.0338
.229E-01	.2267E-01	.2182E-01	.0376	.2191E-01	.0336
.209E-01	.2067E-01	.1989E-01	.0378	.1999E-01	.0333
.191E-01	.1885E-01	.1814E-01	.0379	.1823E-01	.0330
.174E-01	.1720E-01	.1654E-01	.0380	.1664E-01	.0326
.158E-01	.1568E-01	.1508E-01	.0381	.1518E-01	.0322
.145E-01	.1430E-01	.1376E-01	.0382	.1385E-01	.0317
.132E-01	.1304E-01	.1254E-01	.0383	.1264E-01	.0311
.120E-01	.1190E-01	.1144E-01	.0384	.1153E-01	.0305
.110E-01	.1085E-01	.1043E-01	.0384	.1053E-01	.0298
.100E-01	.9895E-02	.9514E-02	.0385	.9608E-02	.0290
.912E-02	.9024E-02	.8676E-02	.0385	.8770E-02	.0281
.832E-02	.8230E-02	.7912E-02	.0386	.8006E-02	.0272
.759E-02	.7506E-02	.7216E-02	.0386	.7310E-02	.0261
.692E-02	.6845E-02	.6580E-02	.0387	.6675E-02	.0249
.631E-02	.6243E-02	.6001E-02	.0387	.6096E-02	.0236
.575E-02	.5694E-02	.5473E-02	.0388	.5567E-02	.0222
.525E-02	.5193E-02	.4991E-02	.0388	.5086E-02	.0206
.479E-02	.4736E-02	.4552E-02	.0388	.4646E-02	.0189
.437E-02	.4319E-02	.4151E-02	.0389	.4246E-02	.0169
.398E-02	.3939E-02	.3786E-02	.0389	.3880E-02	.0149
.363E-02	.3592E-02	.3453E-02	.0389	.3547E-02	.0125
.331E-02	.3276E-02	.3149E-02	.0389	.3243E-02	.0100
.302E-02	.2988E-02	.2872E-02	.0389	.2966E-02	.0072
.275E-02	.2725E-02	.2619E-02	.0389	.2714E-02	.0042
.251E-02	.2485E-02	.2388E-02	.0390	.2483E-02	.0008
.229E-02	.2267E-02	.2178E-02	.0390		
.209E-02	.2067E-02	.1987E-02	.0390		
.191E-02	.1885E-02	.1812E-02	.0390		
.174E-02	.1719E-02	.1652E-02	.0390		
.158E-02	.1568E-02	.1507E-02	.0390		
.145E-02	.1430E-02	.1374E-02	.0390		
.132E-02	.1304E-02	.1253E-02	.0390		
.120E-02	.1190E-02	.1143E-02	.0391		
.110E-02	.1085E-02	.1042E-02	.0391		

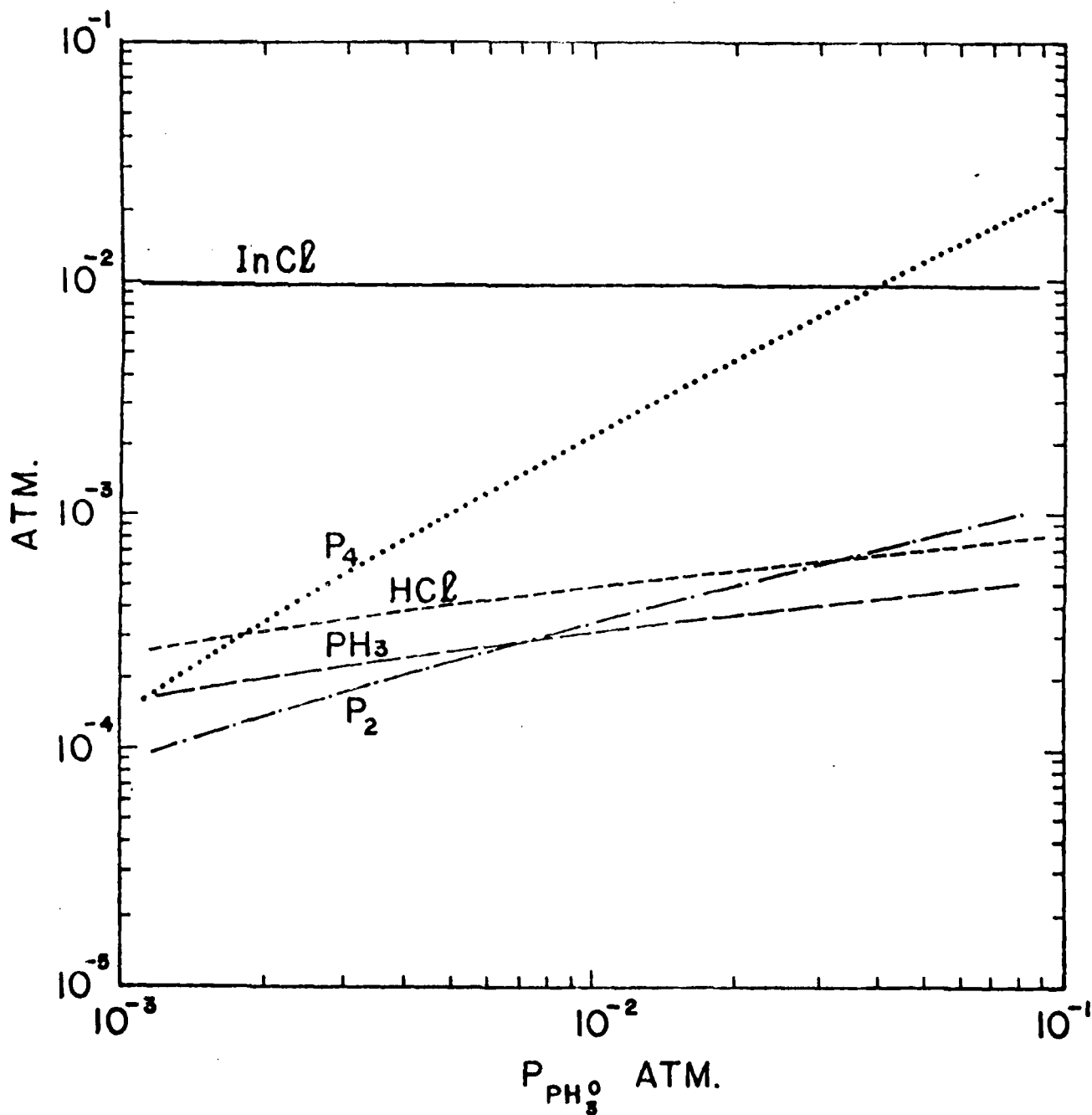


Fig. 13. The InCl, HCl, PH<sub>3</sub>, P<sub>4</sub>, and P<sub>2</sub> equilibrium partial pressures plotted as a function of the input PH<sub>3</sub> concentration, PH<sub>3</sub><sup>0</sup> when T<sub>S</sub> = 850°C, T<sub>D</sub> = 700°C, HCl<sup>0</sup> = .01 atm., and HCl<sup>2</sup> = 0.

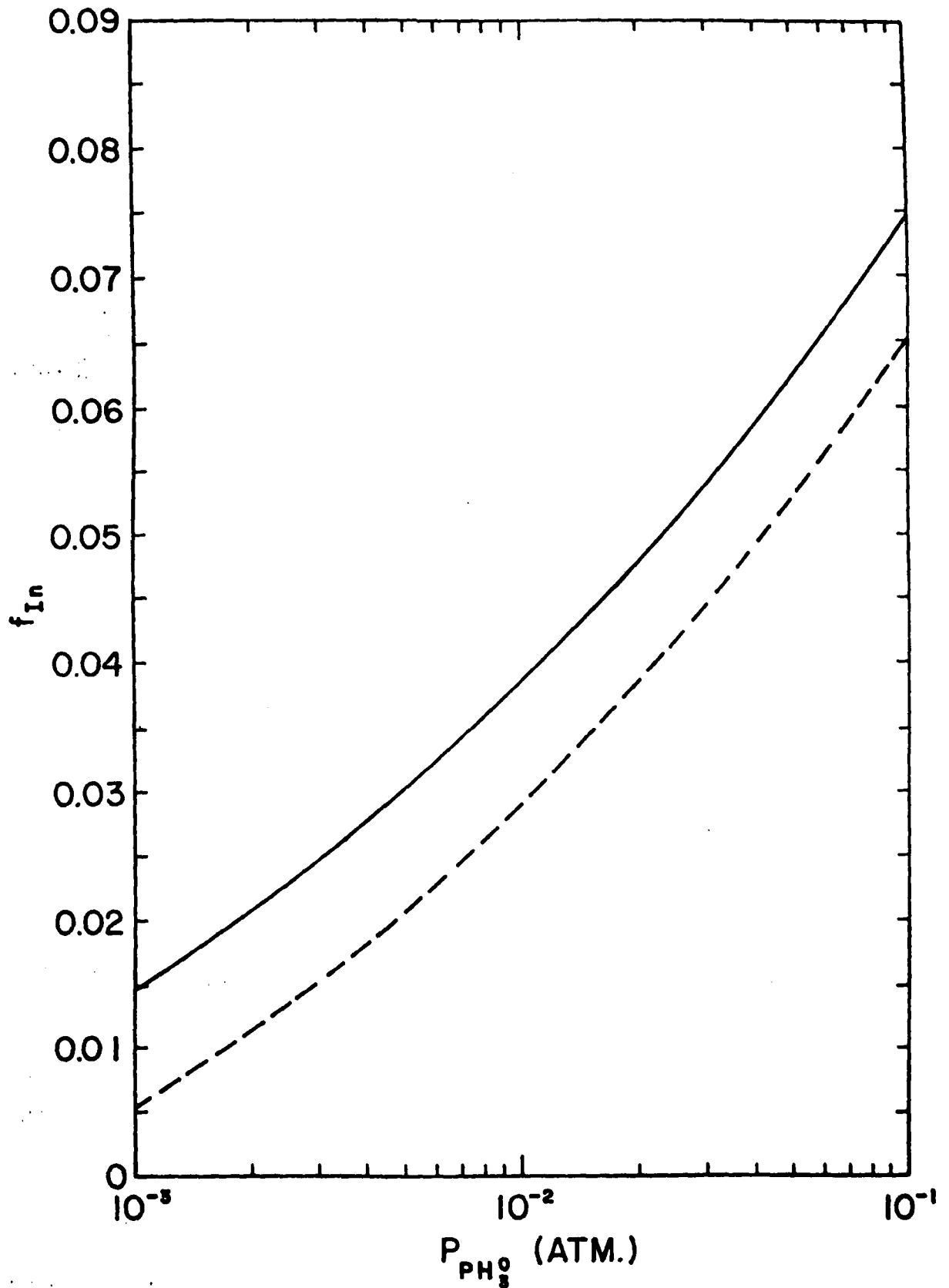


Fig. 14. The fraction of indium deposited,  $f_{In}$ , plotted as a function of the input  $PH_3$  partial pressure,  $P_{PH_3^0}$ , when the downstream HCl concentration is 0 (—) and  $10^{-4}$  atm. (-----).

Table 8. The equilibrium InCl, HCl, PH<sub>3</sub>, P<sub>4</sub>, P<sub>2</sub> and H<sub>2</sub> partial pressures calculated for different input PH<sub>3</sub> concentrations, PH<sub>3</sub><sup>0</sup>, when T<sub>S</sub> = 850°C, T<sub>D</sub> = 700°C, HCl<sup>0</sup> = .01 atm., and HCl<sup>2</sup> = a.) 0, and b.) 10<sup>-4</sup>.

PH <sub>3</sub> <sup>0</sup>	T <sub>S</sub>	HCl <sup>0</sup>	InCl <sup>1</sup>	HCl <sup>1</sup>	HCl <sup>2</sup>	T <sub>D</sub>	H <sub>2</sub>
	850.	.100E-01	.989E-02	.105E-03	0.	700.	
	PH <sub>3</sub>	InCl	HCl	PH <sub>3</sub>	P <sub>4</sub>	P <sub>2</sub>	
.100E+0	.915E-02	.846E-03	.555E-03	.241E-01	.115E-02	.9642	
.912E-01	.917E-02	.828E-03	.544E-03	.219E-01	.110E-02	.9664	
.832E-01	.919E-02	.811E-03	.531E-03	.200E-01	.105E-02	.9685	
.759E-01	.921E-02	.795E-03	.518E-03	.182E-01	.100E-02	.9703	
.692E-01	.922E-02	.778E-03	.511E-03	.163E-01	.954E-03	.9720	
.631E-01	.924E-02	.762E-03	.495E-03	.150E-01	.910E-03	.9736	
.575E-01	.925E-02	.746E-03	.483E-03	.137E-01	.868E-03	.9750	
.525E-01	.927E-02	.730E-03	.475E-03	.124E-01	.828E-03	.9763	
.479E-01	.929E-02	.715E-03	.464E-03	.113E-01	.789E-03	.9774	
.437E-01	.930E-02	.699E-03	.455E-03	.103E-01	.753E-03	.9785	
.398E-01	.932E-02	.684E-03	.443E-03	.934E-02	.717E-03	.9795	
.363E-01	.933E-02	.669E-03	.435E-03	.849E-02	.684E-03	.9804	
.331E-01	.935E-02	.655E-03	.425E-03	.771E-02	.652E-03	.9812	
.302E-01	.936E-02	.641E-03	.415E-03	.700E-02	.621E-03	.9820	
.275E-01	.937E-02	.626E-03	.405E-03	.636E-02	.592E-03	.9826	
.251E-01	.939E-02	.613E-03	.397E-03	.577E-02	.564E-03	.9833	
.229E-01	.940E-02	.599E-03	.386E-03	.524E-02	.537E-03	.9838	
.209E-01	.941E-02	.586E-03	.377E-03	.475E-02	.512E-03	.9844	
.191E-01	.943E-02	.572E-03	.366E-03	.431E-02	.487E-03	.9848	
.174E-01	.944E-02	.559E-03	.359E-03	.391E-02	.464E-03	.9853	
.158E-01	.945E-02	.547E-03	.352E-03	.354E-02	.442E-03	.9857	
.145E-01	.947E-02	.534E-03	.343E-03	.321E-02	.421E-03	.9860	
.132E-01	.948E-02	.522E-03	.334E-03	.291E-02	.400E-03	.9864	
.120E-01	.949E-02	.510E-03	.326E-03	.263E-02	.381E-03	.9867	
.110E-01	.950E-02	.498E-03	.318E-03	.238E-02	.362E-03	.9869	
.100E-01	.951E-02	.486E-03	.311E-03	.215E-02	.345E-03	.9872	
.912E-02	.953E-02	.475E-03	.303E-03	.193E-02	.328E-03	.9874	
.832E-02	.954E-02	.463E-03	.296E-03	.176E-02	.311E-03	.9876	
.759E-02	.955E-02	.452E-03	.288E-03	.159E-02	.296E-03	.9878	
.692E-02	.956E-02	.441E-03	.281E-03	.143E-02	.281E-03	.9880	
.631E-02	.957E-02	.431E-03	.274E-03	.129E-02	.267E-03	.9882	
.575E-02	.958E-02	.420E-03	.267E-03	.117E-02	.254E-03	.9883	
.525E-02	.959E-02	.410E-03	.260E-03	.105E-02	.241E-03	.9884	
.479E-02	.960E-02	.400E-03	.253E-03	.946E-03	.228E-03	.9886	
.437E-02	.961E-02	.390E-03	.247E-03	.850E-03	.216E-03	.9887	
.398E-02	.962E-02	.380E-03	.240E-03	.764E-03	.205E-03	.9888	
.363E-02	.963E-02	.370E-03	.234E-03	.686E-03	.194E-03	.9889	
.331E-02	.964E-02	.360E-03	.227E-03	.615E-03	.184E-03	.9890	
.302E-02	.965E-02	.351E-03	.221E-03	.551E-03	.174E-03	.9891	
.275E-02	.966E-02	.342E-03	.215E-03	.493E-03	.165E-03	.9891	
.251E-02	.967E-02	.333E-03	.209E-03	.441E-03	.156E-03	.9892	
.229E-02	.968E-02	.324E-03	.204E-03	.394E-03	.147E-03	.9893	
.209E-02	.969E-02	.315E-03	.198E-03	.351E-03	.139E-03	.9893	
.191E-02	.969E-02	.306E-03	.192E-03	.313E-03	.131E-03	.9894	
.174E-02	.970E-02	.297E-03	.187E-03	.278E-03	.124E-03	.9894	
.158E-02	.971E-02	.289E-03	.181E-03	.247E-03	.117E-03	.9895	
.145E-02	.972E-02	.281E-03	.176E-03	.219E-03	.110E-03	.9895	
.132E-02	.973E-02	.272E-03	.170E-03	.194E-03	.103E-03	.9895	
.120E-02	.974E-02	.264E-03	.165E-03	.171E-03	.971E-04	.9896	
.110E-02	.974E-02	.256E-03	.160E-03	.151E-03	.912E-04	.9896	

(a)

TS	HCL0	INCL1	HCL1	HCL2	TD	
850.	.100E-01	.989E-02	.105E-03	.100E-03	700.	
PH30	INCL	HCL	PH3	P4	P2	H2
.100E+00	.925E-02	.854E-03	.555E-03	.241E-01	.115E-02	.9641
.912E-01	.926E-02	.837E-03	.543E-03	.220E-01	.110E-02	.9663
.832E-01	.928E-02	.820E-03	.530E-03	.200E-01	.105E-02	.9683
.759E-01	.930E-02	.803E-03	.518E-03	.182E-01	.100E-02	.9702
.692E-01	.931E-02	.786E-03	.505E-03	.165E-01	.955E-03	.9719
.631E-01	.933E-02	.770E-03	.497E-03	.151E-01	.911E-03	.9734
.575E-01	.935E-02	.754E-03	.488E-03	.137E-01	.869E-03	.9749
.525E-01	.936E-02	.738E-03	.477E-03	.125E-01	.829E-03	.9761
.479E-01	.938E-02	.722E-03	.464E-03	.113E-01	.790E-03	.9773
.437E-01	.939E-02	.707E-03	.454E-03	.103E-01	.753E-03	.9784
.398E-01	.941E-02	.691E-03	.446E-03	.936E-02	.718E-03	.9794
.363E-01	.942E-02	.677E-03	.436E-03	.851E-02	.685E-03	.9803
.331E-01	.944E-02	.662E-03	.423E-03	.773E-02	.653E-03	.9811
.302E-01	.945E-02	.647E-03	.415E-03	.702E-02	.622E-03	.9818
.275E-01	.947E-02	.633E-03	.405E-03	.638E-02	.593E-03	.9825
.251E-01	.948E-02	.619E-03	.395E-03	.575E-02	.565E-03	.9831
.229E-01	.949E-02	.606E-03	.388E-03	.520E-02	.539E-03	.9837
.209E-01	.951E-02	.592E-03	.378E-03	.478E-02	.513E-03	.9842
.191E-01	.952E-02	.579E-03	.368E-03	.433E-02	.489E-03	.9847
.174E-01	.953E-02	.566E-03	.360E-03	.393E-02	.466E-03	.9851
.158E-01	.955E-02	.553E-03	.352E-03	.357E-02	.443E-03	.9855
.145E-01	.956E-02	.540E-03	.343E-03	.323E-02	.422E-03	.9859
.132E-01	.957E-02	.528E-03	.336E-03	.293E-02	.402E-03	.9862
.120E-01	.958E-02	.516E-03	.327E-03	.265E-02	.383E-03	.9865
.110E-01	.960E-02	.504E-03	.319E-03	.240E-02	.364E-03	.9868
.100E-01	.961E-02	.492E-03	.311E-03	.218E-02	.346E-03	.9871
.912E-02	.962E-02	.481E-03	.304E-03	.197E-02	.330E-03	.9873
.832E-02	.963E-02	.470E-03	.296E-03	.178E-02	.313E-03	.9875
.759E-02	.964E-02	.458E-03	.289E-03	.161E-02	.298E-03	.9877
.692E-02	.965E-02	.448E-03	.282E-03	.146E-02	.283E-03	.9879
.631E-02	.966E-02	.437E-03	.275E-03	.132E-02	.269E-03	.9880
.575E-02	.967E-02	.426E-03	.268E-03	.119E-02	.256E-03	.9882
.525E-02	.968E-02	.416E-03	.261E-03	.107E-02	.243E-03	.9883
.479E-02	.969E-02	.406E-03	.254E-03	.967E-03	.231E-03	.9884
.437E-02	.970E-02	.396E-03	.248E-03	.872E-03	.219E-03	.9886
.398E-02	.971E-02	.386E-03	.242E-03	.786E-03	.208E-03	.9887
.363E-02	.972E-02	.376E-03	.235E-03	.707E-03	.197E-03	.9888
.331E-02	.973E-02	.367E-03	.229E-03	.636E-03	.187E-03	.9888
.302E-02	.974E-02	.358E-03	.223E-03	.572E-03	.178E-03	.9889
.275E-02	.975E-02	.349E-03	.217E-03	.514E-03	.168E-03	.9890
.251E-02	.976E-02	.340E-03	.212E-03	.462E-03	.160E-03	.9891
.229E-02	.977E-02	.331E-03	.206E-03	.414E-03	.151E-03	.9891
.209E-02	.978E-02	.322E-03	.201E-03	.371E-03	.143E-03	.9892
.191E-02	.979E-02	.314E-03	.195E-03	.333E-03	.135E-03	.9892
.174E-02	.979E-02	.305E-03	.190E-03	.298E-03	.128E-03	.9893
.158E-02	.980E-02	.297E-03	.185E-03	.266E-03	.121E-03	.9893
.145E-02	.981E-02	.289E-03	.180E-03	.238E-03	.115E-03	.9894
.132E-02	.982E-02	.282E-03	.174E-03	.213E-03	.108E-03	.9894
.120E-02	.983E-02	.274E-03	.170E-03	.190E-03	.102E-03	.9894
.110E-02	.983E-02	.266E-03	.165E-03	.169E-03	.966E-04	.9895

(b)

Table 9. The equilibrium InCl partial pressures in the source (INCL1) and deposition (INCL) zones and the fraction of the indium deposited,  $f_{In}$ , for different input  $PH_3$  partial pressures,  $PH_{30}$ , when the downstream HCl concentrations are 0 and  $10^{-4}$  atm.

TS 850. PH30	TD 700. INCL1	HCL2 0.0000 INCL	HCL0 .01 $f_{In}$	HCL2 .0001 INCL	$f_{In}$
.100E+00	.9895E-02	.9154E-02	.0748	.9246E-02	.0656
.912E-01	.9895E-02	.9172E-02	.0731	.9263E-02	.0638
.832E-01	.9895E-02	.9189E-02	.0714	.9280E-02	.0621
.759E-01	.9895E-02	.9205E-02	.0697	.9297E-02	.0604
.692E-01	.9895E-02	.9222E-02	.0680	.9314E-02	.0587
.631E-01	.9895E-02	.9238E-02	.0664	.9330E-02	.0570
.575E-01	.9895E-02	.9254E-02	.0647	.9346E-02	.0554
.525E-01	.9895E-02	.9270E-02	.0631	.9362E-02	.0538
.479E-01	.9895E-02	.9285E-02	.0616	.9378E-02	.0522
.437E-01	.9895E-02	.9301E-02	.0600	.9393E-02	.0507
.398E-01	.9895E-02	.9316E-02	.0585	.9409E-02	.0491
.363E-01	.9895E-02	.9331E-02	.0570	.9423E-02	.0476
.331E-01	.9895E-02	.9345E-02	.0555	.9438E-02	.0461
.302E-01	.9895E-02	.9359E-02	.0541	.9453E-02	.0447
.275E-01	.9895E-02	.9374E-02	.0527	.9467E-02	.0432
.251E-01	.9895E-02	.9387E-02	.0513	.9481E-02	.0418
.229E-01	.9895E-02	.9401E-02	.0499	.9494E-02	.0404
.209E-01	.9895E-02	.9414E-02	.0485	.9508E-02	.0391
.191E-01	.9895E-02	.9428E-02	.0472	.9521E-02	.0377
.174E-01	.9895E-02	.9441E-02	.0459	.9534E-02	.0364
.158E-01	.9895E-02	.9453E-02	.0446	.9547E-02	.0351
.145E-01	.9895E-02	.9466E-02	.0433	.9560E-02	.0339
.132E-01	.9895E-02	.9478E-02	.0421	.9572E-02	.0326
.120E-01	.9895E-02	.9490E-02	.0409	.9584E-02	.0314
.110E-01	.9895E-02	.9502E-02	.0397	.9596E-02	.0302
.100E-01	.9895E-02	.9514E-02	.0385	.9608E-02	.0290
.912E-02	.9895E-02	.9525E-02	.0373	.9619E-02	.0278
.832E-02	.9895E-02	.9537E-02	.0362	.9630E-02	.0267
.759E-02	.9895E-02	.9548E-02	.0351	.9642E-02	.0256
.692E-02	.9895E-02	.9559E-02	.0340	.9653E-02	.0245
.631E-02	.9895E-02	.9569E-02	.0329	.9663E-02	.0234
.575E-02	.9895E-02	.9580E-02	.0318	.9674E-02	.0223
.525E-02	.9895E-02	.9590E-02	.0308	.9684E-02	.0213
.479E-02	.9895E-02	.9600E-02	.0297	.9694E-02	.0202
.437E-02	.9895E-02	.9610E-02	.0287	.9704E-02	.0192
.398E-02	.9895E-02	.9620E-02	.0277	.9714E-02	.0183
.363E-02	.9895E-02	.9630E-02	.0267	.9724E-02	.0173
.331E-02	.9895E-02	.9640E-02	.0258	.9733E-02	.0163
.302E-02	.9895E-02	.9649E-02	.0248	.9742E-02	.0154
.275E-02	.9895E-02	.9658E-02	.0239	.9751E-02	.0145
.251E-02	.9895E-02	.9667E-02	.0230	.9760E-02	.0136
.229E-02	.9895E-02	.9676E-02	.0220	.9769E-02	.0127
.209E-02	.9895E-02	.9685E-02	.0212	.9778E-02	.0118
.191E-02	.9895E-02	.9694E-02	.0203	.9786E-02	.0110
.174E-02	.9895E-02	.9703E-02	.0194	.9795E-02	.0101
.158E-02	.9895E-02	.9711E-02	.0185	.9803E-02	.0093
.145E-02	.9895E-02	.9719E-02	.0177	.9811E-02	.0085
.132E-02	.9895E-02	.9728E-02	.0169	.9818E-02	.0077
.120E-02	.9895E-02	.9736E-02	.0161	.9826E-02	.0069
.110E-02	.9895E-02	.9744E-02	.0153	.9834E-02	.0062

reason  $P_{\text{HCl}}$ , but it appears to be larger because the plot is a log-log plot. The partial pressures of the phosphorous containing compounds increase because the  $\text{PH}_3^0$  pressure increases faster than the InP deposition.  $P_{\text{P}_4}$  increases more rapidly than  $P_{\text{P}_2}$  and  $P_{\text{PH}_3}$  due to the fact that in this temperature-pressure region the enthalpy has a stronger effect than the entropy.

Again in Table 8b it is seen that introducing HCl downstream reduces the deposition reaction, since for a given  $\text{PH}_3^0$  concentration  $P_{\text{InCl}}$  is greater when  $\text{HCl}^2$  has been introduced.

That increasing  $P_{\text{PH}_3^0}$  increases the deposition of InP and introducing  $\text{HCl}^2$  reduces it, is shown in Figure 14 and Table 9 where the dependence of  $f_{\text{In}}$  on  $P_{\text{PH}_3^0}$  is illustrated.

#### F. The Effects of Varying $\text{HCl}^2$

In the previous sections it was shown that introducing HCl downstream reduces the tendency for InP to deposit. In this section this tendency is discussed in more detail. In Figure 15 and Table 10 it is seen that all of the constituent partial pressures increase slightly with  $P_{\text{HCl}^2}$  up to  $P_{\text{HCl}^2} = 4 \times 10^{-4}$  atm. at which point deposition ceases. The HCl concentration increases because  $P_{\text{HCl}^2}$  increases faster than the rate of deposition of InP decreases, and the other pressures increase since there is less InP deposited.

That increasing the  $\text{HCl}^2$  concentration reduces the deposition of InP is also shown in Figure 16 and Table 11 where  $f_{\text{In}}$  is determined as a function of  $P_{\text{HCl}^2}$ . The value of  $f_{\text{In}}$  decreases with increasing  $P_{\text{HCl}^2}$ , and the rate of decrease increases as  $P_{\text{HCl}^2}$  approaches the value of  $P_{\text{HCl}}$ .

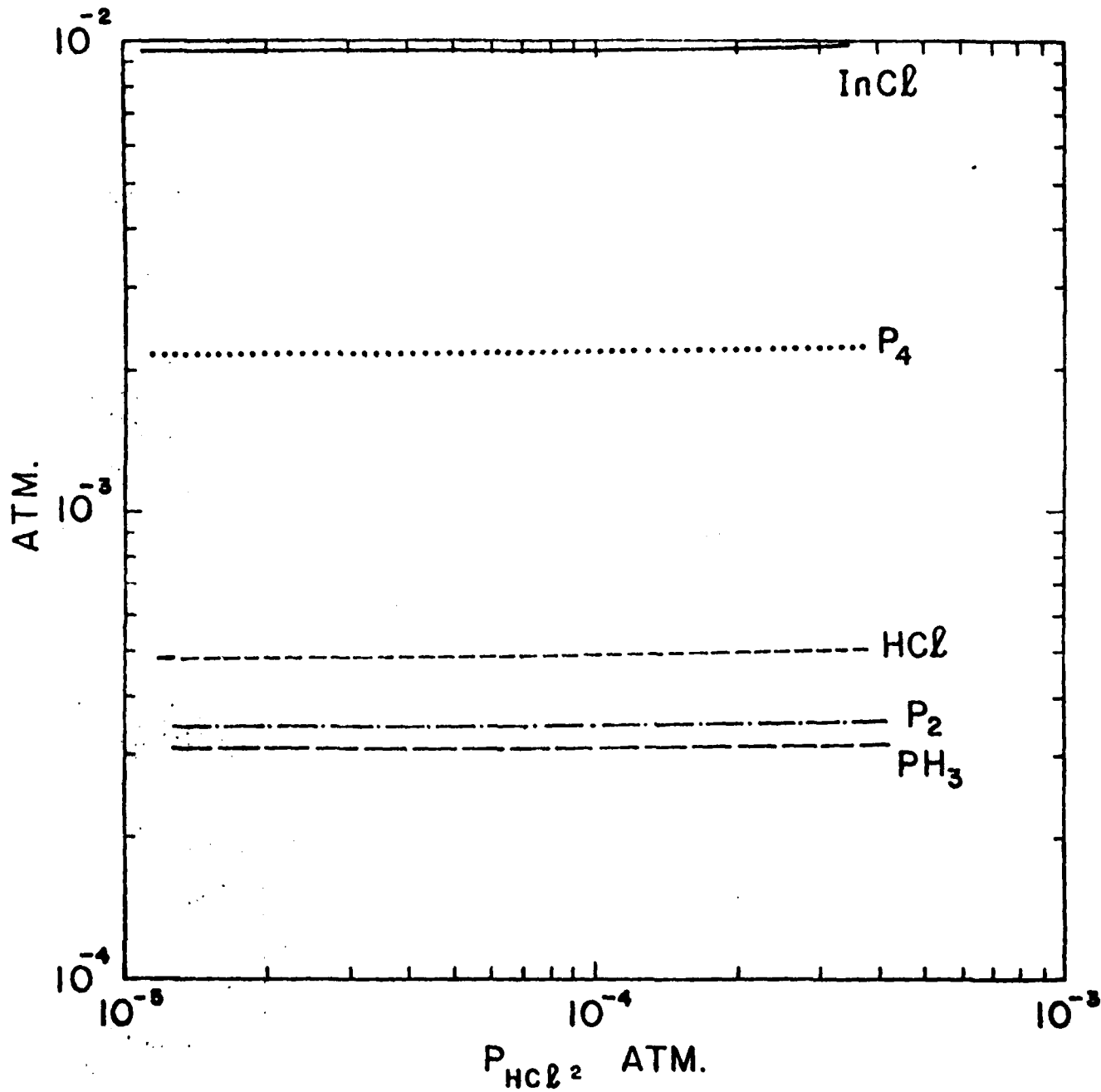


fig. 15. The InCl, HCl,  $PH_3$ ,  $P_4$ , and  $P_2$  equilibrium partial pressures plotted as a function of the downstream input HCl concentration,  $HCl^0$ , when  $T_S = 850^\circ C$ ,  $T_D = 700^\circ C$ ,  $HCl^0 = .01$  atm., and  $PH_3^0 = .01$  atm.

Table 10. The equilibrium  $\text{InCl}$ ,  $\text{HCl}$ ,  $\text{PH}_3$ ,  $\text{P}_4$ ,  $\text{P}_2$  and  $\text{H}_2$  partial pressures calculated for different input downstream  $\text{HCl}$  concentrations,  $\text{HCl}^2$ , when  $T_S = 850^\circ\text{C}$ ,  $T_D = 700^\circ\text{C}$ ,  $\text{HCl}^0 = .01 \text{ atm.}$ , and  $\text{PH}_3^0 = .01 \text{ atm.}$

TS	PD	INCL1	HCL1	TD	PH30	P2IN
850.	.100E-01	.907E-02	.109E-03	700.	.100E-01	1.0107
HCL2	INCL	HCL	PH3	P4	P2	H2
.110E-04	.952E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.120E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.132E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.145E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.158E-04	.953E-02	.487E-03	.310E-03	.216E-02	.345E-03	.9872
.174E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.191E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.209E-04	.953E-02	.487E-03	.311E-03	.216E-02	.345E-03	.9872
.229E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.251E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.275E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.302E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.331E-04	.954E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.363E-04	.955E-02	.488E-03	.311E-03	.216E-02	.345E-03	.9872
.398E-04	.955E-02	.489E-03	.311E-03	.216E-02	.345E-03	.9872
.437E-04	.955E-02	.489E-03	.311E-03	.216E-02	.345E-03	.9872
.479E-04	.956E-02	.489E-03	.311E-03	.217E-02	.345E-03	.9872
.525E-04	.956E-02	.489E-03	.311E-03	.217E-02	.346E-03	.9872
.575E-04	.957E-02	.490E-03	.311E-03	.217E-02	.346E-03	.9872
.631E-04	.957E-02	.490E-03	.311E-03	.217E-02	.346E-03	.9872
.692E-04	.958E-02	.490E-03	.311E-03	.217E-02	.346E-03	.9872
.759E-04	.959E-02	.491E-03	.311E-03	.217E-02	.346E-03	.9872
.832E-04	.959E-02	.491E-03	.311E-03	.217E-02	.346E-03	.9872
.912E-04	.960E-02	.492E-03	.311E-03	.218E-02	.346E-03	.9872
.100E-03	.961E-02	.492E-03	.311E-03	.218E-02	.346E-03	.9872
.110E-03	.962E-02	.493E-03	.311E-03	.218E-02	.347E-03	.9872
.120E-03	.963E-02	.494E-03	.312E-03	.218E-02	.347E-03	.9872
.132E-03	.964E-02	.494E-03	.312E-03	.218E-02	.347E-03	.9872
.145E-03	.965E-02	.495E-03	.312E-03	.219E-02	.347E-03	.9872
.158E-03	.966E-02	.496E-03	.312E-03	.219E-02	.347E-03	.9872
.174E-03	.968E-02	.497E-03	.312E-03	.219E-02	.348E-03	.9872
.191E-03	.969E-02	.498E-03	.312E-03	.220E-02	.348E-03	.9872
.209E-03	.971E-02	.499E-03	.312E-03	.220E-02	.348E-03	.9869
.229E-03	.973E-02	.500E-03	.312E-03	.221E-02	.349E-03	.9869
.251E-03	.975E-02	.501E-03	.313E-03	.221E-02	.349E-03	.9869
.275E-03	.977E-02	.503E-03	.313E-03	.222E-02	.350E-03	.9868
.302E-03	.980E-02	.505E-03	.313E-03	.222E-02	.350E-03	.9868
.331E-03	.982E-02	.506E-03	.313E-03	.223E-02	.351E-03	.9868
.363E-03	.985E-02	.508E-03	.313E-03	.224E-02	.351E-03	.9867
.398E-03	.989E-02	.510E-03	.314E-03	.224E-02	.352E-03	.9867

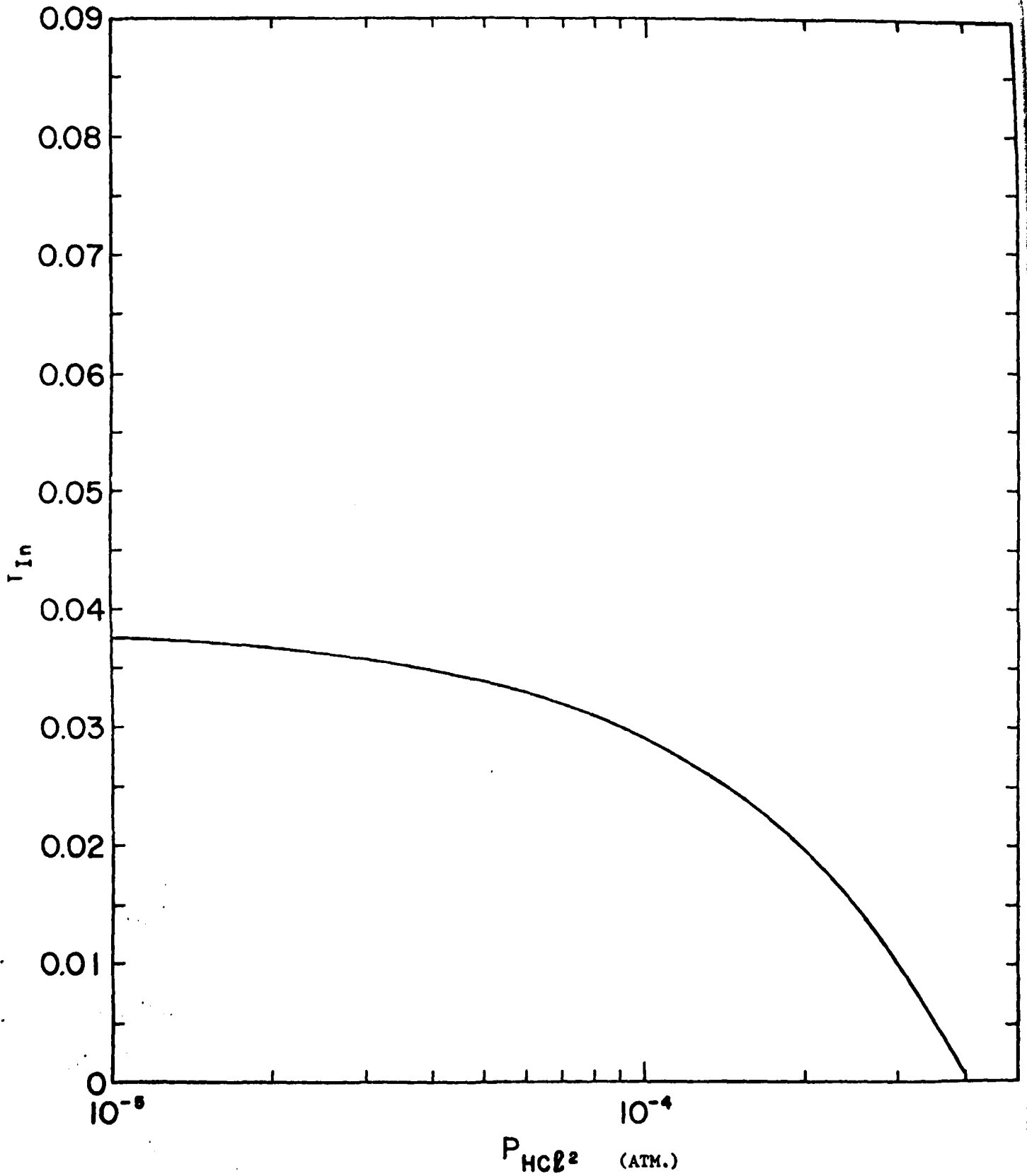


Fig. 16. The fraction of indium deposited,  $f_{In}$ , plotted as a function of the downstream HCl partial pressure,  $P_{HCl_2}$ .

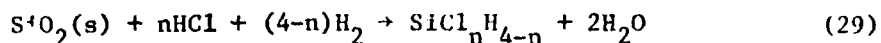
Table 11. The equilibrium InCl partial pressures in the source (INCL1) and deposition (INCL) zones and the fraction of indium deposited,  $f_{In}$ , for different downstream HCl concentrations, HCL2.

TS 850. HCL2	ID 700. INCL1	PH3 101 INCL	HCL0 101 $f_{In}$
.100E-04	.9895E-02	.9526E-02	.0375
.110E-04	.9895E-02	.9524E-02	.0374
.120E-04	.9895E-02	.9525E-02	.0373
.132E-04	.9895E-02	.9526E-02	.0372
.145E-04	.9895E-02	.9527E-02	.0371
.158E-04	.9895E-02	.9529E-02	.0370
.174E-04	.9895E-02	.9530E-02	.0368
.191E-04	.9895E-02	.9532E-02	.0367
.209E-04	.9895E-02	.9533E-02	.0365
.229E-04	.9895E-02	.9535E-02	.0363
.251E-04	.9895E-02	.9537E-02	.0361
.275E-04	.9895E-02	.9540E-02	.0359
.302E-04	.9895E-02	.9542E-02	.0356
.331E-04	.9895E-02	.9545E-02	.0353
.363E-04	.9895E-02	.9548E-02	.0350
.398E-04	.9895E-02	.9551E-02	.0347
.437E-04	.9895E-02	.9555E-02	.0343
.479E-04	.9895E-02	.9559E-02	.0339
.525E-04	.9895E-02	.9563E-02	.0335
.575E-04	.9895E-02	.9568E-02	.0330
.631E-04	.9895E-02	.9573E-02	.0325
.692E-04	.9895E-02	.9579E-02	.0319
.759E-04	.9895E-02	.9585E-02	.0313
.832E-04	.9895E-02	.9592E-02	.0306
.912E-04	.9895E-02	.9599E-02	.0298
.100E-03	.9895E-02	.9608E-02	.0290
.110E-03	.9895E-02	.9617E-02	.0281
.120E-03	.9895E-02	.9627E-02	.0271
.132E-03	.9895E-02	.9638E-02	.0260
.145E-03	.9895E-02	.9650E-02	.0248
.158E-03	.9895E-02	.9663E-02	.0234
.174E-03	.9895E-02	.9677E-02	.0220
.191E-03	.9895E-02	.9693E-02	.0204
.209E-03	.9895E-02	.9710E-02	.0187
.229E-03	.9895E-02	.9729E-02	.0167
.251E-03	.9895E-02	.9750E-02	.0146
.275E-03	.9895E-02	.9773E-02	.0123
.302E-03	.9895E-02	.9797E-02	.0098
.331E-03	.9895E-02	.9825E-02	.0070
.363E-03	.9895E-02	.9855E-02	.0040
.398E-03	.9895E-02	.9886E-02	.0007

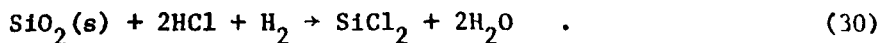
### G. Silicon Contamination

It is thought that one of the primary contaminants in systems grown in silica growth tubes is silicon, and that the silicon activity increases as the HCl concentration decreases. (17,18) This is a consequence of the fact that the HCl discourages the decomposition of the chlorosilanes more than it encourages their formation from reactions with the SiO<sub>2</sub> growth tube. In the previous sections it was shown that the best way to increase the HCl concentration is to increase the source input HCl concentration,  $P_{HCl}^0$ . Thus, computations were made of the silicon activity as a function of  $P_{HCl}^0$  at three different temperatures.

Following the formalism of Dilorenzo (18) and Chaudhury, (17) the activity of silicon is found by examining the formation and decomposition of the silicon chlorides. According to Lever (19) these should include the chlorosilanes and SiCl<sub>2</sub>. The chlorosilanes are formed by the following reaction



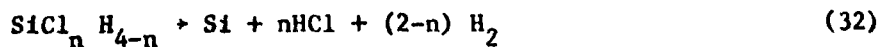
and the reaction for the formation of SiCl<sub>2</sub> is



The sum of the silicon chloride partial pressures is

$$P_{SiCl_2} + \sum P_{SiCl_n H_{4-n}} = (K_{SiCl_2} P_{HCl}^2 P_{H_2} + \sum K_{SiCl_n H_{4-n}} P_{HCl}^n P_{H_2}^{4-n}) / P_{H_2O}^2 \quad (31)$$

For the decomposition reaction



and



the sum of the silicon chloride partial pressures is

$$P_{\text{SiCl}_2} + \sum P_{\text{SiCl}_n \text{H}_{4-n}} = \frac{a_{\text{Si}} P_{\text{HCl}}^2 P_{\text{H}_2}^{-1}}{K_{\text{SiCl}_2}} + a_{\text{Si}} \sum \frac{P_{\text{HCl}}^n P_{\text{H}_2}^{2-n}}{K_{\text{SiCl}_n \text{H}_{4-n}}} \quad (34)$$

where the prime (') is used to differentiate the decomposition reaction from the formation reaction. From an oxygen balance it is seen that

$$\begin{aligned} P_{\text{H}_2\text{O}} &= 2 (P_{\text{SiCl}_2} + \sum P_{\text{SiCl}_n \text{H}_{4-n}}) \\ &= \{2[K_{\text{SiCl}_2} P_{\text{HCl}}^2 P_{\text{H}_2}^{-1} + \sum K_{\text{SiCl}_n \text{H}_{4-n}} P_{\text{HCl}}^n P_{\text{H}_2}^{2-n}]\} \end{aligned} \quad (35)$$

so that

$$a_{\text{Si}} = P_{\text{H}_2\text{O}}/2 \left\{ \frac{P_{\text{HCl}}^2 P_{\text{H}_2}^{-1}}{K'_{\text{SiCl}_2}} + \sum \frac{P_{\text{HCl}}^n P_{\text{H}_2}^{2-n}}{K_{\text{SiCl}_n \text{H}_{4-n}}} \right\} \quad (36)$$

The equilibrium constants are determined using the free energy to absolute temperature ratios computed using the JANAF<sup>(20)</sup> tables, and they are listed in Table 12. The  $P_{\text{HCl}}$  and  $P_{\text{H}_2}$  values are those which are calculated in Section II-D.

The activity of silicon is plotted as a function of  $P_{\text{HCl}}^0$ . There it is seen that  $a(\text{Si})$  decreases as the HCl concentration increases and the temperature decreases. It decreases with increasing temperature both because  $P_{\text{HCl}}$  increases with decreasing temperature and the equilibrium constants change in such a way that for a given HCl concentration,  $a(\text{Si})$  decreases with decreasing temperature. The effects are large as  $a(\text{Si})$

can vary from a high of  $3.9 \times 10^{-3} \text{ cm}^{-3}$  for  $T_D = 1100 \text{ K}$  and  $P_{\text{HCl}^\circ} = .001 \text{ atm.}$  to a low of  $9.1 \times 10^{-8} \text{ cm}^{-3}$  for  $T_D = 900 \text{ K}$  and  $P_{\text{HCl}^\circ} = .1 \text{ atm.}$

(Note that these computations are for °K and not °C as were the previous computations since in this case the JANAF tables were used).

Table 12. The free energy to absolute temperature ratio for the formation and decomposition of the silicon chlorides.

T° (K)	FORMATION						DECOMPOSITION					
	SiClH <sub>3</sub>	SiCl <sub>2</sub> H <sub>2</sub>	SiCl <sub>3</sub> H	SiCl <sub>4</sub>	SiCl <sub>2</sub>	SiClH <sub>3</sub>	SiCl <sub>2</sub> H <sub>2</sub>	SiCl <sub>3</sub> H	SiCl <sub>4</sub>	SiCl <sub>2</sub>	SiClH <sub>3</sub>	SiCl <sub>2</sub>
900	86.810	85.095	74.375	56.779	93.726	6.581	8.284	19.005	36.601	-	-	-
1000	78.962	77.656	68.442	53.241	82.268	3.530	4.826	14.040	29.241	-	-	-
1100	72.582	71.601	63.605	50.358	72.929	1.035	2.007	10.002	23.250	-	-	-

ΔG/T (cal./K)

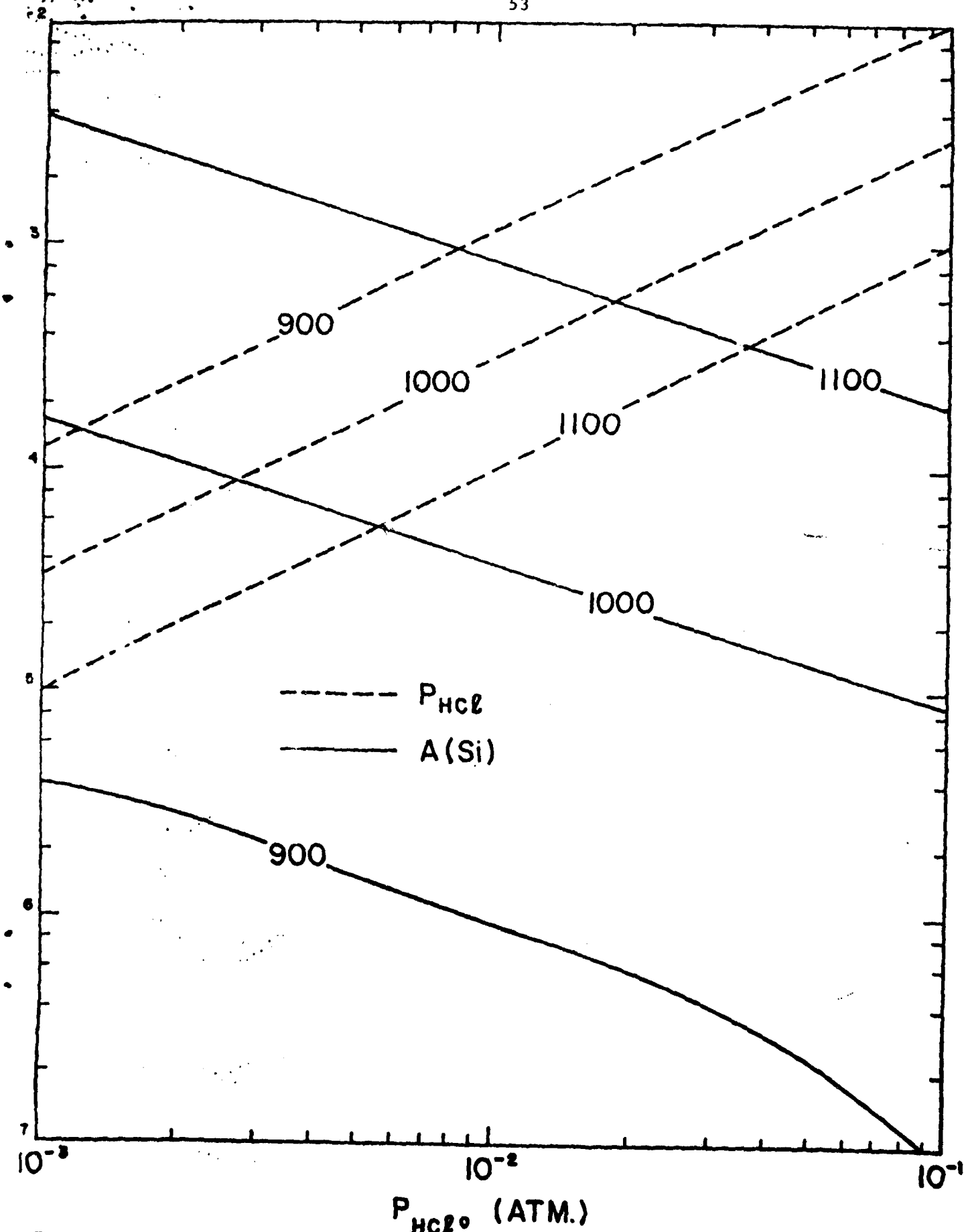


Fig. 17. The equilibrium HCl concentration (----) and the silicon activity,  $a(Si)$  (—), for  $T = 900, 1000$  and  $1100K$  plotted as a function of the source input HCl partial pressure,  $HCl^0$ .

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