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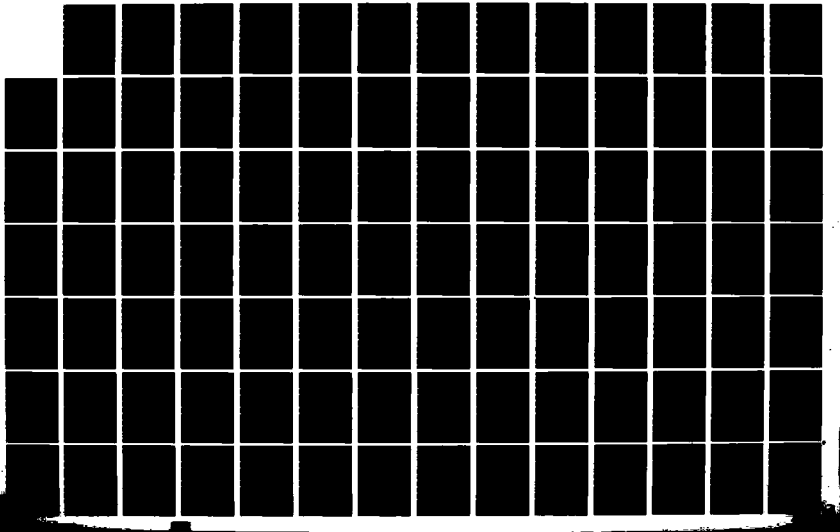

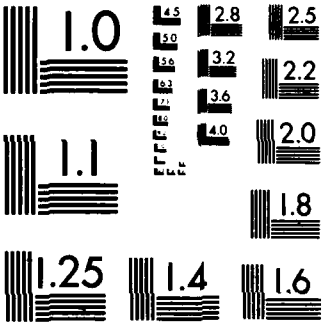

Report AFOSR-81-0164

A COMPARATIVE THERMODYNAMIC ANALYSIS OF IMPURITY INCORPORATION IN VAPOR PHASE EPITAXIAL InP AND GaAs.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The maximum extent of unintentional Si incorporation has been defined for deposition of GaAs and InP by both the chloride and hydride processes. The extents were determined on the basis of constrained chemical equilibrium being achieved in the CVD reactor. The input species consisted of the input gas components and excess condense phases of the group III source material and quartz reactor wall. The work performed included incorporation of a novel psuedo-steady state

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constraint for the liquid source, identifying vapor species not included before, and establishing the vapor composition relation to the point defect structure. The results indicate that Si incorporation levels can be significant. In general, the activity of Si was less in the hydride system and with the compound source in the chloride system. Furthermore, the activity of Si decreased significantly with temperature, small additions of H_2O, HCl or VCl_3 to the mixing zone, and replacing the H_2 carrier gas by an inert in the chloride system. However, the activity of Si displayed a maximum with system pressure and was somewhat insensitive to input composition. Reviews of the literature are included for the thermochemical properties employed and unintentional doping in experimental GaAs and InP VPE films. Algorithms for computing complex chemical equilibrium using both stoichiometric and non-stoichiometric approaches were generated.

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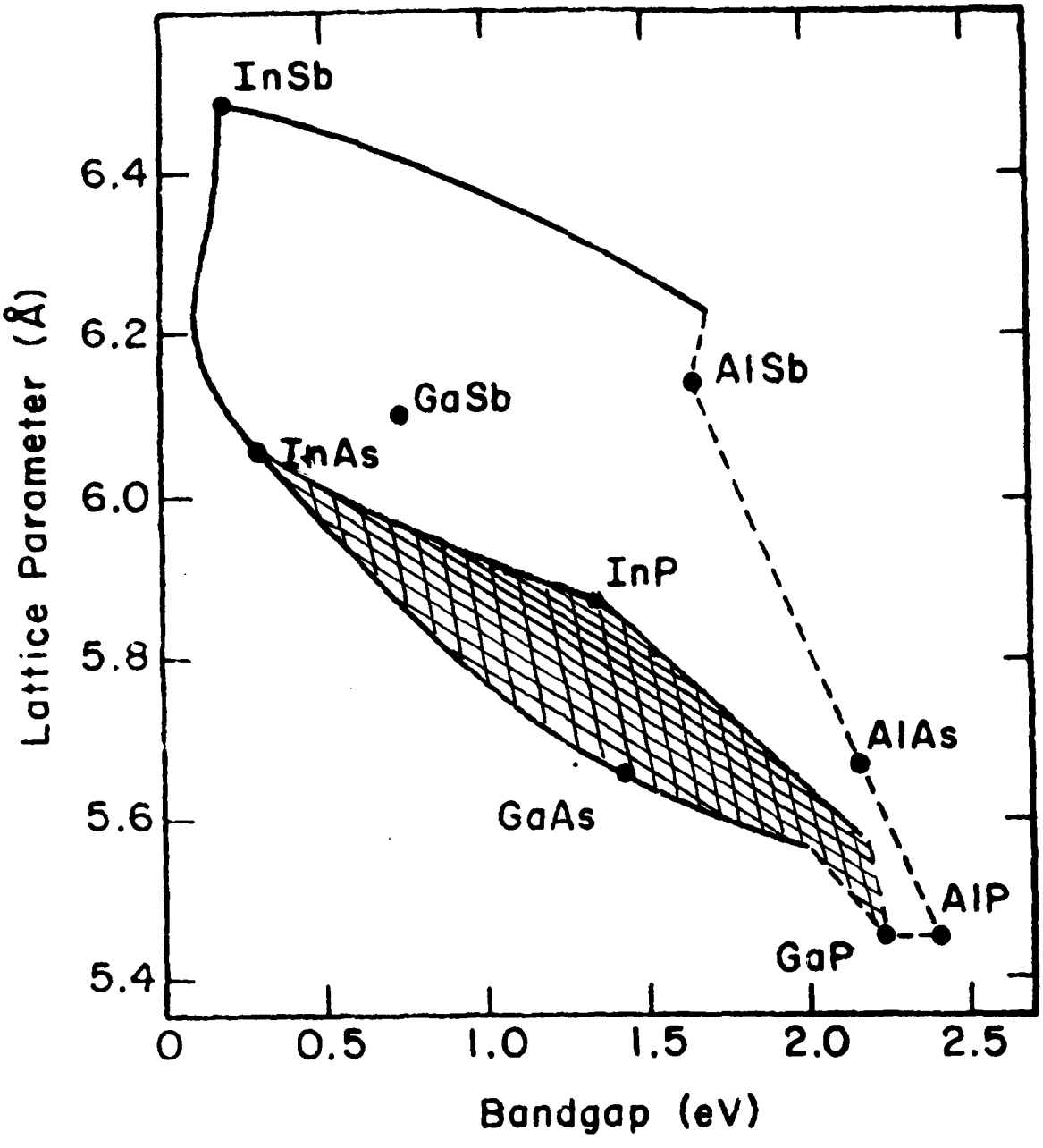
1. INTRODUCTION

1.1 Importance of III-V Materials

The development of the solid-state electronics industry has principally centered around the semiconductor material Si, mainly as a result of its ease of preparation, available high purity, existence of an excellent native oxide and good electrical properties. The explosive growth in semiconductor technology has nurtured a multitude of ingenious solid-state device structures and functions that place an ever increasing demand upon the physical and electrical properties of the host semiconductor material. Although the material Si has satisfied a large number of the requirements for solid-state device applications, there exists no degree of freedom in the inherent electrical properties of this material. Because of this inflexibility, a considerable amount of the current research has focused on the development of alternative semiconductor materials to meet the demands of tomorrow's devices.

In particular, Group III-V compounds and solid solutions are presently receiving intense investigation. The motivation for the research resides in two principal advantages offered by III-V materials: the existence of three degrees of freedom in the properties of the material and improved inherent electrical properties. The first degree of freedom is found in the choice of the base binary system (nine possible compounds with the Group III elements Al, Ga and In and the Group V elements P, As and Sb). While the second and third degrees of freedom are realized as a result of the ability to often form completely miscible substitutional solid solutions on both the Group III and the Group V sublattices independently. Thus, for example, it would be possible to specify a lattice parameter, bandgap energy and thermal conductivity (within a certain range of values) to satisfy the constraints for a given device structure. This point is illustrated in Figure 1.1 which plots the lattice parameter of III-V binary compounds versus the observed room temperature bandgap energy. The solid dots represent binary compounds and the lines connecting each pair represent ternary solid solutions



Lattice parameter of III-V compounds and solid solutions versus bandgap energy.

Figure 1.1

of the two binary limits. Solid lines signify direct bandgap materials while broken lines indicate indirect materials. Essentially, the entire area enclosed in Figure 1.1 is accessible to the designer when employing ternary and quaternary III-V solid solutions. Such flexibility as encountered with III-V materials is extremely useful for optimal design of new solid-state electronic devices. Of interest here is the quaternary system $In_x Ga_{1-x} As_y P_{1-y}$. The available range of lattice parameter and bandgap energy for this system is given by the cross hatched surface shown in Figure 1.1. Thus the lattice parameter and bandgap energy may be specified independently with the composition of the quaternary solution chosen to meet these specifications. The application of one degree of freedom to the lattice parameter is extremely important since currently only GaAs, GaSb, GaP, InP and InSb are available in bulk crystal form for use as substrate materials. A disparity of greater than 0.1% between the lattice parameter of the substrate and epitaxial layer induces the formation of interface defects in the crystal structure which can degrade the device performance. One important application of the quaternary $In_x Ga_{1-x} As_y P_{1-y}$ is in the development of heterojunction lasers for use as transmitters in optical fiber communication systems (11). Currently available optical fibers exhibit minima in attenuation and dispersion characteristics for radiation of approximately 1 eV (11). Choosing the values of x=0.8 and y=0.35 yields an emission energy of ~1.11 eV (12) with a lattice parameter which closely matches that of the InP substrate.

The second advantage III-V materials offer is a general improvement in electrical properties. As examples, Table 1.1 illustrates some measured room temperature electron mobilities, bandgap energies and lattice parameters observed for III-V compounds and for Si (10). This summary indicates that as much as two orders of magnitude improvement can be encountered with the use of III-V compounds over Si and this improvement is extremely important in high speed or high frequency device applications. Thus, in the future, III-V materials are expected to play an increasing role as the host material for semiconductor devices. However, the widespread use of these

materials is currently limited, mainly as a result of technological problems.

Table 1.1

Some Properties of Si and III-V Binary Semiconductors at 300K

	Bandgap		Electron Mobility	Lattice Constant
	Type	Energy (eV)	($cm^2/V \cdot S$)	(Å)
Si	indirect	1.12	1350	5.43
InSb	direct	0.17	80000	6.48
InAs	direct	0.36	33000	6.06
GaSb	direct	0.72	5000	6.10
InP	direct	1.35	4000	5.87
GaAs	direct	1.42	8500	5.65
GaP	indirect	2.26	300	5.45

1.2 Epitaxy of III-V Materials

There exist three primary methods for growing epitaxial III-V films: liquid phase epitaxy (LPE), molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). LPE is the growth of thin single crystal layers from a liquid solution. The driving force (lowering the Gibbs energy of the solid surface below that of the contacting melt) can be provided by a variety of sources such as Peltier cooling and electromigration (electroepitaxy), initial supersaturation (isothermal LPE) and, most commonly, by decreasing the temperature. The advantages of LPE include:

1) The method is capable of growing multicomponent layers with a high reactivity disparity among the elements.
2) The equipment is relatively simple and inexpensive.
3) A large selection of dopants is available.
4) The process is near equilibrium at the surface thus allowing reproducibility.
5) The growth occurs below the film melting temperature.
6) The growth rate can be high.
7) The impurity distribution coefficients are generally favorable ($K < 1$).

There are, however, several drawbacks with LPE. Often there exists the presence of surface defects such as incomplete melt removal, terraces, pinholes, and miniscus

lines. The thickness uniformity can be poor and, for solid solution films, inherent composition gradients are present. Furthermore, LPE is a small scale, batch operation and heteroepitaxy can be difficult.

Molecular beam epitaxy is a method for growing epitaxial thin films of semiconductors by impinging one or more thermal energy beams of atoms or molecules onto a heated substrate under ultra-high vacuum conditions. The distinguishing characteristic of MBE is the slow growth rate ($0.1-2\ \mu m/hr$) that permits precise control of layer thickness, composition and doping profiles. Furthermore, it is possible to achieve spatial resolution not offered by other techniques. As with LPE, the growth temperatures are reduced. In addition, in situ analysis of the surface structure and reaction conditions during growth is possible. However, the equipment is very expensive and the throughput is low.

Commercially the most successful technique for depositing epitaxial semiconductor *films is chemical vapor deposition. Three source chemistries dominate the CVD process for III-V materials: Group III and/or Group V metalorganic (MOCVD), Group V hydride and Group V halide sources. The MOCVD technique involves an irreversible pyrolysis reaction in which a Group III metalorganic gaseous specie is fed to a cold-wall reactor along with a Group V specie (usually a hydride). These species then contact a heated (inductive or radiative) substrate, decompose, and deposit an epitaxial layer onto the substrate.

The focus of this work is with the halide (specifically the chloride) and hydride CVD processes. A schematic representation of the chloride CVD system is shown in Figure 1.2. The reactor consists of source, mixing and deposition zones which are usually operated at 100 kPa pressure. Due to the exothermic nature of the overall deposition reaction, the reactor is hot-wall in design and the temperature of the mixing zone is greater than or equal to that of the source zone while the deposition zone temperature is normally less than that of the source zone. Typically, hydrogen is used as the

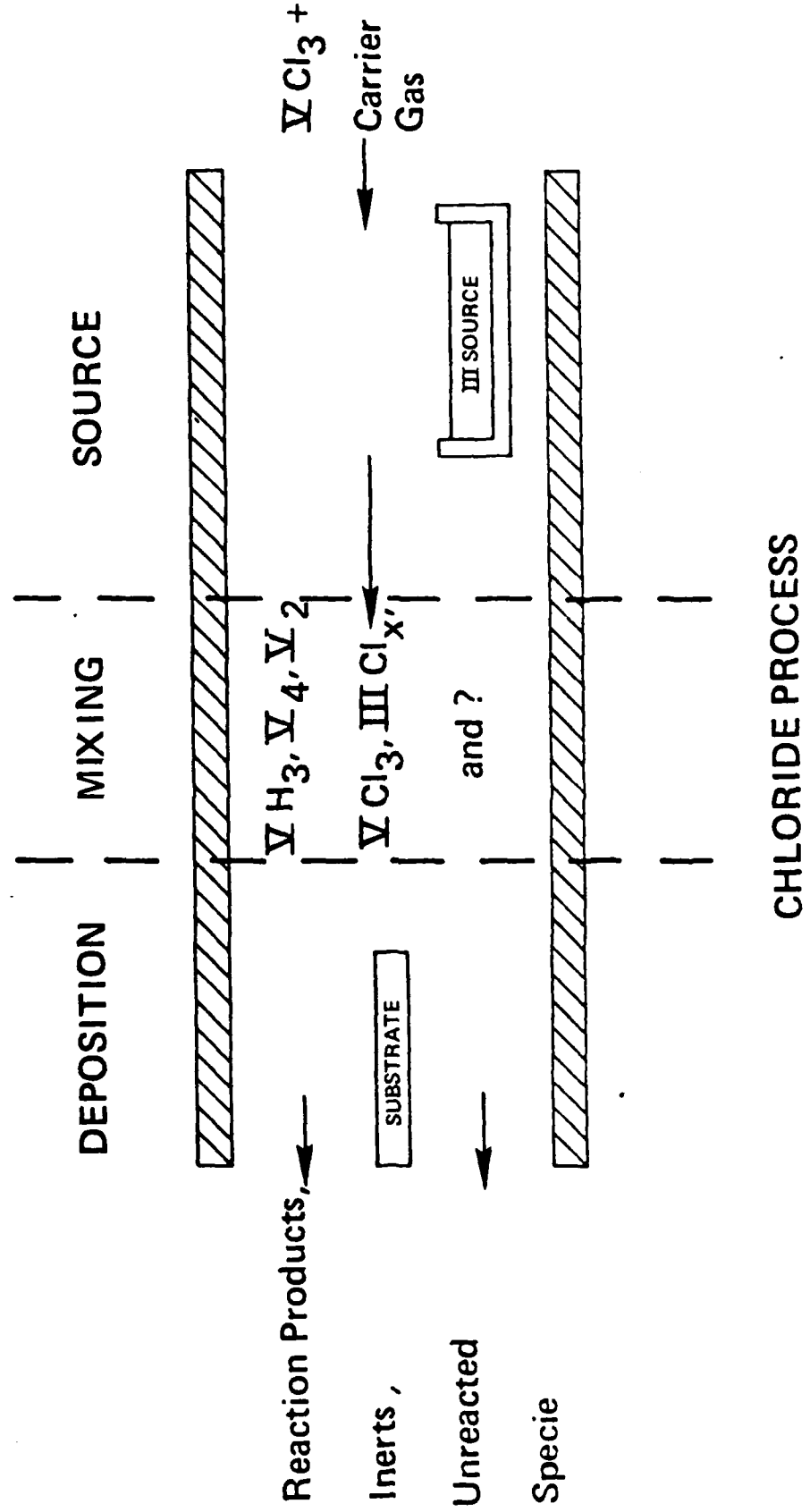
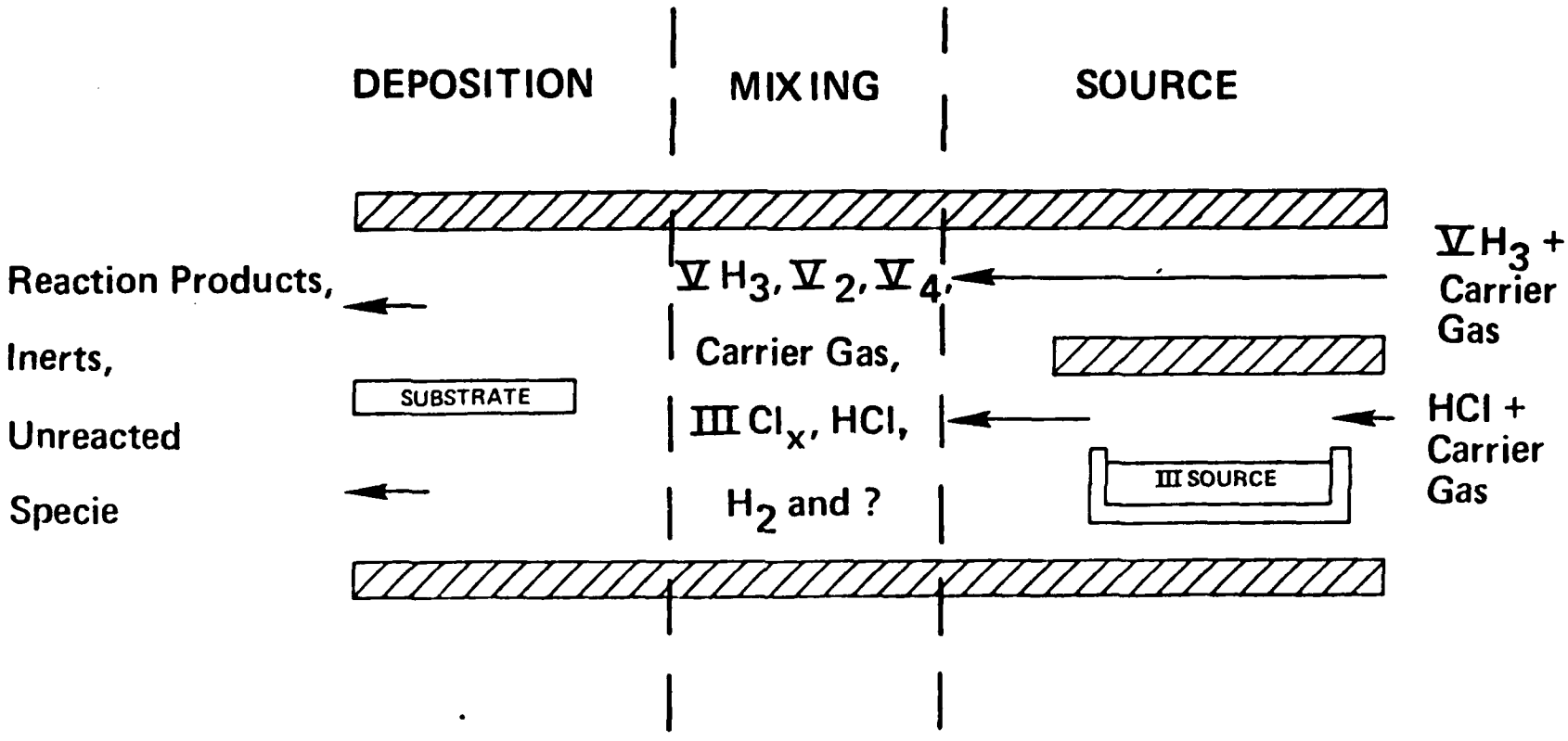

DEPOSITION
MIXING
SOURCE
CHLORIDE PROCESS
V H3, V4, V2
V Cl3, III Clx'
and ?
V Cl3 +
Carrier Gas
III SOURCE
SUBSTRATE
Reaction Products,
Inerts,
Unreacted
Specie

Figure 1.2

carrier gas with the concentration of the Group V chloride in the inlet being on the order of 1 volume percent. The Group III source is either the III-V stoichiometric compound (avoids initial source transient) or the Group III liquid metal saturated with the Group V element (generally available in higher purity). Upon entering the reactor the Group V chloride decomposes (either homogeneously or heterogeneously) to form primarily V_2, V_4 and HCl vapor species. The HCl then reacts with the Group III source to form III-Cl and other higher chlorides. The mixing zone allows the species in the vapor to equilibrate while transporting to the lower temperature deposition zone where the Group III and V vapor species react at the substrate surface to deposit an epitaxial layer. When a liquid Group III source is used the ratio of Group III to Group V atoms in the vapor is fixed at approximately 3 since essentially all of the chlorine atoms on the Group V chlorides react to predominantly form III-Cl. The use of a III-V stoichiometric compound as the Group III source limits the III/V ratio to a maximum value of 1 since one Group V atom is released from the solid for each Group III atom that reacts to form III-Cl.

The hydride CVD process is shown schematically in Figure 1.3. The source zone of the hydride system consists of two mass transfer isolated inputs; one for the Group V specie and one for the Group III specie. The Group V hydride, at a typical inlet composition of 1%, is introduced into the source zone where it decomposes to form primarily V_2, V_4 and H_2. As in the chloride process, the Group III element is transported principally as the mono-chloride by the reaction of HCl (typical HCl inlet concentration is 1%) with the liquid Group III metal. One major advantage the hydride system provides over the chloride system is the ability to vary, in a continuous fashion, the vapor III/V ratio by simply adjusting the input compositions or flowrates of VH_3 and HCl. Typically the source and mixing zones in the hydride system are operated at higher temperatures than those of the chloride system in order to increase the rate of VH_3 thermal decomposition (the decomposition kinetics of VH_3 are much slower than VCl_3). Again, hydrogen is usually used as the carrier gas and the mixing and deposition zones



HYDRIDE PROCESS

Figure 1.3

provide functions equivalent to those in the chloride system. Indeed, the equilibrium chemistry of the two systems are identical after the source zone.

Both the chloride and hydride systems are hot-wall designs (heating from the outside of the reactor tube by conduction). Therefore, interactions between the vapor phase and the reactor wall (usually quartz) can be thermodynamically favorable and not kinetically limited for the introduction of impurities into the vapor. The gas flowrates through these reactors are generally small (Re ~ 10) such that the flow is decidedly laminar.

An understanding of the chemistry involved in the chloride and hydride CVD processes is essential in order to advance these technologies. The complex chemical equilibrium analysis of these systems developed in this study identifies the principal vapor phase species which must be accounted for in order to understand these CVD systems. The influence these species exert on the point defect structure of the epitaxial layers is discussed and the importance of these defects as undesired dopants is evaluated. This analysis also provides information regarding the degrees of supersaturation expected in the deposition zones and suggests methods for reducing the unintentional incorporation of silicon in III-V epitaxial layers. Both the chloride and hydride processes were investigated for the deposition of homoepitaxial GaAs and InP and thus allow direct comparisons to be made.

2. REVIEW OF THE LITERATURE

2.1 Impurities in GaAs and InP Epitaxial Films Grown by the Chloride Process

The feasibility of applying the chloride system CVD technique to the epitaxial growth of high purity GaAs was first demonstrated by Knight et al. [16] and Effer [17]. Initially, the commercially available $AsCl_3$ contained sufficient impurities to cause significant contamination of the epitaxial layers and therefore the purity of the feed materials was believed to be the controlling factor for this system [19]. As better quality $AsCl_3$ became available Cairns and Fairman [20,21] and DiLorenzo et al. [22] found that an increase in the $AsCl_3$ mole fraction in the inlet gas stream resulted in a decrease in unintentional impurity incorporation in the epitaxial layer.

For materials grown in their laboratory, DiLorenzo and Moore [23] identified the primary unintentional dopant as being silicon, through the use of photoluminescence spectra. Further, they proposed a thermodynamic model for the generation of vapor phase chlorosilanes as a result of the interaction of HCl with the quartz (SiO_2) reactor wall and presented an expression for the activity of solid silicon (i.e. as an impurity) as a function of the partial pressures of the chlorosilanes. Their model showed that increasing the vapor HCl concentration (e.g. as a result of $AsCl_3$ decomposition) decreased the condensed phase silicon activity by further stabilizing the silicon species in the vapor phase in the form of chlorosilanes. Additionally, their model predicted that the generation of vapor phase silicon species could be suppressed by the introduction of H_2O in the vapor.

Rai-Choudhury [27] performed a thermodynamic analysis on the incorporation of silicon into GaAs epitaxial layers. His results reflected those of DiLorenzo and Moore [23] when considering the effects of H_2O and HCl but he also showed that higher temperatures increase the amount of vapor phase silicon species.

The work of Ashen et al. [26] further supported the conclusion that silicon was an impurity in GaAs. A BN lined reactor was used to grow epitaxial layers from liquid Ga

sources which were doped with Si. Comparing the electrical characteristics of these epi-layers to layers grown from pure Ga sources provided qualitative evidence for the presence of Si in GaAs. The effect of $AsCl_3$ concentration on the amount of Si incorporated into the epi-layer was also verified by their experiments. Additionally, they provided evidence which indicated that Si was much more likely to reside on a Ga site than an As site and therefore behaves as a donor. This conclusion was also supported by Beiden et al. [29].

Wolfe, Stillman and Korn [24] have identified, through intentional doping and determination of ionization energies, three unintentional impurities, Si, C and one unknown (possibly Te), in GaAs grown by the chloride CVD system. Also, due to concerns over oxygen possibly being a shallow donor in GaAs [25], they attempted to dope the epitaxial layer with oxygen by adding Ga_2O_3 to the liquid gallium source. The oxygen, however, was not incorporated into the epitaxial layer but the presence of oxygen in the system did reduce the amount of unintentional silicon which was incorporated into the epitaxial layer. This reduction in background doping due to the presence of oxygen was also investigated by Palm et al. [28] by injecting a hydrogen-oxygen mixture into the mixing zone of a chloride system CVD reactor. Using silane as an intentional dopant the presence of oxygen was found to reduce the incorporation of silicon in the epitaxial layers by as much as four orders of magnitude.

Seki et al. [33] performed a thermodynamic analysis of the GaAs chloride process in order to identify the effects of inerts, HCl and substrate temperature on the activity of silicon in the epitaxial layers. They found, in agreement with others, that increasing the HCl content or decreasing the substrate temperature lowered the silicon activity. They also found that replacing the hydrogen carrier gas with an inert caused a very large reduction in the silicon activity.

The effect of replacing the hydrogen carrier gas with an inert was investigated by Ozeki et al. [34]. They found, through far infrared photoconductivity measurements,

that sulfur was the dominant residual donor present in epitaxial GaAs when N_2 was used in place of H_2 as the carrier gas. They also found that the dominant residual donor when H_2 was used as the carrier gas was sometimes Si and sometimes S. A possible source of S in the system was not discussed (although it was presumably in the feed gases) and elaboration on the growth conditions which caused Si or S to be dominant was not provided.

A thermodynamic analysis of the chloride CVD system performed by Boucher and Hollan [30] assumed solid GaAs as the Group III source material. They concluded, by comparison with experiment, that the dominant Group III and Group V species present in the vapor were GaCl and As_4. They further found that the deposition process was kinetically controlled with an activation energy of ~ 40 kcal mol^{-1}, and that reproducible growth conditions could only be assumed if 10% or less of the thermodynamically available GaAs was deposited in the vapor phase.

Gentner, Bernard and Cadoret [31] also studied the chloride process thermodynamically and experimentally but over a greater range of temperature, pressure and inlet $AsCl_3$ composition than did previous investigators. They found that As_2 became the dominant Group V specie below 10 kPa pressure and that GaCl was always the dominant Group III specie. At large $AsCl_3$ inlet compositions the higher gallium chlorides became more pronounced but never competed with the monochloride as the dominant specie. They concluded, based on Cadoret's [32] kinetic model, a mass transfer model and experimental results, that the deposition of GaAs was kinetically rather than mass transfer controlled.

Shaw [7] studied the transport kinetics of the GaAs chloride system in the source and deposition zones. He found an activation energy of 49.1 kcal mol^{-1}, in reasonable agreement with that of Boucher and Hollan [30], for a surface reaction associated with the deposition process.

The epitaxial growth of homoepitaxial InP using a chloride CVD system was first

demonstrated by Joyce et al. [40] and later by Hales et al. [41]. Both groups of investigators reported limitations on the purity of their epitaxial layers due to unintentional dopants. Joyce and Williams [42] tentatively identified the impurities as being Si and/or Zn acceptors. They also found evidence of a donor which was thought to be amphoteric Si.

The dependence of unintentional doping on PCl_3 mole fraction in the InP chloride system was first reported by Clarke [43]. The similarity between the GaAs and InP chloride system reactors combined with the analogous dependencies on the Group V hydride mole fraction supported the belief that Si was an impurity in InP epitaxial layers. Clarke [44] later studied the effect of III/V ratio in the vapor phase on the unintentional doping of InP epi-layers and found p-type conductivity for III/V < 3 and n-type for III/V > 3, with a minimum in the free carrier concentration at III/V ≈ 3. No explanation was offered for these observations.

Easton [45] investigated the unintentional doping of InP epitaxial layers grown by the chloride system and concluded that sulfur (acting as a donor) was the major impurity and that the origin of the sulfur was the PCl_3 liquid source. Using mass spectrometric analysis Easton found Si, S and Zn present in the PCl_3 source at levels between 1 ppm and 10 ppm (atomic) and Fe, Cu, Cd and Sn at ~ 0.7 ppm. These same elements were found in the unused bulk In liquid at levels below 0.1 ppm. Analysis of the used In source liquid revealed impurity levels approximately 10 times larger than those in the unused liquid.

These results support the work of Weiner [9] who proposed models for the contamination of a Ga liquid source by Si in the GaAs and GaP systems. Weiner's results showed that the liquid Group III metal impurity level increased as the exposure to the CVD environment increased. He also found the level of Si contamination to be inversely related to the partial pressure of H_2O in the system.

Fairhurst et al. [46] studied the InP halide system using both PCl_3 and PBr_3. They

found that oxyhalide salts were present in both phosphorous liquids at approximately the 100 ppm level. The presence of oxygen was expected to decrease the level of impurity incorporation in the epitaxial layers. This effect was not observed however, presumably due to this level of oxygen contamination being too low to be significant. Equilibrium calculations were performed which showed InCl and P_4 to be the dominant Group III and V species in the vapor over a temperature range of 850 K to 1150 K and an inlet PCl_3 mole fraction range of 0.1% to 6%. These results agreed with those of Boucher and Hollan [30] for the analogous GaAs system.

Hales and Knight [47] investigated the effect of introducing oxygen into the system in order to reduce the level of impurities in InP. They observed a monotonic decrease in free electron density for additions of O_2 up to 24 ppm. The electron mobility (measured at 77 K) however reached a very broad maximum at approximately 16 ppm of added oxygen, which suggests that oxygen was becoming incorporated into the epitaxial layer and that there is a limit to the degree of benefit which may be obtained through oxygen addition. They also observed $POCl_3$ to be an impurity in the liquid PCl_3 used in the chloride system.

Investigations of the dependence of impurity incorporation on PCl_3 inlet composition, total flowrate and deposition zone temperature were carried out by Chevrier, Huber and Linh [48]. They observed a decrease in free carrier concentration with increasing PCl_3 concentration, as did other investigators, but also found that the impurity concentration increased with increasing total flowrate. This velocity effect had not been reported before and suggests the presence of a mass transfer resistance at the Group III source (if impurities are picked up from the liquid metal) and/or at the substrate in the deposition zone. They also studied the intentional doping of InP as a function of deposition zone temperature using $SnCl_4$. Lower free electron concentrations and higher electron mobilities were observed when the deposition zone temperature was decreased from 950 K to 910 K. Thus, the uptake of Group IV impurities (Sn, Si, etc.) was apparently reduced by lowering the deposition zone temperature.

Cardwell et al. [49] found kinetic limitations in both the source and deposition zones. The previously reported effect of PCl_3 mole fraction on impurity levels in the epitaxial layers was observed. Intentional doping of InP using Sn followed the same behavior as that of unintentional dopants and therefore supports the use of Sn for studies regarding the reduction of unintentional impurities. In contrast to Chevrier et al. [48] no dependence of impurity uptake on total flowrate was found.

A thermodynamic analysis comparing the GaAs and InP chloride systems using the stoichiometric III-V solid as the Group III source material was reported by Shaw [50]. His results also confirmed GaCl, As_4, InCl and P_4 to be the dominant Group III and V vapor species in these systems. Further, the degree of supersaturation in the deposition zone was calculated to be less for InP than for GaAs under analogous conditions. Since solid III-V source materials were employed etching conditions were predicted whenever the deposition zone temperature was greater than that of the source zone.

2.2 Impurities in GaAs and InP Epitaxial Films Grown by the Hydride Process

The feasibility of the hydride CVD system for the growth of high purity GaAs was demonstrated by Enstrom and Peterson [18]. Since the hydride system consists of a hot-wall quartz reactor with the elements H, Cl, Ga and As present in the vapor one would expect it to show an unintentional impurity incorporation problem similar to that of the chloride system. Pogge and Kemlage [35] investigated the effects of HCl, AsH_3 and PH_3 on the unintentional doping of GaAs and GaP grown by the hydride system. They found that the free carrier concentration decreased with increasing HCl, AsH_3 or PH_3 composition. The effect of HCl was less than that of the Group V hydrides and changes in PH_3 showed larger effects than did AsH_3. They concluded that the HCl effect on the vapor phase composition was similar to that of the chloride system. Further, they concluded that As_4 and P_4 caused blocking of the available surface sites on the substrate surface due to the large size of these molecules. The unintentional dopant was assumed to be Si generated from reactions with the quartz wall.

Kennedy, Potter and Davies [36] investigated the effect of HCl inlet composition and additions of HCl downstream of the source zone on the unintentional doping of GaAs grown in a hydride CVD reactor. They found that increasing the HCl inlet composition (by decreasing the H_2 carrier gas flowrate) greatly reduced the free carrier density in the epitaxial layer. In contrast to this result, however, when HCl was added downstream of the source zone the free carrier density was found to increase. This led to the conclusion that the equilibrium model as proposed by DiLorenzo and Moore [23] for the chloride system was not applicable to the hydride system. However, the HCl which was injected may not have been as pure as that which was generated from the decomposition of $AsCl_3$ in the chloride system and therefore may have introduced additional impurities into the epi-layer.

The problem of obtaining sufficiently pure HCl for use in the hydride system was addressed by Enstrom and Appert [37]. When the HCl tank was cooled in dry ice and the "light" impurities were bled out of the tank, the purity of epitaxial GaAs layers grown with this HCl was found to increase significantly. Using photoluminescence measurements they found C, Be, Zn or O, Si, Mn and Cu in epitaxial GaAs grown with HCl before the HCl cylinder was cooled and bled. Epitaxial GaAs layers grown after the cooling and bleeding procedure displayed essentially unchanged Zn and Si concentrations but the other previously found impurities were undetectable.

The work of Skromme et al. [38] identified some of the unintentional donors and acceptors present in GaAs and InP prepared by the hydride CVD system. They found C, Zn, Cu and Mn as acceptors and Si, S and Ge as donors in GaAs. Epitaxial InP was found to contain Zn, C or Mg and an unidentifiable acceptor along with Si and S as donors. Additionally, in one of the laboratories (Honeywell) where the epi-layers were grown an increase in the impurity concentration in epitaxial GaAs was noted as the HCl gas cylinders "aged". This effect, however, was not observed at the other (Hanscom AFB) laboratory.

The effect of pressure was studied experimentally by Putz et al. [39] from 1 kPa to 100 kPa. They found that the unintentional doping of GaAs was reduced at pressures below 100 kPa.

Growth of InP epitaxial layers using the hydride system has been demonstrated by Olsen [51] and Hyder [52] among others. Both of these investigators observed unintentional impurity incorporation similar to that occurring in the GaAs system. Hyder also found that for the ternary $In_xGa_{1-x}As$ (x=0.53) a maximum in electron mobility occurred when the III/V ratio in the vapor phase was approximately 2 but the effect of III/V ratio on free carrier concentration was not discussed. Zinkiewicz et al. [53] also studied the growth of InP and the ternary $In_xGa_{1-x}As$ in the hydride system. They found Zn, Cu and Hg to be present as unintentional donors.

Anderson [54] studied the hydride system for InP growth in order to determine the effect of HCl mole fraction, H_2 flowrate and mixing zone temperature on unintentional impurity incorporation. He found that these parameters caused only minor changes in the electrical characteristics of the InP epitaxial layers. This suggests that the InP hydride system may perform somewhat differently than the GaAs hydride system.

Jones [55] performed a thermodynamic analysis of the InP hydride system in order to understand the effect of process parameters on unintentional silicon incorporation. The calculations predicted that decreasing temperatures lowered the silicon activity in the epitaxial layer. Additionally, the silicon activity was decreased by increasing the PH_3 and/or HCl inlet composition. Very little effect was noted when HCl was added downstream of the source zone. His analysis used liquid In as the Group III source material and showed InCl and P_4 to be the dominant Group III and V vapor species.

Bans and Ettenberg [56] coupled a mass spectrometer to a hydride system reactor used for the growth of $In_xGa_{1-x}P$. They compared measured vapor species to those predicted by a thermodynamic model and concluded that the model yielded an acceptable representation of the system. The major shortcomings of the model were

an overprediction of the amount of InCl generated from the heterogeneous reaction of HCl and In liquid, and a predicted greater degree of dissociation for PH_3 than was measured. Due to the known slow decomposition kinetics of PH_3 and the potential mass transfer and kinetic limitations associated with heterogeneous reactions these discrepancies were not surprising. Their mass spectrometric measurements identified the major vapor phase species as being InCl, GaCl, HCl, PH_3, P_2, P_4 and H_2.

Usui and Watanabe [57] investigated the effects of temperature and oxygen additions on the unintentional doping of hydride grown InP. Additions of O_2 in the 1 ppm to 10 ppm range decreased the free carrier concentration about one order of magnitude but further additions caused the free carrier concentration to increase, presumably due to uptake of oxygen by the epitaxial layer. The liquid In source that was used in these experiments was found to have a gettering effect on impurities in the inlet gases. Unused In showed less than 1 ppm levels of Si, S, Sn, Te, Zn, Fe and Cu while In exposed to the CVD environment contained increased levels ($\sim$ 2 ppm) of Fe, Cu and Sn. Increasing the source zone temperature caused a decrease in the free carrier concentrations in InP epi-layers due to an increased ability of the In liquid to getter impurities at high temperature. Thus, the purity of source gases still appears to be a major problem in the hydride system.

3. METHOD OF CALCULATION FOR COMPLEX CHEMICAL EQUILIBRIUM

The calculation of complex chemical equilibrium in multicomponent, multiphase systems has been reviewed most completely by Smith [1]. Essentially, there are two statements of the solution to this problem. Nonstoichiometric methods, such as the popular Rand algorithm [2], directly minimize the Gibbs energy of the total system in order to obtain a solution without recourse to a specific set of formation reaction equations. Stoichiometric methods [3] require that an independent set of chemical reactions be in equilibrium. Generally a formation reaction is written for each specie present in the system and the corresponding equilibrium constant for each reaction is generated from the Gibbs energy change of the reaction.

An extension of the Rand algorithm to include not only a gas phase with an inert specie, but also a multicomponent solution and pure condensed phases is presented in Appendix A. This extension, which was suggested in the original research proposal [4], was initially applied to the hydride and chloride CVD systems but was susceptible to finding local minima. In particular, component mole fractions were sought as low as 10^{-10}. The contribution to the system Gibbs energy for these components is then quite small and the resulting component mole changes were not capable of releasing the Gibbs energy of the system from the local minima.

A stoichiometric algorithm, presented in Appendix B, was therefore developed which was superior to the extended Rand algorithm since a linearized Gibbs energy function was not required and dilute components were required to satisfy equilibrium reaction constraints. The stoichiometric algorithm performed well for all of the systems studied (comparison to standard literature calculations and independence with respect to initial guesses) and yielded results which were in agreement with those of the extended Rand algorithm, when successfully applied (~ 95% of the cases examined). Also, the amount of computer memory required for the stoichiometric algorithm was found to be much less than that required by the extended Rand algorithm in order to

solve identical systems.

The input data which was required in order to perform the calculations consisted of the standard enthalpy and entropy of formation and heat capacity for each specie along with the constraints of system temperature, pressure and inlet composition.

Aside from numerical difficulties, there are two major factors which must be considered in determining the overall accuracy of the calculated equilibrium compositions: 1) the choice of species postulated to be present in the system and 2) the accuracy of the thermodynamic data chosen for each specie. Choosing an appropriate set of species which accurately represent the system at equilibrium is an inherent difficulty in the calculation of multicomponent equilibrium. A true calculation of equilibrium in a given system would require the inclusion of any chemical specie which may be formed from any combination of the elements present in the system. The compilation of such a complete thermodynamic data base can represent a nearly impossible task, even for systems consisting of only a few elements.

It is important to realize that anytime a possible specie is not included in the data set a constrained equilibrium calculation will result. This is most easily understood if the calculation of chemical equilibrium is considered from the viewpoint of the Rand algorithm. In the Rand algorithm multicomponent equilibrium represents the optimal distribution of a given quantity of elements among a set of chemical species. The optimizing function for a constant pressure system is the minimization of the total Gibbs energy. Therefore, as the number of available chemical species is decreased the elements are constrained to reside in a smaller selection of molecules. This causes a shift in the calculated compositions in order to satisfy the atom balance while keeping the Gibbs energy of the system as low as possible. In general, the exclusion of a specie will impact the equilibrium composition of the remaining species containing similar atoms that are in the vicinity or below the equilibrium composition of the excluded specie.

The procedure for developing a specie list first excludes those species not expected to be present because of severe kinetic limitations. In practice this specie set is developed by including only those species which have been experimentally observed in the system or for dilute systems, in constrained subsystems. For example, mass spectroscopic work in the CVD of GaAs has indicated approximately 10 species but observations in the subsystem Si-H-Cl indicates approximately 15 additional species. The next step consists of generating an initial thermodynamic data base for all species. In practice this includes the sources: thermodynamic compilations, data bases of other investigators for similar systems and crude estimates for the remaining species. An initial equilibrium calculation is then performed at the extreme conditions and those species whose composition is more than ~ three orders of magnitude in mole fraction below the range of interest are excluded. Finally, the initial thermodynamic data base is fully developed by reference to the literature and the performance of internal consistency tests.

The sensitivity of the results to errors in the thermodynamic data was investigated by Smith [5] in terms of a Jacobian which relates the changes in the calculated results to changes in the input parameters. The first order approximation to the result was

$$|\delta n_i| < \sum_{j=1}^{N} \left| \frac{\partial n_i}{\partial \mu_j^o} \right| \delta \mu_j^o| \tag{3.1}$$

Here, n_i is the number of moles of specie i present, μ_j^o is the standard chemical potential of specie j and N is the total number of components. This expression, while simple in form, is extremely difficult to evaluate due to the complicated and implicit nature of the function $n_i(\mu_j^o)$ for all values of i. If problems seem apparent for some species this function can be numerically evaluated. The work of Sirtl and Hunt [6] and similar calculations performed here (Section 5) showed by means of a calculated example the effects of changes in the enthalpy of formation of $SiHCl_3$ on the predicted equilibrium ratio of $SiCl_4/SiHCl_3$. This ratio was found to change by approximately two orders of

magnitude for a 10% change in enthalpy of formation. The shape of the curve relating this ratio to temperature was also found to change markedly. Therefore, it is extremely important to critically review the thermodynamic data set in order to perform meaningful equilibrium calculations. The absolute composition of the calculated solution can be no better than the data set employed. Extreme care must also be used when comparing equilibrium compositions to experimental process compositions as the latter include possible kinetic limitations. However, these calculations are of great value in predicting directions of composition change or function process constraints, particularly at the high temperatures and low pressures encountered in this study.

4. THERMODYNAMIC MODELS OF CVD

4.1 Models for the CVD Source and Pre-Source Zones

The CVD system is naturally segmented on the basis of temperature or composition into four equilibrium zones: the pre-source, source, mixing and deposition regions. The pre-source zone was investigated as a source of Si by considering the equilibrium gas phase Si-content in the system: $SiO_2(c)$ in excess, carrier gas (H_2 or inert) and vapor reactant (VH_3, VCl_3 or HCl). As the activity of Si(c) monotonically increased with increasing temperature, an uniform temperature equal to the source zone was used for a "worst" case calculation.

For the chloride process two different Group III source materials are generally employed (IIIV(c) and $III(l)$) and thus required two separate formulations of a model. In the pre-source zone, there is no "sink" (i.e. condensed phase) for the elements in vapor input compounds and $SiO_2(c)$ is in excess while the source zone in both situations also had $SiO_2(c)$ in excess. Thus, the equilibrium activity of Si is independent of the pre-source results. For the III-V(c) chloride source zone the model considered the inputs $SiO_2(c)$ in excess, III-V(c) in excess, carrier gas (H_2 or inert) and $VCl_3(g)$ as a function of temperature, pressure and input vapor composition.

For the chloride process using Group III(l) as the Group III source material the situation is somewhat more complicated. Shaw [7] has studied this source zone and found that, following an initial transient, a constant rate of mass loss of material occurred. An overall mass balance on the source boat yields the following expression:

$$\frac{d}{dt}\left[\frac{1}{2}\,n^c(M_{III}+M_V)+n^l(xM_{III}+(1-x)M_V)\right]=\dot{n}^V(yM_{III}+(1-y)M_V)=\text{constant} \qquad (4.1.1)$$

while a Group III component mass balance on the source boat produces the constraint:

$$\frac{d}{dt}\left[\frac{1}{2}\,n^c M_{III}+n^l xM_{III}\right]=\dot{n}^V yM_{III} \qquad (4.1.2)$$

In these expressions: n^c and n^l are the moles of the solid source GaAs crust and of the liquid III-V mixture, respectively, M_{III} and M_V are the molecular weights of the Group III and V elements, x and y are the mole fractions of the Group III element in the liquid and vapor phase, respectively, and $\dot{n}^V$ is the molar rate at which vapor species are formed on an atomic basis. If it is assumed that the solid and liquid phases are in equilibrium the liquid phase mole fraction is a function of temperature only and therefore constant for a given process condition. Furthermore if the actual kinetic processes produce a steady state value of the crust thickness the first term on the left side of both equations is zero. With these assumptions, equations (4.1.1) and (4.1.2) can be solved to show that $\dot{n}^V = \frac{dn^l}{dt}$ and x=y. That is, the rate at which Group III and V atoms are introduced into the vapor phase is equal to the rate of loss for the melt and the vapor composition is the same as that in the melt. Another way of viewing the situation is to consider the three phase equilibrium problem. The activity of the Group III and V elements in the solid compound can vary to a large degree though the stoichiometry (~ 1:1) can be very small and therefore the sum of these two activities is nearly constant. The large amount of melt in equilibrium with the solid will, however, fix the activity of each element in the solid, with the Group III activity being considerably higher than the Group V one, which in turn fixes the vapor phase fugacity. In the event that the assumption of constant crust thickness is not valid the dn^S/dt terms in equations (4.1.1) and (4.1.2) must be retained and solution results in

$$\dot{n}^V = \text{constant} = \frac{(2x-1)}{2(x-y)}\frac{dn^c}{dt} = \frac{(2x-1)}{2y-1}\frac{dn^l}{dt} \qquad (4.1.3)$$

The limit that $\frac{dn^l}{dt} = 0$ implies that $y = 1/2$ and the source can be considered to be pure solid compound. This limit is simply the first case examined (solid compound source). Thus an investigation of the two source zones described here should establish the limits of operation for the liquid source in the chloride process. In practice, the conditions of operation may lie somewhere in between with the observed III/V

ratio providing an indicator of the relative rates. However, if x is a constant as determined by the condition of solid-liquid equilibrium and y is also a constant as witnessed by a constant growth rate, it follows that both $\frac{dn^l}{dt}$ and $\frac{dn^c}{dt}$ are constant. If dn^l/dt is dependent upon the crust thickness, n^c, (i.e. a diffusion limited process) then it is impossible for dn^l/dt to be constant for a finite value of dn^c/dt, which implies operation at one of the limits.

The above considerations motivated a model for the liquid Group III source zone to consist of an ideal vapor phase in equilibrium with excess $SiO_2(c)$ and $III_x V_{1-x}(l)$. The gas input stream contained VCl_3 and carrier gas (H_2 or inert). The development of a thermodynamic data set for the hypothetical specie $III_x V_{1-x}(l)$ is presented in Section 5.2. Thus, with this formulation, the compound crust does not contribute elements to the system.

Two source zones, one for the thermal decomposition of the Group V hydride and one for volatilization of the Group III liquid, are found in the hydride CVD process. The Group V source zone was modeled as an ideal vapor phase in equilibrium with excess $SiO_2(c)$. The input gas reactants were the hydride (VH_3) and carrier gas (H_2 or inert) at a constant temperature and pressure. The Group III source zone included excess pure Group III liquid in equilibrium with excess $SiO_2(c)$ and an ideal vapor phase (HCl plus carrier gas).

4.2 Models for the CVD Mixing and Deposition Zones

Since the only differences between the chloride and hydride systems exist in the source regions the mixing and deposition zone models were identical in both systems. An ideal vapor phase in equilibrium with excess $SiO_2(c)$ was used for the mixing zone model. Formation of solid III-V compound was postulated to be kinetically hindered and thus assumed not to exist in the mixing zone. As a result it was possible for this region to be supersaturated. The model also allowed the addition of various species (i.e. HCl, H_2O, VCl_3, VH_3) in order to study their effects on silicon activity. The gas

reactant input for the mixing zone was identical to that calculated from the equilibrium source zone(s). Consistent with the source and mixing zone models, the vapor phase of the deposition zone was assumed to behave ideally. Due to the large volumetric flowrate of gases and the relatively small deposition rates in these CVD processes, the depletion of Group III, Group V and silicon species in the vapor phase as a result of film deposition or wall interaction was neglected. The equilibrium mixing zone gas mixture serves as the input to the deposition zone. Essentially, the above assumption fixes the gas phase atom numbers and the new equilibrium composition is produced as a result of a temperature change only. This model therefore provides an upper bound for the computed value of the Si activity. A lower temperature would shift the wall interactions towards $SiO_2(c)$ formation while including the compound deposition with Si incorporation would remove Si from the gas phase. In addition, this would be enhanced by chlorine atom production. This model, therefore, assumes that the epi-film grows from a supersaturated vapor mixture of pseudo-steady state properties. Furthermore this procedure avoided having knowledge of the silicon activity coefficient. In order to implement this model the III-V solid phase was not included in the deposition zone, thus allowing calculation of the degree of supersaturation in this zone.

The effect of not accounting for depletion of the Group III and V atoms from the vapor phase can be tested by the following simple analysis. The molar growth rate of an epitaxial layer is just

$$\dot{g}_m = \dot{g}_l \rho_m A \tag{4.1.4}$$

where:

$\dot{g}_m$ = molar growth rate (moles/time)

$\dot{g}_l$ = linear growth rate (length/time)

ρ = compound molar density (moles/length^3)

A = substrate area (length^2)

A typical set of operating parameters for a hydride CVD process would specify a total volumetric flowrate of 500 SCCM through each source zone having an inlet composition of 1% HCl to the Group III source zone and 1% NH_3 composition to the Group V source zone. Assuming that all of the HCl reacts to form III-Cl results in 3.7 $\mu-moles/s$ of Group III atoms transported. The molar flowrate of Group V atoms would also be 3.7 $\mu-moles/s$. Choosing as typical deposition parameters a 2.54 cm diameter circular substrate, a linear growth rate of 1 $\mu m/min$ and the molar density of GaAs as 0.0367 $moles/cm^3$ [8] the resulting molar growth rate is 0.31 $\mu-moles/s$. Thus, in the worst case less than 10% of the III and V atoms are depleted. The smaller the growth rate and substrate surface area or the larger the volumetric flowrate the better the approximation becomes. If reaction depletion were indeed important, highly non-uniform film thickness would be generated. However, this is not experimentally observed. Similar analyses applied to the GaAs chloride system and the analogous InP systems yield equivalent results.

The activity of silicon in the epi-layer was further studied in the presence and absence of the SiO_2 reactor wall. Since the deposition zone is typically operated at a lower temperature than the source and mixing zones, inclusion of the reactor wall would be expected to decrease the silicon activity as some of the silicon in the vapor phase is redeposited on the reactor wall via reactions with H_2O. Neglecting interactions with the reactor wall in the deposition zone therefore, provides an additional method of bounding the maximum value of the silicon activity in the epitaxial layer. Justification for neglecting the reactor wall lies in the heterogeneous nature of the gas-wall reaction. Due to the lower temperature of the deposition zone (~ 873K) it is expected that this heterogeneous reaction does not equilibrate as rapidly as it should in the source and mixing zones (~ 973K). This expectation arises from the fact that adsorption reaction rates decrease strongly, and to a lesser extent molecular diffusivities, with decreasing temperature. Additionally, the mean residence time is typically much smaller in the deposition zone. Thus the reactor wall in the deposition

zone should not interact with the vapor phase as strongly as it does in the source and mixing zones.

In order to carry out parametric analyses of the two processes "base cases" were chosen for each system around which each parameter could be varied. The base cases were chosen from commonly used operating parameters reported in the literature, shown in Tables 4.1 and 4.2, thus providing results which may be compared to experimental results. The chloride system base case parameters were:

Source Zone Temperature = Mixing Zone Temperature : 973K
Deposition Zone Temperature : 873K
Inlet VCl_3 Composition : 1%
Carrier Gas : H_2
System Pressure : 100 kPa

For the hydride system the following base case was chosen:

Source Zone Temperature = Mixing Zone Temperature : 973K
Deposition Zone Temperature : 873K
Inlet HCl Concentration = Inlet VH_3 Concentration : 1%
Carrier Gas : H_2
Pressure : 100 kPa

Typically the source zone of the hydride system is operated at a higher temperature than that of the chloride system in order to augment the decomposition of VH_3. Due to the strong influence of temperature on the species present the same temperatures were used in both systems in order to provide direct comparisons between the chloride and hydride CVD systems.

Table 4.1

Some Typical Operating Parameters for the GaAs and InP Chloride Systems

System	Group III Source Material	% VCl_3 in Feed	Total Flowrate (SCCM)	Zone Temperatures (K)			Pressure (kPa)	Reference
				Source	Mixing	Deposition		
GaAs	liquid	0.1-0.7	250-800	1123	1123	983-1043	100	58
GaAs	solid	0.05-10.0	80	1100	1100	850-1050	0.5-100	31
GaAs	liquid	0.06-0.6	180-800	1123	1123	1000-1100	100	7
GaAs	liquid	0.6-1.2	> 100	1073	1073	1023	100	59
GaAs	solid	0.6-1.2	> 100	1073	1073	1023	100	59
GaAs	liquid	0.15-1.0	600	1123	1123	1023	100	28
GaAs	liquid	0.1-0.8	130	1123	1123	1023	100	23
GaAs	liquid	0.05-0.9	650	1073	1073	973	100	60
GaAs	liquid	0.08-0.35	600	1073	1073	943-993	100	61
GaAs	liquid	?	50	1073	1073	1023	100	17
GaAs	liquid	?	50	1073	1073	1023	100	16
InP	liquid	0.23-0.75	100-800	1023	1023	873-1023	100	62
InP	solid	0.23-0.75	100-800	1023	1023	873-1023	100	62
InP	liquid	?	?	973-1123	973-1123	873-1023	100	40
InP	liquid	0.2-2.0	?	1023	1023	923	100	43
InP	liquid	0.2-4.0	150-250	1023	1023	923	100	63
InP	liquid	0.1-2.9	250	973	973	923	100	44
InP	liquid	1.2	100	1023	1023	923	100	45
InP	solid	?	?	973	973	873	100	64
InP	liquid	0.9-4.6	56	873-1100	873-1100	848-973	100	46
InP	solid	4.6	66	1012-1113	1012-1113	887-991	100	46
InP	liquid	2.0-10.0	200	923-1023	923-1023	823-993	100	49
InP	liquid	0.9-4.5	100-200	1023	1023	933-953	100	48

Table 4.2

Some Typical Operating Parameters for the GaAs and InP Hydride Systems

System	% HCl in Feed	% VH_3 in Feed	Total Flowrate (SCCM)	Zone Temperatures (K)			Pressure (kPa)	Reference
				Source	Mixing	Deposition		
GaAs	0.2-1.0	0.3-1.4	560-2475	1048	1138	973	100	36
GaAs	0.3-3.0	0.3-6.0	30	1023	1073	1023	1-100	39
GaAs	5.0-25	0.2-1.6	1410-2650	1123	1123	1023	100	35
GaAs	0.3-2.4	0.7-1.4	420-980	?	?	973-1023	100	38
GaAs	0.2-2.0	0.05-2.0	?	1023	1023	1023	100	65
InP	2.0-2.6	2.0-2.6	177-1510	?	?	923	100	38
InP	0.65	1.2	500-900	1053-1123	1053-1123	923	100	53
InP	?	?	400-2400	?	973-1223	?	100	54
InP	0.11	0.11	5200	1043-1193	1043-1193	943	100	57
InP	0.3-0.9	0.3-1.9	1690-2400	1173	943-1250	923	100	66

4.3 Solid State Defect Chemistry

The model developed for the deposition zone specifies that reactant depletion is not important. That is the growing compound film is exposed to a vapor phase that is invariant with respect to composition. Therefore the vapor phase fugacity of Si is constant and the compound with impurity that is in equilibrium with this vapor phase also has a constant value of Si activity. The problem thus reduces to finding the Si concentration as a function of the fixed vapor composition and temperature. Necessary for this analysis is a description of the solid state composition dependence of the Si activity. Presented below is a point defect model which relates the Si concentration, [Si], to the temperature and gas phase composition.

Hurle (67-70) has recently proposed a model for native defects in GaAs and for Te, Sn and Ge doped GaAs. Strong evidence is presented to support this model and a similar model is developed here to include Si doped III-V compounds. The general model includes the presence of Frenkel disorder on the V sub-lattice and Schottky disorder in the compound. The Si can reside either on a III sub-lattice site (donor) or V sub-lattice site (acceptor). Furthermore, Si substituted on a III site is postulated to complex with both a Group III vacancy and Si substituted on a V site. For convenience of symbol usage, the model described here will specify the compound GaAs. An independent set of native defect reactions is postulated to consist of:

$$As_{As} + V_i = A_{Si} + V_{As} \tag{4.3.1}$$

$$O = e^- + h^+ \tag{4.3.2}$$

$$As_i = As_i^+ + e^- \tag{4.3.3}$$

$$V_{As} = V_{As}^+ + e^- \tag{4.3.4}$$

$$\tfrac{1}{2} As_2(g) + V_i = As_i \tag{4.3.5}$$

$$V_{Ga} = V_{Ga}^- + h^+ \tag{4.3.6}$$

$$O = V_{Ga} + V_{As} \tag{4.3.7}$$

Reaction 4.3.1 represents Frenkel disorder on the As sub-lattice with As on a normal lattice site, As_{As}, moving to a vacant interstitial site, V_i, to produce an arsenic intersti-

tial, As_i, and a vacant arsenic site, V_{As}. Reaction 4.3.2 displays an electron, e^-, hole, h^+, generation step while reactions 4.3.3, 4.3.4 and 4.3.6 describe ionization of As_i, V_{As} and a gallium vacancy, V_{Ga}. Interaction with gas phase is allowed for through reaction 4.3.5 while 4.3.7 entails Schottky disorder. An independent set of incorporation reactions considered here is:

$$Si(g) + V_{Ga} = Si_{Ga}^{+} + e^{-} \tag{4.3.8}$$

$$Si(g) + V_{As} = Si_{As}^{-} + h^{+} \tag{4.3.9}$$

$$Si_{Ga}^{+} + V_{Ga}^{-} = Si_{Ga}\,V_{Ga}^{-} + h^{+} \tag{4.3.10}$$

$$Si_{Ga}^{+} + Si_{As}^{-} = Si_{Ga}\,Si_{As} \tag{4.3.11}$$

The amphoteric nature of Si in GaAs is illustrated in reactions 4.3.8 and 4.3.9 while the last two reactions show the formation of the two complexes mentioned earlier. Assuming that Boltzmann statistics are applicable, the defects are sufficiently dilute so that their activities are equal to their concentrations, and the concentrations of As_{As}, V_i and 0 are constant and normalized to unity, the following equilibrium relations can be written:

$$K_1 = [As_i][V_{as}] \tag{4.3.12}$$

$$K_2 = np \tag{4.3.13}$$

$$K_3 = [As_i^{+}]n / [As_i] \tag{4.3.14}$$

$$K_4 = [V_{As}^{+}]n / [V_{As}] \tag{4.3.15}$$

$$K_5 = [As_i] / P_{As_2} \tag{4.3.16}$$

$$K_6 = [V_{Ga}^{-}]p / [V_{Ga}] \tag{4.3.17}$$

$$K_7 = [V_{Ga}][V_{As}] \tag{4.3.18}$$

$$K_8 = [Si_{Ga}^{+}]n / [V_{Ga}]a_{Si} \tag{4.3.19}$$

$$K_9 = [Si_{As}^{-}]p / [V_{As}]a_{Si} \tag{4.3.20}$$

$$K_{10} = [Si_{Ga}\,V_{Ga}^{-}]p / [V_{Ga}][Si_{Ga}^{+}] \tag{4.3.21}$$

$$K_{11} = [Si_{Ga}\,Si_{As}] / [Si_{As}^{-}][Si_{Ga}^{+}] \tag{4.3.22}$$

In addition the condition of charge neutrality requires that:

$$p + [Si_{Ga}^{+}] + [As_i^{+}] + [V_{As}^{+}] = n + [V_{Ga}^{-}] + [Si_{As}^{-}] + [Si_{Ga}\,V_{Ga}^{-}] \tag{4.3.23}$$

In these equations K_1 through K_{11} are equilibrium constants and a function of temperature only. It is seen that equations 4.3.12 through 4.3.25 contain 15 variables. The problem considered here is to determine the 12 defect concentrations from the 11 equilibrium relationships and the electroneutrality condition given the external parameters T, P_{As_2} and a_{Si}. An analytical solution to these equations is possible with the results summarized below.

$$[As_i] = K_5 P_{As_2}^{1/4} \tag{4.3.24}$$

$$[V_{As}] = (K_1/K_5) P_{As_2}^{1/4} \tag{4.3.25}$$

$$[V_{Ga}] = (K_7 K_5/K_1) P_{As_2}^{1/4} \tag{4.3.26}$$

$$[As_i^+] = K_3 K_5 P_{As_2}^{1/4}\, n^{-1} \tag{4.3.27}$$

$$[V_{As}^+] = (K_1 K_4/K_5) P_{As_2}^{-1/4}\, n^{-1} \tag{4.3.28}$$

$$[V_{Ga}^-] = (K_5 K_6 K_7/K_1 K_2) P_{As_2}^{1/4}\, n \tag{4.3.29}$$

$$P = K_2\, n^{-1} \tag{4.3.30}$$

$$[Si_{Ga}^+] = (K_5 K_7 K_8/K_1) P_{As_2}^{1/4}\, a_{Si}\, n^{-1} \tag{4.3.31}$$

$$[Si_{As}^-] = (K_1 K_9/K_2 K_5) P_{As_2}^{-1/4}\, a_{Si}\, n \tag{4.3.32}$$

$$[Si_{Ga}\, V_{Ga}^-] = (K_5^2 K_6 K_7^2 K_8 K_{10}/K_1^2 K_2^2) P_{As_2}\, a_{Si}\, n \tag{4.3.33}$$

$$[Si_{Ga}\, Si_{As}] = (K_7 K_8 K_9 K_{11}/K_2) a_{Si}^2 \tag{4.3.34}$$

and the concentration of electrons by

$$n = \left[\frac{K_2 + K_3 K_5 P_{As_2}^{1/4} + (K_1 K_4/K_5) P_{As_2}^{-1/4} + (K_5 K_7 K_8/K_1) P_{As_2}^{1/4} a_{Si}}{1 + (K_5 K_6 K_7/K_1 K_2) P_{As_2}^{1/4} + (K_1 K_9/K_2 K_5) P_{As_2}^{-1/4} a_{Si} + (K_5^2 K_6 K_7^2 K_8 K_{10}/K_1^2 K_2^2) P_{As_2} a_{Si}} \right]^{1/2} \tag{4.3.35}$$

Thus the total equilibrium concentration of Si in the solid compound can be determined as a function of the gas phase composition and system temperature. It is seen to be a very complex function of the arsenic partial pressure and silicon activity.

Somewhat simpler expressions can be proposed under the conditions of light doping that are of interest here. At the temperature of growth the material may be considered to be intrinsic (i.e. the presence of Si in small concentrations does not contri-

bute significantly to the total ionized content of the defect structure). Furthermore, the analysis of Hurle suggests that for GaAs the dominant ionized native defects under VPE conditions are e^- and V_{As}^+. Under these assumptions the electroneutrality conditions reduces to:

$$n \cong [V_{As}^+] \tag{4.3.36}$$

and the value of n at growth temperature can be shown to be

$$n = (K_1 K_4 / K_5)^{\frac{1}{2}} P_{As_2}^{-\frac{1}{4}} \tag{4.3.37}$$

With this value for n equations 4.3.24 to 4.3.34 remain valid for the defect concentrations. With these assumptions the total Si concentration is

$$\sum [Si] = [Si_{Ga}^+] + [Si_{As}^-] + [Si_{Ga} V_{Ga}^-] + 2[Si_{Ga} Si_{As}] = (a\ P_{As_2}^{-\frac{1}{4}} + b\ P_{As_2}^{\frac{1}{4}}) a_{Si} + c\ a_{Si}^2 \tag{4.3.38}$$

where:

$$a = (K_1 / K_5)^{3/2} (K_9 / K_2) K_4^{\frac{1}{2}}$$
$$b = (K_5 / K_1)^{3/2}\ K_4^{-\frac{1}{2}} K_7 K_8 [1 + (K_4 K_6 K_7 K_{10} / K_2^2)]$$
$$c = K_7 K_8 K_9 K_{11} / K_2$$

At room temperature the intrinsic defects become negligible when compared to typical unintentional doping levels examined here ($\sim 10^{\frac{1}{4}} / cm^3$). The room temperature compensation ratio then becomes

$$\frac{N_D}{N_A} = \frac{[Si_{Ga}^+]}{[Si_{As}^-] + [Si_{Ga} V_{Ga}^-]} = \frac{P_{As_2}^{3/2}}{g + h\ P_{As_2}^{3/2}} \tag{4.3.39}$$

where

$$g = (K_1 / K_5)^3\ K_4 K_9 / (K_2 K_7 K_8)$$
$$h = K_4 K_6 K_7 K_{10} / K_2^2$$

This relationship indicates that the room temperature compensation ratio does not depend on the a_{Si} and if the $[Si_{As}] > [Si_{Ga} V_{Ga}]$ then $N_D / N_A \propto P_{As_2}^{3/2}$ or if the reverse is

true then there should be no P_{As_2} dependence for N_D/N_A. Since the observed compensation ratio for LPE and VPE material is nearly the same, though P_{As_2} varies by nearly two orders of magnitude, it is suggested that the dominant acceptor is $Si_{Ga}\,V_{Ga}^{-}$. For the intentional doping of both GaAs and InP with Si in the light doping region it is found that the free carrier concentration, N_D-N_A, is directly proportional to the total ionized impurity concentration. Therefore in this region of doping the $[Si_{Ga}\,Si_{As}]$ should not be important and the last term in equation 4.3.38 is negligible. In this simplified version of the defect chemistry associated with Si incorporation the total [Si] is

$$\sum [Si] \cong [Si_{Ga}^{+}] + [Si_{Ga}\,V_{Ga}^{-}] = b\ P_{As_2}^{3/4}\ a_{Si} \tag{4.3.40}$$

Thus, the concentration of Si in the compound semiconductor should increase with both the external As_2 partial pressure and silicon activity.

In order to complete the thermodynamic model, a means of relating the external gas phase variables introduced above (P_{As_2} and a_{Si}) must be related to the supersaturated external gas phase composition calculated in the deposition zone. The model stipulates a growing solid surface in equilibrium with the vapor just above it. The Ga partial pressure is determined from the equilibrium reaction

$$GaAs(c) = Ga(g) + \frac{1}{2}\,As_2(g) \tag{4.3.41}$$

with the relation

$$P_{Ga}^{s} = K_{41}\,P_{As_2}^{s\,1/2} \tag{4.3.42}$$

Of course all of the other species originally postulated exist above the vapor as determined from equilibrium relationships. The solid-gas interface is next assumed to be separated from the equilibrium deposition zone gas phase (supersaturated) by a mass transfer barrier. In the steady state, the flux of molecules is constant across the

barrier with the atomic flux of As equal to the Ga flux as required by stoichiometry. In addition the flux of Cl, H and O atoms is zero since there is no net incorporation of these atoms into the growing film. The flux of a specie i is assumed to be given by

$$J_i = K(P_i^o - P_i^s) \tag{4.3.43}$$

where P_i^o and P_i^s is the partial pressure of specie i, in the equilibrium bulk gas phase and at the surface, respectively. The proportionality constant is furthermore assumed to be the same for all species (e.g. for diffusion limited mass transfer $K = -D_i / RT\delta$, where D_i is the diffusion coefficient of specie i and δ is the diffusion boundary layer thickness). With this assumption the following relations hold

$$\sum P^o_{Ga\ species} - \sum P^o_{As\ species} = \sum P^s_{Ga\ species} + \sum P^s_{As\ species} \tag{4.3.44}$$

$$\sum P^o_{Cl\ species} = \sum P^s_{Cl\ species} \tag{4.3.45}$$

$$\sum P^o_{H\ species} = \sum P^s_{H\ species} \tag{4.3.46}$$

$$\sum P^o_{O\ species} = \sum P^s_{O\ species} \tag{4.3.47}$$

In addition, the temperature and pressure are specified and all the equilibrium relationships solved for the gas phase deposition zone are also valid at the surface (involves al the P_i^s variables). However, an additional mixture phase has been included (the Si-GaAs defect solid solution) which is in equilibrium with the surface gas phase, with equation 4.3.42 now also valid and independent. Finally, the flux of Si atoms must be equal to the solid incorporation rate by

$$\left[\sum P^o_{Si\ species} - \sum P^s_{Si\ species}\right] \sum [Si] = \sum P^o_{Ga\ species} - \sum P^s_{Ga\ species} \tag{4.3.48}$$

Given T, P, $K_{eq}(T)$ and all P_i^o, the equations 4.3.40, 4.3.42, 4.3.44-48, and the gas phase equilibrium relations can be solved for the total concentration of Si atoms in the solid.

The above procedure was not performed here for the following reasons. The solution to these equations is extremely difficult due to their non-linear behavior. Also the distribution coefficient of Si (amount in solid/ amount in gas) is much less than unity

and thus the surface a_{Si}^{s} should not be much different than the bulk a_{Si}^{g}. Since the solid represents a "sink" for equal amounts of Ga and As atoms the $P_{As_2}^{s}$ will necessarily decrease at the substrate surface. The amount by which $P_{As_2}^{s}$ will differ from the bulk value, $P_{As_2}^{g}$, depends upon the III/V ratio and the supersaturation ratio.

In summary, the total concentration of Si in the growing compound can be seen to increase with a_{Si} found in the vapor phase and with the partial pressures of the Group V species. Because of a lack of knowledge of the defect reaction equilibrium constants the quantification of this dependence is not possible. However, the results of this parametric analysis should provide correct directions of change in Si content for changes in operating conditions.

5. THERMOCHEMICAL PROPERTIES

5.1 Introduction

Summarized in this section are the thermochemical properties used for the complex chemical equilibrium analysis. The proper selection of a consistent data set is of extreme importance as a small error in a property value can greatly influence the eventual calculated equilibrium composition. That this sensitivity can be important is nicely illustrated in the Si-Cl-H sub-system as discussed later. Essentially, what is required for these calculations is a means of specifying the partial molar Gibbs energy of each specie believed to be present as a function of temperature, pressure and composition. Approximately 150 species were initially examined while only those species that would be present at a mole fraction $> 10^{-14}$ were included in the analysis. The scheme of representing the data was to fix the zero enthalpy scale at 298K and 1 atm with the pure components (standard states) Ga(c), As(c), In(c), white P(c), $H_2(g)$, Si(c), $Cl_2(g)$ and $O_2(g)$. The enthalpy of forming the remaining components at the standard conditions from the reference components was determined. In addition, the absolute entropy at the standard conditions for each specie was selected which allows a calculation of the standard Gibbs energy change for all possible reactions at 298K ad 1 atm. Finally, knowledge of the constant pressure heat capacity and assuming ideal gas behavior allows the Gibbs energy to be determined at any temperature and pressure. The gas phase was assumed to be a solution of ideal gases as is justified by the low pressure and high temperatures investigated. As a result of this simplification the pressure and composition dependence of the partial molar Gibbs energy is explicit in both formulations of the solution procedure. For the condensed solutions the pressure dependency of the thermochemical properties was neglected, however the moderate deviations from ideal behavior in the composition dependence was accounted for and represents one of the significant refinements contained in these calculations. As must be the case, this data base is sufficient for achieving a solution with either the stoichiometric or non-stoichiometric algorithms.

Thus three pieces of information were required for each species with the standard enthalpy of formation being the most critical, particularly at the lower temperatures. It is for this quantity that the most uncertainty exists in the reported values. On the other hand, the standard entropy is generally quite accurately known, either from low temperature heat capacity measurements or spectroscopic studies. The high temperature heat capacities were sometimes estimated, but there exists a partial cancellation of its effect when calculating Gibbs energy changes. Presented below is a discussion of the properties selected. It is noted that in many instances the thermochemical data presented in the JANAF (29-31) tables were used and is discussed in these tables, therefore precluding a discussion here. A summary of the selected thermochemical properties is presented in Table 5.1. In order that the stability of various species might easily be compared, the standard molar Gibbs energy of formation is listed at various temperatures in Table 5.2.

5.2 Pseudo-Steady State Constraint for Liquid Source Boat

It has been observed that during VPE of GaAs and InP with a liquid source boat of pure Group III metal in the chloride process an initial transient period exists in which the composition of the gas stream leaving the source region is a function of time. Initially, the pure metal boat is dissolving the Group V atom thus producing an excess of Group III chloride. As the metal becomes saturated with the Group V element a thin crust of the compound is formed at the top surface since the density of the compound is less than that of the saturated liquid. It is observed that the crust thickness reaches a steady state value and therefore, from a simple mass balance, the vapor phase will contain all of the Group V atom in the input stream plus the amount of Group V atom generated from the saturated liquid (due to reaction of chlorine with the Group III atom). The exact amount of Group V element produced from the source boat is therefore a function of the temperature (i.e. the equilibrium Group V mole fraction in the liquid is a function of temperature and the amount of Group III atom

Table 5.1 Selected Thermochemical Values

Specie	$\Delta H^{\circ}_{f,298K}$ kcal mol^{-1}	Ref.	S°_{298} cal mol^{-1}K^{-1}	Ref.	C°_{p} cal mol^{-1}K^{-1}				Form*	Ref.
					a	b×10^{3}	c×10^{-6}	d		
As(c)	0	--	8.53±0.1	1	6.736	1.50	-0.1504	-0.1967	1	1
As(g)	68.7±1.0	1	41.611±0.1	1	4.968	--	--	--	1	1
$As_2(g)$	45.95±10.0	••	57.546±0.1	1	7.630	-0.169	-0.3708	0.212	1	1
$As_3(g)$	52.2±1.0	1	74.121±0.1	1	13.836	-0.1365	-0.5589	0.172	1	1
$As_4(g)$	37.5±0.6	••	78.232±0.1	1	18.516	-0.1756	-1.1128	0.218	1	1
AsCl(g)	27±3	48	66.24±2.0	48	8.878	0.0453	-0.3815	--	1	48
$AsCl_2(g)$	14.5±4	48	72.04±2	48	13.79	0.08566	-0.3524	--	1	48
$AsCl_3(g)$	-62.7±4.0	••	77.97±2.0	48	19.76	0.0726	-1.5766	--	1	48
AsH(g)	58±12	••	51±3	••	6.4	1.432	0.108	--	1	29(P
$AsH_3(g)$	16±2	14-16 52	53.22±0.8	83	10.07	5.42	-2.20	--	1	79
Cl(g)	28.992±0.002	82	39.454±0.005	82	5.779	-0.4083	-0.387	--	1	30
$Cl_2(g)$	0	--	53.29±0.01	82	8.8	0.208	-0.67	--	1	29
Ga(c)	0	--	9.758±0.05	1	6.40	--	--	--	1	1
Ga(g)	65.0±0.05	1	40.375±0.05	1	30.138	2.09	-2.652	-3.812	1	1
GaCl(g)	-17.0±5	••	57.36±1.0	56	8.925	1.021	-0.3949	--	1	56
$GaCl_2(g)$	59.2±5	41	72.09±1.5	56	13.84	5.15	-0.8644	--	1	56
$GaCl_3(g)$	-107.3±3	53,54	79.93±2.0	56	19.74	0.0744	-1.690	--	1	56
$Ga_2Cl_6(g)$	-235.6±10	••	127.9±6.0	••	43.06	0.427	-4.922	--	1	29 (Al_2Cl
H(g)	52.103±0.001	82	27.391±0.004	82	4.968	--	--	--	1	31
$H_2(g)$	0	--	31.207±0.008	82	6.956	2.12	-0.3306	-1.462	1	29
HCl(g)	-22.063±0.03	82	44.643±0.008	82	6.724	1.39	0.3351	--	1	29
$H_2O(g)$	-57.795±0.01	82	45.106±0.01	82	8.429	2.44	0.670	0.5682	1	29
In(c)	0	--	13.82±0.2	1	4.59	6.04	--	--	1	1
In(g)	57.3±1.0	••	41.507±0.2	1	5.076	4.426	--	-1.689×10^{-6}	2	1
InCl(g)	-16.8±1.0	••	59.26±0.8	78	8.93	--	-0.209	--	1	79
$InCl_2(g)$	-58.4±1.0	80	73.4±1.0	80	13.84	0.0515	0.8644	--	1	56 ($GaCl$
$InCl_3(g)$	-89.4±4	14	83.8±1.0	14	18.0	1.7	--	--	1	15
$In_2Cl_6(g)$	208.5±10	60	129.7±2.0	60	40.0	3.4	--	--	1	60
O(g)	59.553±0.2	82	38.467±0.005	82	5.542	0.061	0.1688	-0.0899	1	31
$O_2(g)$	0	--	49.005±0.008	82	-7.902	-1.15	0.8877	2.504	1	29

Table 5.1 Continued

Specie	$\Delta H^{\circ}_{f,298K}$ kcal mol^{-1}	Ref.	S°_{298} cal mol^{-1}K^{-1}	Ref.	C°_p cal mol^{-1}K^{-1}				Form*	Ref.
					a	b×10^3	c×10^{-5}	d		
P(c),white	0	--	9.82±0.02	29	5.7	--	--	--	1	29
P(g)	75.62±0.25	1	38.98±0.02	1	4.968	--	--	--	1	29
$P_2(g)$	34.34±0.9	1	52.11±0.1	1,29	8.236	8.6618	0.6036	--	1	29
$P_4(g)$	12.58±2	**	66.89±0.1	1	19.2	0.5744	-0.2974	--	1	29
PCl(g)	31.0±2.0	29	56.8±1.0	29	7.638	-0.0581	-0.4304	0.2216	1	29
$PCl_3(g)$	-68.67±1.4	29	74.47±0.1	29	11.291	-0.6038	-1.787	0.8773	1	29
$PCl_5(g)$	-95.5±2	49	83.5±1.0	49	23.4	12.0	--	--	1	80
PH(g)	56.2±8	29	46.9±2.0	29	6.4	1.432	0.108	--	1	29
$PH_2(g)$	25.9±20	29	50.8±2.0	29	6.524	6.237	--	-1.506×10^{-6}	2	29
$PH_3(g)$	1.3±0.4	81	50.24±1.0	29	4.77	14.97	--	-4.388×10^{-6}	2	29
PO(g)	-5.5±1.5	30	53.218±0.005	30	-5.225	-1.256	0.7156	2.173	1	30
Si(c)	0	--	4.486±0.02	82	5.73	0.6811	-1.056	--	1	29
Si(g)	108±1.0	**	40.123±0.003	1	4.82	0.18	0.42	--	1	29
SiCl(g)	47.4±0.6	93	56.82±0.04	29	8.87	0.1387	-0.328	--	1	29
$SiCl_2(g)$	-40.4±0.6	**	67.36±1.0	30	11.263	-0.234	-1.105	0.4061	1	30
$SiCl_3(g)$	-93.3±0.6	93	76.17±1.5	29	12.797	-0.762	-1.761	1.112	1	29
$SiCl_4(g)$	-158.4±0.3	30	79.07±0.05	30	14.511	-1.21	-2.416	1.778	1	30
SiH(g)	90.0±2.0	29	47.306±0.05	29	6.63	-1.423	0.0988	--	1	29
$SiH_4(g)$	8.2±0.6	29	48.89±0.01	29	-74.824	-6.17	3.329	14.597	1	29
$SiHCl_3(g)$	-119.5±1.0	**	74.924±2.0	29	-7.913	-2.42	-1.535	4.983	1	29
$SiH_2Cl_2(g)$	-75.5±2.0	97	68.531±2.0	29	-31.537	-3.85	-0.3446	8.408	1	29
$SiH_3Cl(g)$	-32.7±2.5	97	59.9±2.0	29	-53.526	-5.04	1.248	11.554	1	29
SiO(g)	-24±2	29	50.54±1.0	29	-6.471	-1.39	0.4755	2.368	1	29
$SiO_2(c)$	-217.7±0.2	82	9.91±0.05	82	31.588	14.14	-3.761	-3.703	1	29
$SiO_2(g)$	-73±8	29	54.7±1.0	29	-14.368	-2.70	0.095	4.4884	1	29
Si_2Cl_6	-236±8	86	101.0±3.0	86	42.15	1.03	-8.46	--	1	86
Si_2H_6	17.1±3	99	70±5	**	2.247	38.20	--	-11.05×10^{-6}	2	C_2H_6
GaAs(c)	-19.52±1.0	32	15.34±0.1	42	10.16	2.8	--	--	1	43
InP(c)	-14.0±1.0	32	14.28±0.1	42	12.27	-	-0.114	298<T<910	1	68
					5.89	6.40	--	T>910	1	68

* Form 1: $C_p(T/K) = a + bT + c/T^2 + d\ln T$
Form 2: $C_p(T/K) = a + bT + cT^2 + dT^3$

** See text

Table 5.2 The Molar Gibbs Energy of Formation of Various Species (kcal mol^{-1})

Specie	Temperature (K)					
	273.2	873.2	973.2	1073.2	[illegible]	1273.2
As(g)	59.657	38.009	34.140	30.220	[illegible]	22.244
$As_2(g)$	34.880	7.467	2.436	-2.686	[illegible]	-13.172
$As_3(g)$	38.926	4.566	-1.934	-8.586	[illegible]	-22.294
$As_4(g)$	25.429	-7.959	-14.549	-21.342	[illegible]	-35.465
AsCl(g)	19.204	-2.576	-6.669	-10.854	[illegible]	-19.465
$AsCl_2(g)$	11.694	0.735	-1.807	-4.491	[illegible]	-10.235
$AsCl_3(g)$	-59.852	-60.388	-61.496	-62.806	[illegible]	-65.962
AsH(g)	50.652	31.956	28.451	24.866	[illegible]	17.479
$AsH_3(g)$	16.570	13.767	12.613	11.305	[illegible]	8.255
Cl(g)	25.487	15.858	13.970	12.026	[illegible]	7.995
$Cl_2(g)$	-0.009	-3.088	-4.061	-5.126	[illegible]	-7.501
Ga(g)	56.629	35.966	32.200	28.376	[illegible]	20.578
GaCl(g)	-22.735	-38.459	-41.543	-44.719	[illegible]	-51.314
$GaCl_2(g)$	-61.684	-71.946	-74.373	-76.943	[illegible]	-82.457
$GaCl_3(g)$	-104.652	-105.596	-106.769	-108.145	[illegible]	-111.430
$Ga_2Cl_6(g)$	-221.574	-205.303	-204.797	-204.734	[illegible]	-205.779
H(g)	48.877	40.006	38.266	36.474	[illegible]	32.757
$H_2(g)$	-0.007	-2.534	-3.326	-4.192	[illegible]	-6.122
HCl(g)	-22.725	-26.697	-27.736	-28.853	[illegible]	-31.295
$H_2O(g)$	-54.907	-51.561	-51.471	-51.482	[illegible]	-51.779
In(g)	49.731	31.230	27.846	24.397	[illegible]	17.324
InCl(g)	-21.942	-36.010	-38.793	-41.666	[illegible]	-47.649
$InCl_2(g)$	-60.132	-68.743	-70.895	-73.189	[illegible]	-78.153
$InCl_3(g)$	-86.700	-87.525	-88.669	-90.016	[illegible]	-93.249
$In_2Cl_6(g)$	-195.220	-181.003	-180.857	-181.156	[illegible]	-182.945
O(g)	55.732	45.999	43.528	41.505	[illegible]	37.324
$O_2(g)$	-0.008	-2.662	-3.513	-4.450	[illegible]	-6.553
OH(g)	8.453	3.622	2.443	1.188	[illegible]	-1.524
P(g)	67.648	48.353	44.876	41.348	[illegible]	34.156
$P_2(g)$	25.468	4.172	0.257	-3.743	[illegible]	-11.972
$P_4(g)$	5.020	-17.964	-22.780	-27.796	[illegible]	-38.361
PCl(g)	25.436	10.119	7.102	3.994	[illegible]	-2.467
$PCl_3(g)$	-64.512	-61.973	-62.552	-63.332	[illegible]	-65.427
$PCl_5(g)$	-79.260	-53.983	-51.421	-49.220	[illegible]	-45.815
PH(g)	50.325	34.862	31.897	28.851	[illegible]	22.542
$PH_2(g)$	23.221	14.088	12.041	9.880	[illegible]	5.243
$PH_3(g)$	3.036	3.028	2.360	1.536	[illegible]	-0.544
PO(g)	-10.671	-24.850	-27.644	-30.526	[illegible]	-36.527

Table 5.2 Continued

Specie	Temperature (K)					
	273.2	873.2	973.2	1073.2	1173.2	1273.2
Si(g)	98.258	75.012	70.872	66.679	62.440	58.157
SiCl(g)	40.373	21.794	18.231	14.576	10.836	7.020
$SiCl_2(g)$	-42.931	-53.383	-55.830	-58.419	-61.136	-63.971
$SiCl_3(g)$	-91.064	-92.699	-93.970	-95.442	-97.097	-98.919
$SiCl_4(g)$	-149.682	-138.946	-138.446	-138.207	-138.205	-138.420
SiH(g)	82.557	63.612	60.058	56.421	52.718	48.924
$SiH_4(g)$	13.109	19.151	19.295	19.234	19.080	18.544
$SiHCl_3(g)$	-112.662	-104.996	-104.889	-105.028	-105.332	-105.963
$SiH_2Cl_2(g)$	-69.928	-64.060	-64.142	-64.457	-64.965	-65.713
$SiH_3Cl(g)$	-27.784	-22.474	-22.546	-22.835	-23.326	-24.011
SiO(g)	-29.896	-45.574	-48.611	-51.735	-54.939	-58.218
$SiO_2(g)$	-73.342	-78.331	-79.840	-81.493	-83.276	-85.181
$Si_2Cl_6(g)$	-217.500	-190.437	-188.052	-186.103	-184.550	-183.362
$Si_2H_6(g)$	25.991	39.324	40.364	41.106	41.594	41.751
As(c)	-0.006	-2.228	-2.935	-3.714	-4.557	-5.460
Ga(c)	-0.007	-2.324	-3.047	-3.836	-4.685	-5.588
GaAs(c)	-18.727	-21.207	-22.269	-23.467	-24.790	-26.230
In(c)	-0.007	-2.665	-3.561	-4.565	-5.672	-6.878
InP(c)	-11.455	-10.040	-10.433	-10.950	-11.582	-12.317
P(c),white	-0.006	-2.070	-2.714	-3.416	-4.172	-4.977
Si(c)	-0.005	-1.969	-2.605	-3.307	-4.067	-4.883
$SiO_2(c)$	-205.805	-184.503	-181.795	-179.288	-176.973	-174.844

leaving depends on the form in which it leaves (e.g. IIICl, $IIICl_3$, III etc.)) and the flow rate (i.e. mass transfer efficiency). The mechanism by which the Group III and V atoms reach the gas/solid interface is not known but is not required for the thermodynamic model presented here as mass transfer barriers (e.g. the crust) are assumed not to be present. All that is required is to assume a new species exists having a stoichiometry equivalent to the saturated liquid composition.

The thermodynamic properties of the hypothetical liquid specie, $A_{1-x}B_x(l)$, can be estimated in the following manner. Letting A represent the Group III atom and B the Group V atom, consider the reaction sequence:

$$(1-x)\,A(c) = (1-x)\,A(l) \qquad (5.2.1)$$

$$x\;\;B(c) = \quad x\;\;B(l) \qquad (5.2.2)$$

$$(1-x)\,A(l) + xB(l) = A_{1-x}B_x(l) \qquad (5.2.3)$$

all occurring at the source temperature, T. Since the pure state, the

Gibbs energy changes for reactions (5.2.1) and (5.2.2) are the Gibbs energies of formation for the liquid species and can be calculated from the thermodynamic sequence: solid element A or B is taken from T to its melting temperature T_m^A or T_m^B, the solid element is melted, the liquid element is taken from the melting temperature to the original temperature of interest. Assuming the heat capacity difference between the pure liquid and pure solid, ΔC_p, is constant, the Gibbs energy change for reactions (5.2.1) and (5.2.2) are:

$$\Delta G(1) = (1-x)\left\{\Delta H_m^A\left[1 - \frac{T}{T_m^A}\right] + \Delta C_p^A\left[T - T_m^A - T\,ln\left[\frac{T}{T_m^A}\right]\right]\right\} \qquad (5.2.4)$$

and

$$\Delta G(2) = x\left\{\Delta H_m^B\left[1 - \frac{T}{T_m^B}\right] + \Delta C_p^B\left[T - T_m^B - T\,ln\left[\frac{T}{T_m^B}\right]\right]\right\} \qquad (5.2.5)$$

The Gibbs energy change of the third reaction is simply the Gibbs energy of mixing and, assuming a simple solution model describes the liquid behavior, results in

$$\Delta G(3) = (a + bT)\,x\,(1-x) + RT[x\ln x + (1-x)\ln(1-x)] \qquad (5.2.6)$$

where a and b are adjustable parameters determined in conjunction with solid-liquid equilibrium data.

The sum of reactions (5.2.1) to (5.2.3) is the desired formation reaction

$$(1-x)A(c) + x\,B(c) = A_{1-x}B_x(l) \qquad (5.2.7)$$

while the corresponding Gibbs energy of formation of $A_{1-x}B_x(l)$ is the sum of ΔG (1) to ΔG (3). Given the source temperature, T, the procedure is to first calculate the liquidus composition, x, from the implicit equation:

$$\frac{T}{T_m^{AB}}\,\Delta H_m^{AB} - R\,ln[4x(1-x)] + b\left[\frac{1}{2} - x^2 - (1-x)^2\right] = a\left[\frac{1}{2} - x^2 - (1-x)^2\right] \qquad (5.2.8)$$

where ΔH_m^{AB} and T_m^{AB} are the enthalpy of fusion and melting temperature of the solid compound AB and R is the gas constant. Once the equilibrium Group V composition is determined the standard Gibbs energy of formation of $A_{1-x}B_x$ (l) can be calculated from equations (5.2.4) to (5.2.6) given T, x and the required thermochemical properties. Tables 5.3a and 5.3b summarize the thermochemical properties used in these calculations. The adjustable parameters a and b for GaAs were determined by reduction of the liquidus measurements of Clariou et al. (102), Hall (103), Koster and Thoma (101), Muszynski and Riabeev (104) and Osamura et al. (105) using a maximum likelihood algorithm.

Table 5.3a Thermochemical Properties of GaAs and InP required for calculating $\Delta G_f^o[A_{1-x}B_x(l),T]$

Property	GaAs	Reference	InP	Reference
$T_m^{AB}(K)$	1511	101	1332	71,72,74
ΔH_m^{AB} ($kcal\ mol^{-1}$)	25.14	43	14.4	71,72,73
a ($cal\ mol^{-1}$)	4,666	see text	5,055	75
b ($cal\ mol^{-1} \cdot K^{-1}$)	-8.74	see text	-5.0	75

Table 5.3b Thermochemical properties of the elements Ga, In, As and P required for calculating $\Delta G_f^o[A_{1-x}B_x(l),T]$

Property	Ga	Ref.	In	Ref.	As	Ref.	P	Ref.
$T_m(K)$	302.9	1	429.76	1	1090	17	313.3	29
$\Delta H_m(kcal\ mol^{-1})$	1.336	1	0.78	1	5.123	17	0.157	29
$\Delta C_p(cal\ mol^{-1} \cdot K^{-1})$	0.27	1	-0.2	1	1.0	estimated	0.472	1

5.3 The Ga-As-Cl-H System

The enthalpy of vaporization of As(c) has been investigated quite extensively with a reported range (1-16) of 34.4 to 38.54 $kcal\ mol^{-1}$ $As_4(g)$ and corresponds to the standard enthalpy of formation for $As_4(g)$. The literature has been summarized by Hultgren et al. (1) to 1973, while a more recent measurement of Kusi et al. (2) by a static method produced a value of 38.14 kcal mol^{-1}. In addition, Rau (17) has measured the total vapor pressure over solid and liquid arsenic from 550 to 1150 with a Bourdon

gauge. Analysis of the low temperature results [illegible] $\Delta H_f^\circ(As_4, g, 298K) = 37.31 \pm 0.2$ *kcal mol*$^{-1}$. The value selected was 37.5 *kcal mol*$^{-1}$ on the basis that the static methods are believed to be more reliable.

The dissociation enthalpy, $\Delta H^\circ(As_4 = 2As_2, 298K)$, has received considerable investigation with early mass spectrometric studies producing values in the range of 61.5 to 73.5 *kcal mol*$^{-1}$ (20,24-27). These measurements are suspected of overestimating the As_4 partial pressure as a result of a low condensation coefficient for As_4 thus producing high As_4 ion currents. More recent determinations using $MoAs_2$, Mo_2As_3, GaAs, InAs, and InAs + InSb sources with improved Knudsen-cell mass-spectrometer designs (18,19,21) and reduction of PVT measurements (17) have indicated a much lower value for the dissociation enthalpy (54.21±1.5, 54.26±1.1, 54.2±1.4and 54.8±1.0 *kcal mol*$^{-1}$, respectively). The value selected here is the average of these four measurements, 54.4±1.5 *kcal mol*$^{-1}$. Using the selected values from the standard enthalpies, $\Delta H_f^\circ(GaAs, c, 298K) = 19.52$ *kcal mol*$^{-1}$, $\Delta H_f^\circ(As_4, g, 298K) = 37.5$ *kcal mol*$^{-1}$ and the above dissociation enthalpy yields $\Delta H^\circ(GaAs, c) = Ga(c) + \frac{1}{2} As_2(g), 298K) = 42.5$ *kcal mol*$^{-1}$ and can be compared to the values of 44.85 (18), 45.15 (19) and 45.4 (28) *kcal mol*$^{-1}$.

The value adopted for $\Delta H_f^\circ(GaAs, c, 298K)$ is -19.52 *kcal mol*$^{-1}$ as determined by Martosudirdjo and Pratt (32) with a precipitation calorimetric technique. This value can be compared to the emf work of Abbasov (33) and Sirota et al. (34) in which values of −19.4 and −20.96 *kcal mol*$^{-1}$ were reported, respectively. These latter two values are expected to contain uncertainties due to the assumed valency of Ga in the galvanic cell and the inability to accurately determine the full temperature dependence over a relatively small temperature range of measurement. In addition a considerable number of dissociation pressure studies (18,19,22-26,27,35-43) and flow equilibration investigations with reactive gases (28,41) have been performed which contain information about solid GaAs. However, knowledge of the thermodynamic properties of other

species is required (i.e. $As_2(g)$, $As_4(g)$, GaCl(g), $Ga_xAs_{1-x}(l)$ etc.) to specify the properties of GaAs(c) and thus introduce the uncertainty in their properties in addition to those associated with the measurements. However, this work can be used to impose an internal consistency in the total data set. The standard entropy of GaAs, $S^\circ(GaAs,c,298K)$ was taken from the low temperature heat capacity measurements of Piesbergen (42) while the high temperature heat capacity was taken from the measurements of Lichter and Sommelet (43) and are in good agreement with the work of Cox and Pool (59) and the estimates of Marina et al. (44) and Maslov and Maslov (45).

Very little experimental information is available for the arsenic chlorides. The reported range for the enthalpy of formation of $AsCl_3(g)$ is −52 to −72 *kcal mol*$^{-1}$ (14,16,46-51). The value adopted was $\Delta H_f^\circ(AsCl_3,g,298K)$ = −62.7 *kcal mol*$^{-1}$, taken from the enthalpy of formation of the liquid and the enthalpy of vaporization. The enthalpy of formation of the mono and dichlorides were taken from the estimates of Shaulov and Mosin (48) as was the standard entropy and heat capacity. The enthalpy of formation of arsine was taken as $\Delta H_f^\circ(AsH_3,g,298K)$ = 16.0±1.5 *kcal mol*$^{-1}$ based on the work of Gunn (52) and reported tabulations (14-16). Finally the thermochemical properties of the remaining arsenic hydrides were estimated by comparison with the hydrides of N, P and Sb (29-31).

The thermodynamic information available for the chlorides of gallium is somewhat scarce and inconsistent. The enthalpy of formation for $GaCl_3(g)$ was determined from $\Delta H_f^\circ(GaCl_3,c,298K)$ = −125.0 *kcal mol*$^{-1}$ (53) and the enthalpy of sublimation taken from the vapor pressure measurements of Kubaschewski et al. (54), $\Delta H^\circ(GaCl_3(c) = GaCl_3(g),298K)$ = 17.7 *kcal mol*$^{-1}$, producing $\Delta H_f^\circ(GaCl_3,g,298K)$ = −107.3±3 *kcal mol*$^{-1}$. The enthalpy of formation of gallium monochloride has the reported value $\Delta H_f^\circ(GaCl,g,298K)$ = −19.5 *kcal mol*$^{-1}$ and is taken from the dissociation energy of Barrow (55) and $\Delta H_f^\circ(Ga,g,298K)$ and $\Delta H_f^\circ(Cl,g,298K)$ values selected. However, a value of $\Delta H_f^\circ(GaCl,g,298K)$ = −12.0 *kcal mol*$^{-1}$ is obtained using $\Delta H^\circ(GaAs(c) + HCl,g = GaCl(g) + \frac{1}{4}As_4(g) + \frac{1}{2}H_2,g,298K)$ = −12.52 *kcal mol*$^{-1}$ determined by

Battat et al. (41) and the other thermochemical data selected here for the other species. These results are in sharp contrast to the vapor pressure measurements of Kuniya et al. (54) who report a second law $\Delta H^o(GaCl_3(g) = GaCl(g) + Cl_2,g),1083K) = 45.912$ *kcal mol* $^{-1}$. The value selected was $\Delta H_f^o(GaCl_3,g,298K) = -17.0 \pm 5$ *kcal mol* $^{-1}$ is based on the first two reports, weighting the value of Farrow (55) slightly more due to the uncertainties found in the enthalpy of formation for the other species in the reaction studied by Battat et al. (41). The enthalpy of formation for gallium dichloride was taken from the measurements of Battat et al. (41) using the thermochemical data selected here and correcting the second law entropy to that calculated by Shaulov and Mosin (56). The enthalpy of dimerization has been investigated by several authors (54,57-60) with the reported enthalpy and entropy of dimerization in the range, $\Delta H^o(2GaCl_3(g) = Ga_2Cl_6(g),298K) = -22.6$ to -20.9 *kcal mol* $^{-1}$ and $\Delta S^o(2GaCl_3(g) = Ga_2Cl_6(g),298K) = -31.66$ to -36.0 *cal mol* $^{-1}$ K^{-1}. Accepting the enthalpy and entropy of dimerization as -21.0 *kcal mol* $^{-1}$ and $-$ *cal mol* $^{-1}$ K^{-1}, respectively, and combining with the selected thermochemical data for $GaCl_3$ produces $\Delta H_f^o(Ga_2Cl_6,g,298K) = -235.6 \pm 10$ *kcal mol* $^{-1}$ and $S^o(Ga_2Cl_6,g,298K) = 127 \pm 6.0$ *cal mol* $^{-1}K^{-1}$. The standard entropy and heat capacity for GaCl, $GaCl_2$ and $GaCl_3$ were taken from Shaulov and Mosin (56) while the heat capacity of Ga_2Cl_6 was taken as the same for Al_2Cl_6 (29). In addition other species are expected to exist (i.e. Ga_2Cl_4, Ga_2Cl_2) (61,62) but no thermochemical data available.

5.4 The In-P-Cl-H System

The standard entropy at 298K and the constant pressure heat capacity of solid and vapor In were taken from Hultgren et al. (1). As summarized by Hultgren et al. (1), the standard enthalpy of vaporization of solid In at 298K that results from application of the third law to the vapor pressure measurements reduces the range of 49.8 to 58.1 *kcal mol* $^{-1}$ for $\Delta H_f^o(In,g,298K)$. More recent mass spectrometric results of Danish and Arthur (63) and Farrow (61) suggest the values [illegible] and 58.03 *kcal mol* $^{-1}$, respectively, with the [illegible] favoring the latter. The thermochemical

properties of phosphorus as selected by Fuhrmann et al. (1) or the JANAF tables (29) are in agreement with the more recent results (63) and were adopted for this study. However there exists a small difference in the reported $\Delta H^{\circ}(298K)$ of the reaction $P_4(g) = 2P_2(g)$. Foxon et al. (22) report a value of $\Delta H^{\circ}(298K) = 57.9 \pm 1$ *kcal mol*$^{-1}$ while Panish and Arthur (63) reported $\Delta H^{\circ}(298K) = 53.8 \pm 0.8$ *kcal mol*$^{-1}$ from third law calculations of their mass spectrometric results. The third law reduction of the mass spectrometric results of Farrow (64) produces a value of $\Delta H^{\circ}(298K)$ = 58.04±0.3 *kcal mol*$^{-1}$, while the JANAF tables (29) select $\Delta H^{\circ}(298K)$ = 54.6±1.1 *kcal mol*$^{-1}$. An average value was selected of $\Delta H^{\circ}(298K)$ = 56.1±2.0 *kcal mol*$^{-1}$.

A rather wide range in the reported values for the standard enthalpy of formation of solid InP exists (−13.52 to −22.3 *kcal mol*$^{-1}$). As shown in Table 5.4 the value selected was the average of the two solution calorimetric determinations as this is a direct determination of the property. The results from the vapor pressure measurements are subject to uncertainties in the properties of the vapor phase species and also the heat capacity of solid InP (e.g. Panish and Arthur (63) used C_p for AlSb which produces a decrease in $\Delta H_f^{\circ}(InP,c,298K)$ of 0.5 *kcal mol*$^{-1}$ when compared to $C_p(InP,c,T)$ of Pankratz (68)). The standard entropy of InP(c) was taken from the low temperature heat capacity measurements of Piesbergen (42) while the heat capacity adopted was that measured by Pankratz (68) and is in good agreement with the 298K value of Piesbergen (42) and in fair agreement with the high temperature measurements of Cox and Pool (69) and the suggested value of Maslov and Maslov (45).

Table 5.4 The reported standard enthalpy of formation of InP(c), ΔH_f°(InP,c,298K)

$\Delta H^?_{f,298}[InP(c)]$ *kcal mol*$^{-1}$	Method	Reference
$-18.83 \pm 0.7^{(a)}$	flow equilibration	63
$-18.58 \pm 0.7^{(b)}$	mass spectrometry	63
-22.3 ± 1.5	mass spectrometry	25
$-19.33 \pm 0.1^{(c)}$	vapor pressure	28,65
$-17.83 \pm 1.4^{(d)}$	calculated	28
-21.2	calculated	66
$-20.33^{(e)}$	mass spectrometry	64
-13.52 ± 0.26	solution calorimetry	32
-21.0 ± 2	bomb calorimetry	67
-21.5 ± 1.5	bomb calorimetry	68,70
-14.5 ± 0.44	solution calorimetry	referenced in 32

(a) $InP(c) = In(c) + \frac{1}{2} P_2(g)$, $\Delta H^?_{298} = 360$ *kcal mol*$^{-1}$
$\Delta H^?_{f,298}[P_2(g)]$ taken as 34.34 *kcal mol*$^{-1}$

(b) $InP(c) = In(c) + \frac{1}{4} P_4(g)$, $\Delta H^?_{298} = 22.1$ *kcal mol*$^{-1}$
$\Delta H^?_{f,298}[P_4(g)]$ taken as 14.08 *kcal mol*$^{-1}$

(c) $InP(c) = In(c) + \frac{1}{2} P_2(g)$, $\Delta H^?_{298} = 36.5$ *kcal mol*$^{-1}$
$\Delta H^?_{f,298}[P_2(g)]$ taken as 34.34 *kcal mol*$^{-1}$

(d) $InP(c) = In(c) + \frac{1}{2} P_2(g)$, $\Delta H^?_{298} = 35.0$ *kcal mol*$^{-1}$
$\Delta H^?_{f,298}[P_2(g)]$ taken as 34.34 *kcal mol*$^{-1}$

(e) $InP(c) = In(c) + \frac{1}{2} P_2(g)$, $\Delta H^?_{298} = 37.50 \pm 0.1$ *kcal mol*$^{-1}$
$\Delta H^?_{f,298}[P_2(g)]$ taken as 34.34 *kcal mol*$^{-1}$

Barrow (55) reports the dissociation energy of InCl to be 102.5 kcal/mol and combining this with the value of the enthalpy of formation of In(g) and Cl(g) gives $\Delta H^?_f(InCl,g,298K) = -16.21$ *kcal mol*$^{-1}$. However the atomic fluorescence value for the dissociation energy also reported by Barrow (55) ($D_o = 104.6$ *kcal mol*$^{-1}$) yields $\Delta H^?_f(InCl,g,298K) = -18.31$ *kcal mol*$^{-1}$. Klemm and Brautigan (76) reported $\Delta H^?_f(InCl,c,273K) = -44.6$ *kcal mol*$^{-1}$ (77) and when combined with the enthalpy of sublimation, $\Delta H^?_s(InCl,c,298K) = 27.8$ *kcal mol*$^{-1}$, gives $\Delta H^?_f(InCl,g,298K) = -16.8$ *kcal mol*$^{-1}$ and is the value adopted here. The standard entropy of InCl was taken from the calculations of Malakova and Pashinkin (78) while the heat capacity is that recommended by Kelley (79). The standard enthalpy of formation and entropy of $InCl_2$

was taken from the estimate of Glassner (9) and the heat capacity is the same as listed for $GaCl_2$. The standard enthalpy of formation and entropy of $GaCl_3$ was taken to be the values suggested by Mullins and Burdett (14) and the constant pressure heat capacity estimated by Shaw (15). The thermochemical properties of the dimer, In_2Cl_6, were taken from the values suggested by Schafer and Binnewies (16).

The standard enthalpy of formation of phosphine, PH_3, was taken from the decomposition studies of Gunn and Green (81) and the remaining properties from the JANAF tables (29,30). The JANAF tables were also used for the other phosphorous hydrides, chlorides and oxide vapor phase species listed in Table 5.1.

5.5 The Si-Cl-H System

The thermochemical properties of Si have been reviewed by Hultgren et al. (1) and the JANAF tables (29). In particular, there exists a rather large range in the reported third law values of the standard enthalpy of vaporization, $\Delta H_f^o(Si,g,298K)$ = 86.75 to 109.06 $kcal\ mol^{-1}$. The value selected was in between the Knudsen studies of Davis et al. (84) and Grieveson and Alcock (85).

The Si-Cl-H system has received considerable attention due to its importance in the semiconductor industry. An excellent review of the literature for this system with equilibrium calculations presented is given by Hurd and Sirtl (86,87). The posture taken here is to assume that $SiCl_4$ has the most reliable thermodynamic data with these values being fixed by the JANAF tables (29).

The reaction

$$Si(g) + SiCl_4(g) = 2SiCl_2(g) \qquad (5.5.1)$$

has been investigated extensively (88-93). Employing the thermochemical data for the three species in reaction (5.1) from the JANAF tables (29), third law values of $\Delta H_f^o(SiCl_2,g,298K)$ were calculated from the experimental data of the effusion-mass spectrometric determination of Farber and Srivastava (93) over the temperature

range of 1593K to 1792K produced these values $\Delta H_f^\circ(SiCl_2,g,298K)$ = -40.39 ± 0.3 *kcal mol*$^{-1}$ and showed no temperature dependence. This result is in good agreement with flow equilibration data of Schäfer et al. (88) (1273K to 1473K) and Teichmann and Wolf (89) (1223K to 1575K) and the static measurements of Schafer and Nickl (92) (1398K to 1573K), with third law values of −40.62, −40.54, and −40.44 *kcal mol*$^{-1}$, respectively. The flow equilibration values of Antipin and Sergeev (90) (1273K to 1673K) and the static values of Ishino et al. (91) (1445K to 1573K) were more negative and exhibited a marked temperature dependence. On the basis of these calculations the value, $\Delta H_f^\circ(SiCl_2,g,298K) = -40.4$ *kcal mol*$^{-1}$ was selected. The values for the standard enthalpy of formation of the less stable chlorides SiCl and $SiCl_3$ were computed from the high temperature flow equilibration studies of Farber and Srivastava (93). In the third law analysis the data previously discussed was used in conjunction with the heat capacity for SiCl and $SiCl_3$ suggested by the JANAF tables (29) and produced the value of 47.4±0.6 and −93.3±0.5 *kcal mol*$^{-1}$, respectively. These results are in agreement with the analysis of Rusin et al. (94-96) on the total pressure measurements of Schafer and Nickl (92). No additional thermodynamic studies of Si_2Cl_6 are known to exist and thus the properties suggested by Hunt and Sirtl (86) were adopted and are in agreement with the analysis of Rusin et al. (94-96).

It was pointed out by Hunt and Sirtl (86) that the mole ratio of $SiCl_4$ to $SiHCl_3$ is very sensitive to the assumed value of the standard enthalpy of formation of $SiHCl_3$. Indeed this ratio is seen to vary by nearly four orders of magnitude at 1000K when bounded by the experimental determinations of $\Delta H_f^\circ(SiHCl_3,g,298K)$. Since the work of Hunt and Sirtl (86) was published, two additional experimental investigations of the thermodynamic properties of $SiHCl_3$ have been performed. Farber and Srivastava (97), from effusion-mass spectrometric measurements, determined the reaction enthalpy for

$$SiCl_4(g) + H_2(g) = SiHCl_3(g) + HCl(g) \qquad (5.5.2)$$

over the temperature range 1155K to 1500K. Employing the thermodynamic data listed in Table 5.1 and these results, a relatively temperature insensitive third law value for $\Delta H_f^o(SiHCl_3,g,298K) = -119.30\pm1.0$ is obtained. Using both static and dynamic methods, Wolf and Teichmann (98) investigated reaction (5.5.2) and the reaction

$$4SiHCl_3(g) = 3SiCl_4(g) + Si(c) + 2H_2(g) \qquad (5.5.3)$$

Third law values of $\Delta H_f^o(SiHCl_3,g,298K)$ were calculated from the original results and the thermodynamic data of Table 5.1. The values obtained for reaction (5.5.3) is -119.47 ± 0.40 *kcal mol*$^{-1}$ and for the three data sets with reaction (5.5.2) are -119.83 ± 0.90, -119.58 ± 0.2 and -119.50 ± 0.60 *kcal mol*$^{-1}$ and the results are seen to be in good agreement with the measurements of Farber and Srivastava (97). Since these values are nearly 3 *kcal mol*$^{-1}$ more negative than that developed by Hunt and Sirtl (86), values of $\Delta H_f^o(SiHCl_3,g,298K)$ were calculated for various experimental $SiCl_4/SiHCl_3$ ratios in a fashion similar to Hunt and Sirtl (86). The experimental data consisted of a variety of feed mixtures (e.g. $SiCl_4/H_2$, H_2/HCl, $SiHCl_3/H_2$) which were contacted with Si(c) at different temperatures during a deposition/etching process. The results of these calculations for 14 data sets suggest $\Delta H_f^o(SiHCl_3,g,298K) = -118.16\pm1.70$ *kcal mol*$^{-1}$. Based on these results and the new experimental determinations, the value adopted is $\Delta H_f^o(SiHCl_3,g,298K) = -119.5\pm1.5$ *kcal mol*$^{-1}$.

The standard enthalpy of formation of the di- and mono-chlorosilanes was taken from the recent measurements of Farber and Srivastava (97). In order to obtain a consistent data set, third law values of these quantities were calculated from the original experimental data while using the data base adopted here. The adopted values are $\Delta H_f^o(SiH_2Cl_2,g,298K) = -75.5\pm2$ *kcal mol*$^{-1}$ and $\Delta H_f^o(SiH_3Cl,g,298K) = -32.7\pm2.5$ *kcal mol*$^{-1}$.

No additional experimental information on the thermochemistry of SiH_4 and SiH exists and thus the JANAF tabular recommendations are adopted. The standard

enthalpy of formation of disilane was taken from the calculations of Potzinger et al. (99). $\Delta H_f^o(Si_2H_6,g,298K)$ = 17.1±3 *kcal mol*$^{-1}$ and is compared with the calculations of O'Neal and Ring (100), $\Delta H_f^o(Si_2H_6,g,298K)$ = 19.1 *kcal mol*$^{-1}$ and the value of 16.0 *kcal mol*$^{-1}$ obtained from the estimated enthalpy of formation for SiH_3 (35 *kcal mol*$^{-1}$) and Si-Si (−54 *kcal mol*$^{-1}$). The standard entropy and heat capacity of Si_2H_6 were obtained by comparison with C_2H_6.

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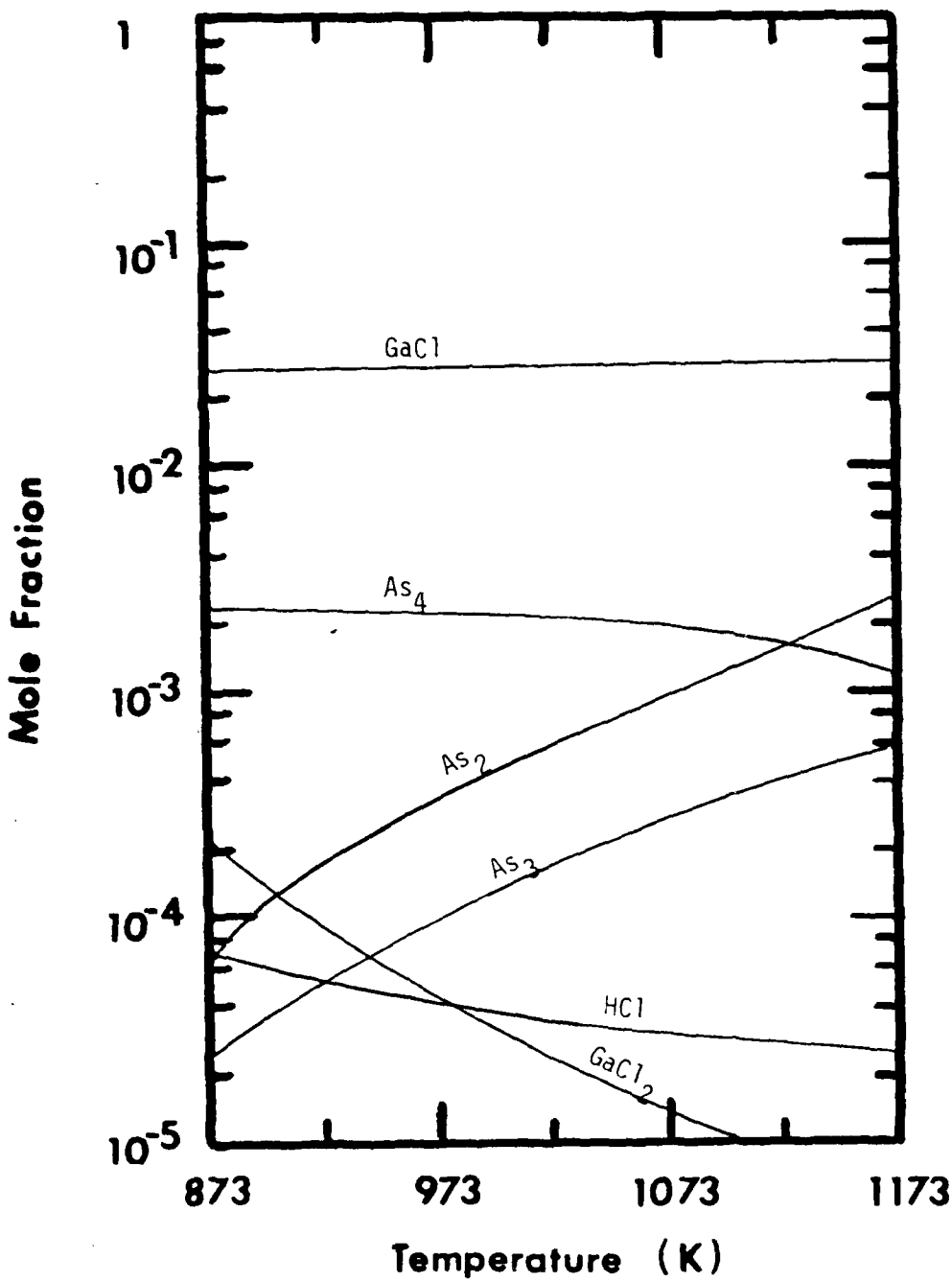
6. RESULTS AND DISCUSSION

6.1 Introduction

The product of these calculations is the equilibrium composition of the vapor phase in the presence of excess condensed phases. The composition is a function of the operating parameters: temperature, pressure, overall inlet gas composition and included condensed phases. The usual procedure was to vary one of the operating conditions while holding the remaining ones at their base values. The graphical representation of these results generally depicts the natural logarithm of the equilibrium vapor mole fractions of each specie versus the parameter varied. Since the primary objective of this study was to examine the unintentional Si incorporation levels, mole fractions are shown typically down to a level of 10^{-10} (0.1 ppb). In order to show the complete detail, these plots were generally limited to fewer orders of magnitude in mole fraction. Furthermore, since the Si species were always found to be below 10^{-5} mole fraction, only the lower range are given, unless the upper range is necessary to understand the results. A full parametric analysis was performed and over 160 plots were generated. In most cases the results were obvious or similar to analogous systems. Thus, this report includes only those necessary for understanding the principal phenomena observed. In interpreting these plots, it should be realized that an excess specie serves to constrain the activity of that specie to a constant value. For example, with solid SiO_2 present the activity of SiO_2 is fixed at unity and therefore the product of the Si and O_2 partial pressures is also fixed. Thus changes in operating parameters that alter the O_2 fugacity will alter the Si activity by the same degree in an inverse fashion.

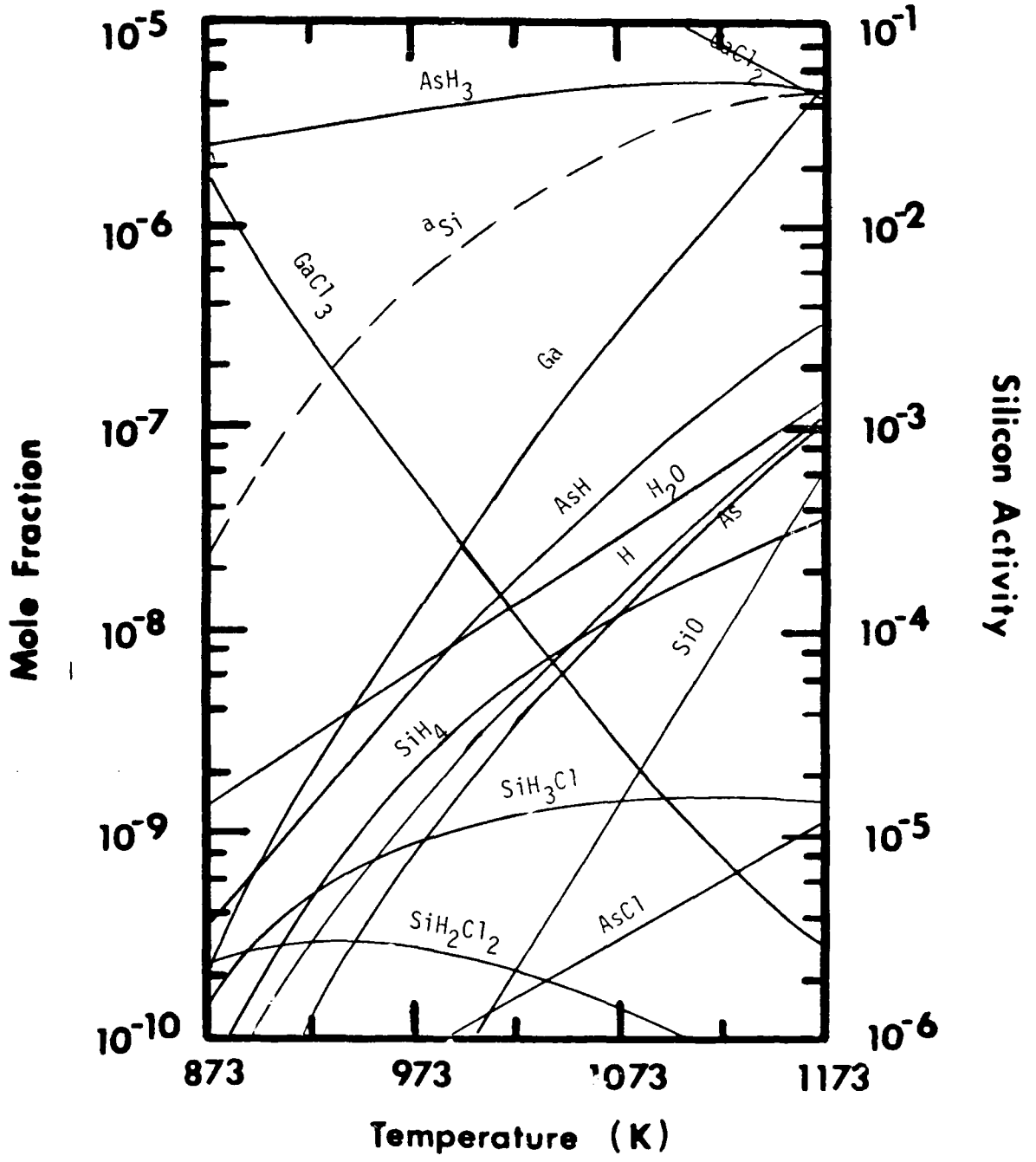
6.2 The GaAs Chloride System

The effect of temperature on the species present in the GaAs chloride system source zone (100 kPa pressure, inlet composition 1% $AsCl_3$ in H_2) is shown in Figures 6.1-6.4. Figures 6.1 and 6.2 apply to the system which used a liquid Group III source,



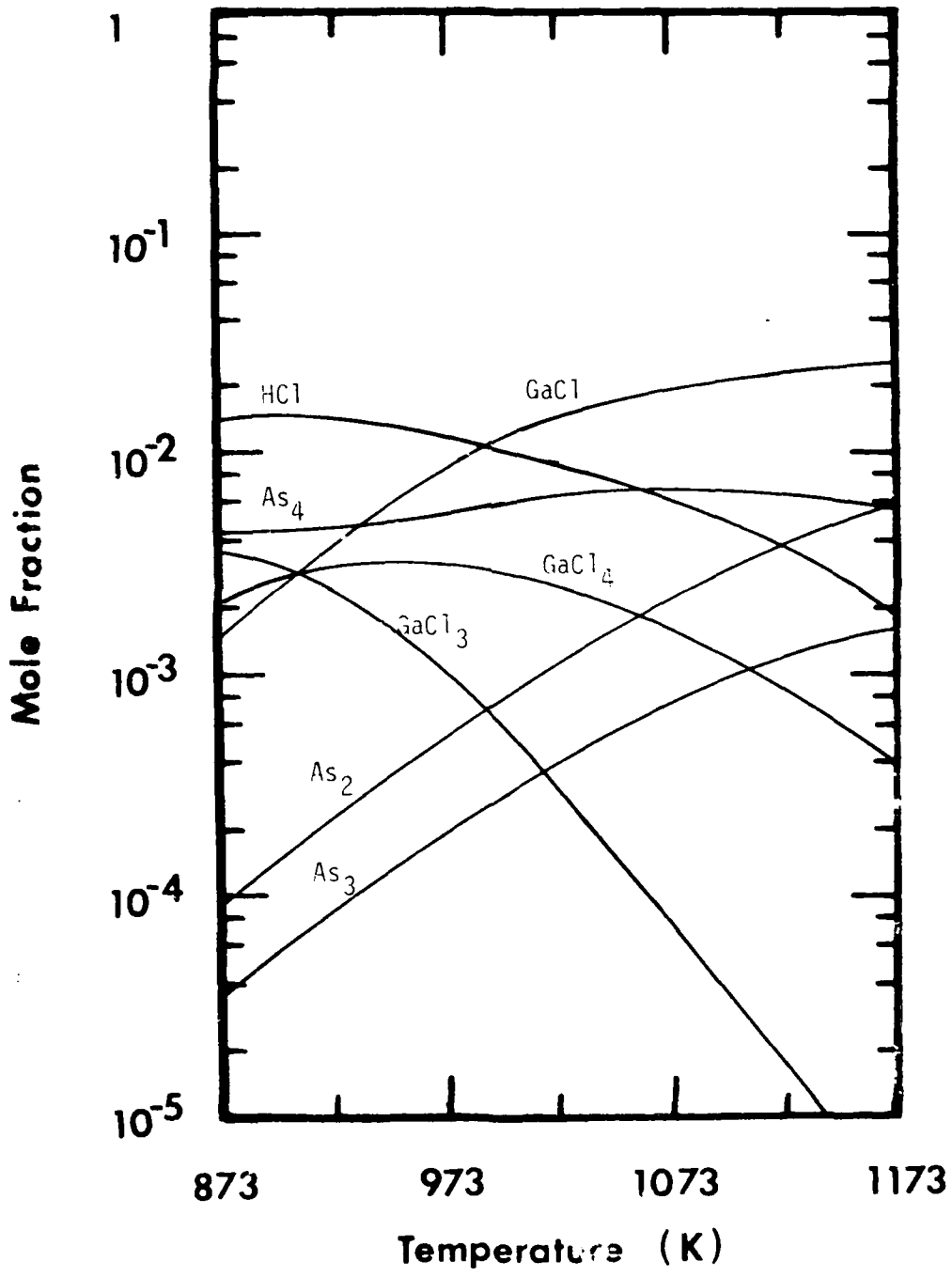
Effect of temperature in the GaAs chloride system source zone (liquid source)

Figure n.1



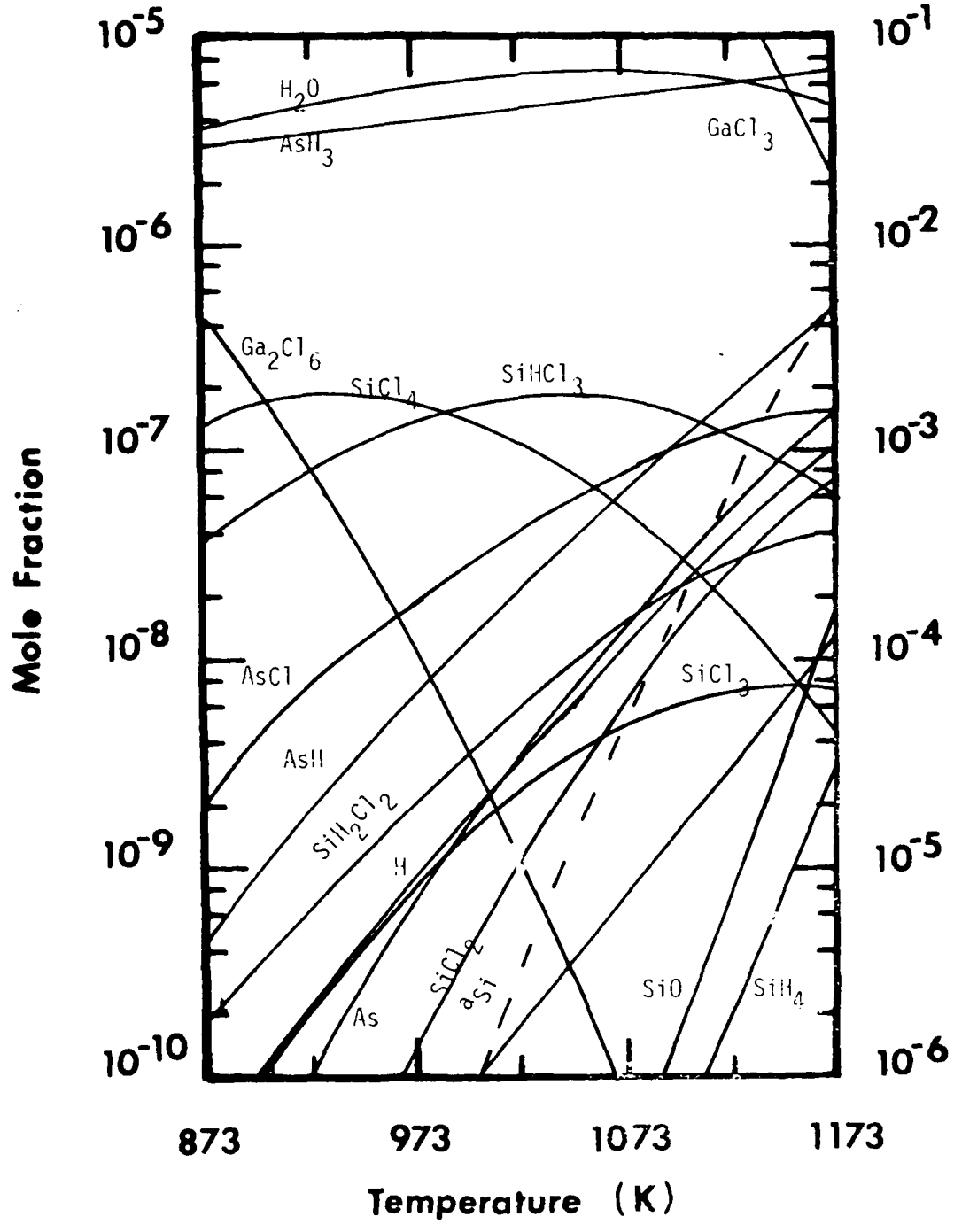
Effect of temperature in the GaAs chloride system source zone (liquid source)

Figure [illegible]



Effect of temperature in the GaAs chloride system source zone (solid source)

Figure 5.



Effect of temperature in the GaAs chloride system source zone

Figure 3.1

Ga_xAs_{1-x}, and Figures 6.3 and 6.4 represent the system which employed GaAs(c) as the Group III source material. At low temperatures $GaCl_2$ and $GaCl_3$ became relatively important gallium vapor species along with GaCl in the solid source system (see Fig. 6.3). In the liquid source system GaCl is the dominant gallium specie over the entire temperature range examined ($873K \leq T \leq 1173K$). In both systems As_4 was the dominant arsenic specie at low temperature while As_2 became important at high temperatures. In contrast to previous studies [30,31], the trimer, As_3, mole fraction was not negligible. In general, comparison of the silicon activity for the two source zones revealed that the silicon activity associated with the GaAs(c) source material was much lower than that which resulted when a liquid source material was employed. The predominant silicon species in the vapor phase of the system which used a solid source were the higher silicon chlorides in contrast to the hydrogen rich silicon species found in the system which used a liquid source. An additional interesting feature is that the total mole fraction of silicon compounds in the vapor for the system which employed a solid source was greater than that for the system which employed a liquid source. At first glance this fact seems contradictory to the lower observed silicon activity.

The following reaction equations may be written to describe the formation of silicon chlorides, chlorosilanes and silane resulting from reactions with the quartz reactor wall.

$$SiO_2(c) + nHCl + (4-n)H_2 = 2H_2O + SiH_{4-n}Cl_n \qquad n=0,1,2,3,4 \qquad (6.2.1)$$

$$kSiO_2(s) + kmHCl + k(2-m/2)H_2 = 2kH_2O + Si_kCl_{km} \qquad k=1,2 \qquad m=0,1,2,3 \qquad (6.2.2)$$

Reactions 6.2.1 and 6.2.2 represent a set of independent formation reactions which describe the interplay between the dominant vapor phase silicon species present in the system. Assuming ideal gas behavior, the equilibrium constants for these reactions are as follows:

$$K_{1,n} = \frac{y_{H_2}^2 o\, y_{SiH_4}\, a_{Si}^n}{y_{H_2}^{4-n}\, y_{HCl}^n\, P_T^{4-n}} \tag{6.2.3}$$

and

$$K_{2,k\,m} = \frac{y_{H_2}^{2k} o\, y_{Si_k Cl_m}\, P_T^{4-km/2}}{y_{H_2}^{k(2-m/2)}\, y_{HCl}^{km}} \tag{6.2.4}$$

where

y_i = vapor phase mole fraction of specie i

P_T = system total pressure ratio (total pressure / reference state pressure)

The activity of silicon residing in a condensed phase which is in equilibrium with the vapor phase may be calculated from any reaction using a vapor Si specie reactant and solid Si product. For example, consider the following reactions and subsequent equilibrium expressions for the activity of Si.

$$Si(c) + 2H_2 = SiH_4 \qquad a_{Si} = \frac{y_{SiH_4}}{K_5\, y_{H_2}^2\, P_T} \tag{6.2.5}$$

$$Si(c) + 4HCl = SiCl_4 + 2H_2 \qquad a_{Si} = \frac{y_{SiCl_4}\, y_{H_2}^2}{K_6\, y_{HCl}^4\, P_T} \tag{6.2.6}$$

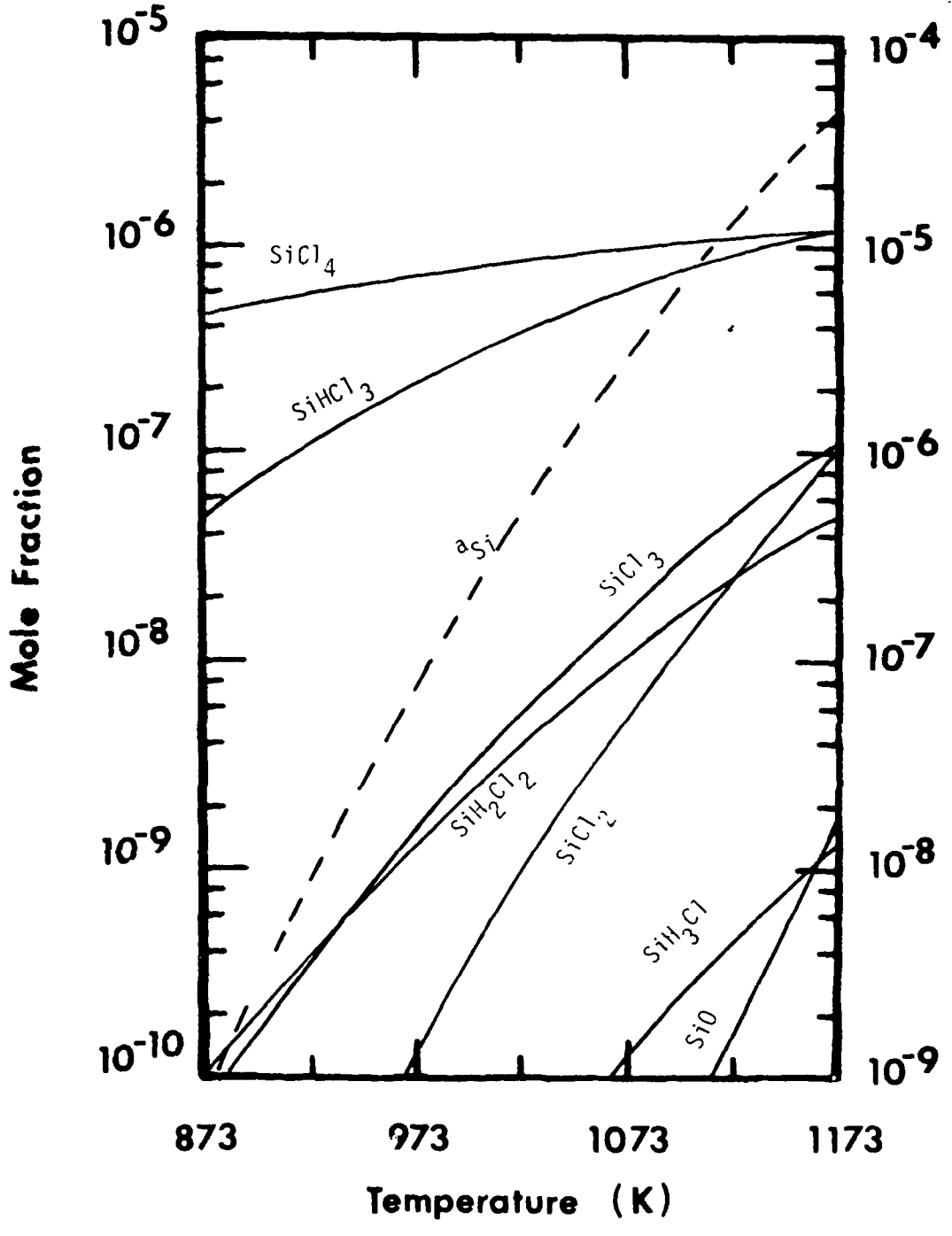
Here K_i is the equilibrium constant for reaction i=5 or 6. Other equivalent relations may be written in order to calculate the condensed phase silicon activity but the models suggested in equations 6.2.5 and 6.2.6 serve as convenient points of focus since either SiH_4 or $SiCl_4$ is usually a significant silicon vapor specie in the systems studied. In particular for those systems using H_2 as the carrier gas, the mole fraction of H_2 is nearly constant with the value unity. Therefore the a_{Si} will track the SiH_4 mole fraction and is inversely proportional to the system pressure. Both models of course yield identical values for the silicon activity when applied to the same situation. The activity of Si presented in these plots can be viewed as the value found in a condensed phase in equilibrium with a vapor having the composition shown. In order to translate this into a solubility the nature of the condensed phase need be reconstructed. Since the

same condensed phase is present (i.e. III-V compound) an increase in activity corresponds to an increase in solubility.

These thermodynamic models for the incorporation of silicon in GaAs epitaxial layers are similar to those proposed by Rai-Choudhury [27] and DiLorenzo and Moore [23]. They differ from the previously proposed models in that a more complete set of species, including condensed phases, are included in the calculation as a result of the application of a digital computer to solve the complex chemical equilibrium problem.

The lower silicon activity associated with the solid GaAs source can therefore be viewed as due to a suppressed SiH_4 concentration when comparing use of the liquid source (equation 6.2.5). In the source zone which employed solid GaAs the presence of primarily higher chlorides and chlorosilanes at the lower source zone temperatures was a result of less gallium being present in the vapor phase than was present when a liquid source was employed. Ga is in excess in both sources thus constraining the activity of Ga with the liquid source having a higher activity. Thus, sufficient HCl was formed due to the decomposition of $AsCl_3$ to enhance reactions 6.2.1 and 6.2.2 for large k and m values. Figure 6.5, which shows the chloride system pre-source zone (1% $AsCl_3$ in H_2, no Group III source material present), further supports this analysis. The absence of Group III chlorides caused the total amount of silicon in the vapor to increase above the level observed in the solid source system while the condensed phase silicon activity decreased even further.

Table 6.1 is a list of the enthalpy of formation at 298K and the Gibbs energy of reaction at 973K for some of the vapor species described by reactions 6.2.1 and 6.2.2. The large negative enthalpies of formation are indicative of strong gas phase atomic bonds and therefore stable species. Since equilibrium represents the lowest Gibbs energy state of the system, species with a lower Gibbs energy of reaction are favored. Therefore, providing sufficient chlorine to react with the silicon species will result in a higher total silicon concentration in the vapor phase but due to the stability of these



Effect of temperature on the GaAs chloride system presource zone

Figure 6.3

species, a lower activity of solid silicon in the condensed phase. The relative stability of silicon halides when compared to silicon hydrides was also recognized by Rai-Choudhury [27].

Table 6.1. Enthalpies of Formation and Gibbs Energies of Reaction for Some Silicon Vapor Species

Vapor Specie	ΔH_f^{298K*} (kcal/ mol^{-1})	ΔG_{rxn}^{973K} (kcal/ mol^{-1})
$SiCl_4$	-158.4	51.4
$SiHCl_3$	-119.5	60.5
$SiCl_3$	-93.3	69.8
SiH_2Cl_2	-75.5	76.9
$SiCl_2$	-40.3	81.8
SiH_3Cl	-32.7	94.0
SiH_4	8.2	111.5
SiCl	47.4	129.8
Si_2Cl_6	-236.0	139.5

*Reference state: Si(c), $Cl_2(v)$, $H_2(v)$ at 298K and 100 kPa

The outlet compositions (equilibrium composition) of the source zones using solid and liquid source materials at 973K were used as input to the mixing zone and the effect of mixing zone temperature was investigated. The system using a liquid source material displayed behavior which was nearly identical to the source zone behavior. This supports Weiner's model [9] which suggested using the outlet composition of the source zone as the inlet composition to the deposition zones. This model is only applicable, of course, if the source and mixing zones are operated at the same temperature. Justification for isothermal operation of the source and mixing zones comes from noting that the condensed phase silicon activity increases with temperature. Therefore, it is desirable to operate the mixing zone at the source zone temperature in order to minimize the silicon activity and at the same time prevent deposition of GaAs in this zone.

The behavior of the mixing zone, when fed from a source zone using solid GaAs as the source material, differs from that of the source zone alone in that the mole fractions of all of the chlorinated vapor phase silicon species increase with temperature, as does the condensed phase silicon activity. Although the silicon activity in the mixing zone increases more slowly with temperature than it does in the source zone, in the interests of attaining the lowest possible silicon activity it is again advisable to operate the mixing zone at a temperature equal to or less than that of the source zone.

The effect of temperature on the deposition zone for source and mixing zone temperatures of 973K, pressures of 100 kPa, a liquid source material and 1% $AsCl_3$ in H_2 inlet to the reactor, has shown GaCl and As_4 to be the dominant Group III and V species. A measure of the supersaturation of the vapor was defined based on the reaction

$$GaAs(c) = Ga + As \tag{6.2.7}$$

using the equilibrium relationship

$$R_{sat} = \frac{P_{Ga} P_{As}}{K_{sat}} \tag{6.2.8}$$

where: $$K_{sat} = \exp(-\Delta G^{\circ}_{rxn} / RT)$$

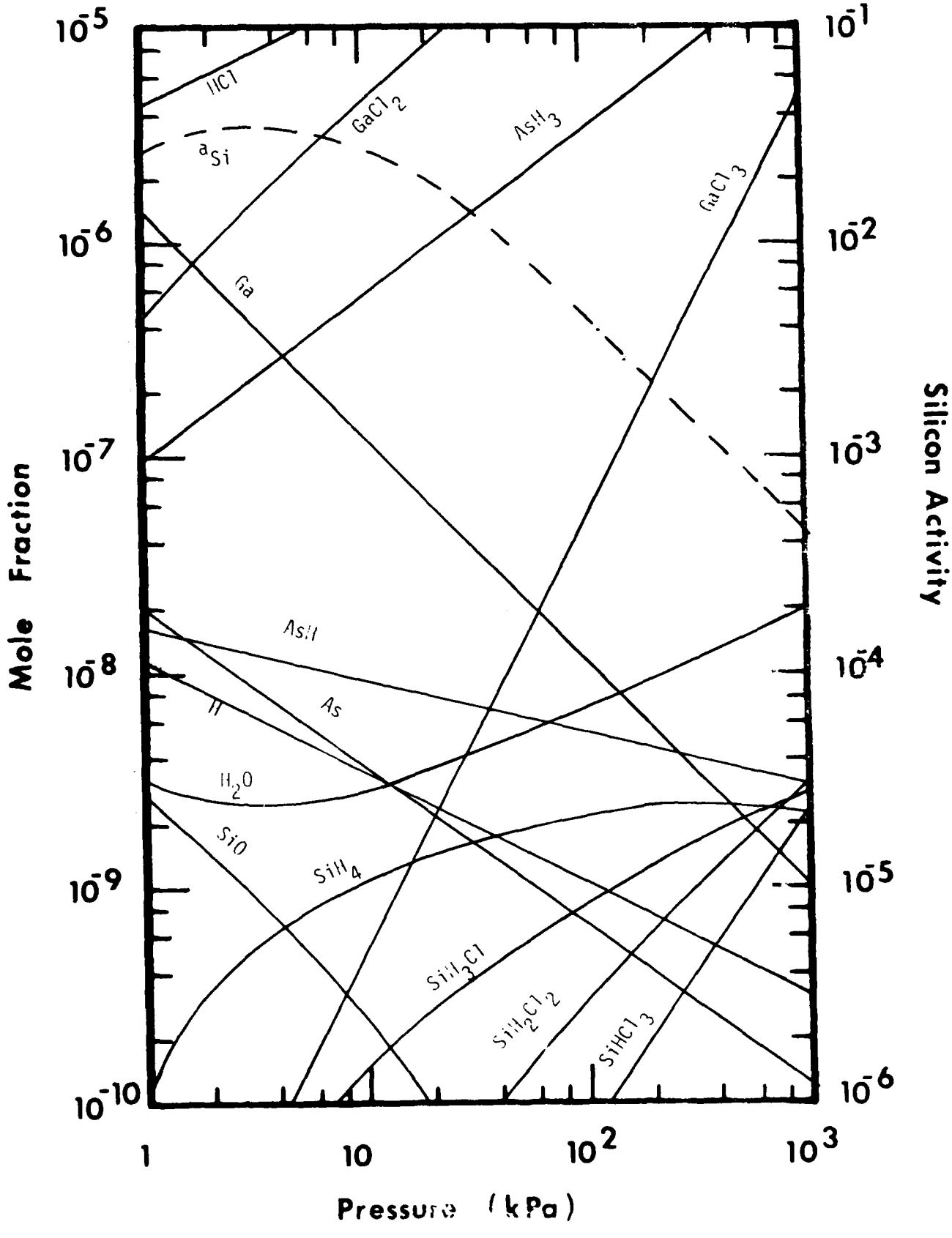
This saturation ratio was observed to decrease from 4×10^{5} at 773K to 700 at 973K which shows the vapor phase to be highly supersaturated. When $SiO_2(c)$ was not included in the deposition zone the condensed phase silicon activity changed only slightly from 9×10^{-3} at 773K to 6×10^{-3} at 973K. Including $SiO_2(c)$ in the deposition zone calculation resulted in the condensed phase silicon activity becoming a strong function of temperature (due to reversal of reactions 6.2.1 and 6.2.2) with the activity value at 973K remaining unchanged and the 773K value falling to 9×10^{-5}.

When solid GaAs was used as the Group III source material the following results were obtained for the deposition zone. The saturation ratio fell from a value of 200 at 773K to the expected value of 1 at 973K, thus showing the system to be much less supersaturated than the liquid source material counterpart. This lower degree of supersaturation was due to much less GaCl being present in the vapor. The dominant Group V specie was As_4 but GaCl, $GaCl_2$ and $GaCl_3$ were all important contributors to the Group III vapor species. The condensed phase silicon activity was found to increase with temperature from 9×10^{-8} at 773K to 7×10^{-7} at 973K for the case where $SiO_2(c)$ was not included in the deposition zone. When $SiO_2(c)$ was included the silicon activity at 773K fell to 2×10^{-9}.

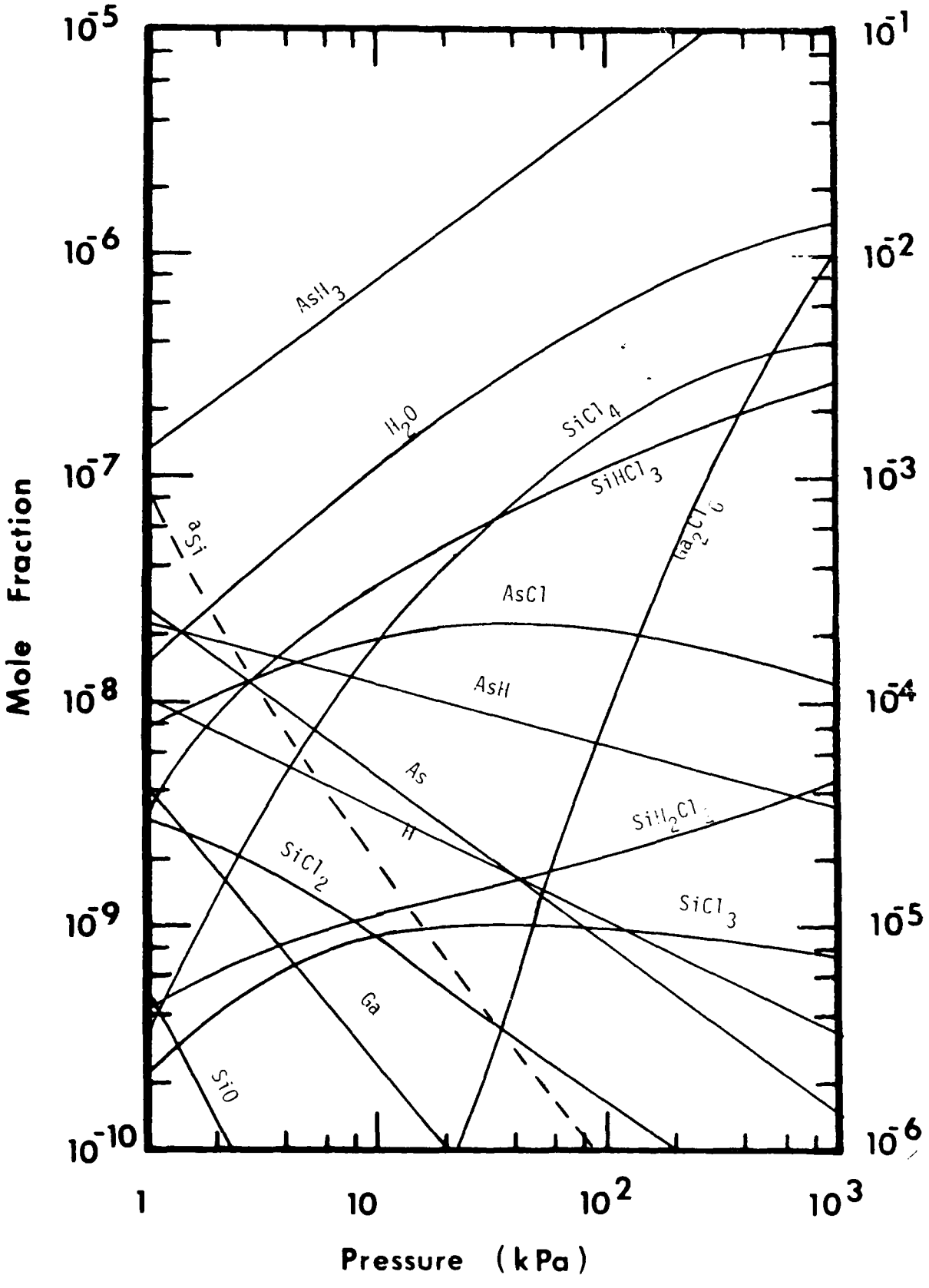
The effect of pressure was investigated over the range of 1 to 1000 kPa (temperature 973K, inlet composition: 1% $AsCl_3$ in H_2) for both the solid and liquid Group III source materials. Over the entire range studied GaCl was the dominant Group III vapor specie in the system using a liquid source material, while for the system using solid GaAs as the source material, GaCl became the dominant Group III specie at pressures below 100 kPa but competed with $GaCl_2$ and $GaCl_3$ at the higher pressures. The dominant Group V vapor specie was As_4 at pressures above 10 kPa with As_2 becoming important below this pressure, in agreement with Gentner et al. [31], in both the liquid and solid sourced systems.

Figures 6.6 and 6.7 show the lower five orders of magnitude in mole fraction and the condensed phase silicon activities in the liquid and solid material source zones. The silicon activity in the system using a liquid source material reaches a maximum at a pressure of 4 kPa and then decreases with increasing pressure. This behavior has not been reported in the literature presumably due to the constrained nature of previous equilibrium calculations. Referring to equation 6.2.5 reveals that the maximum in the silicon activity is due to the SiH_4 mole fraction rising faster than P_T in the 1 to 10 kPa range. Applying equation 6.2.3 to the specie SiH_4 (n=0) and referring to Figure 6.6 shows that the SiH_4 mole fraction dependence on pressure deviates from being linear

Effect of pressure on the GaAs chloride system source zone (liquid source)



Effect of pressure on the GaAs chloride system source zone (solid source)



Figure

due to the H_2O mole fraction changes in this range ($y_{H_2} \approx 1$). The change in H_2O mole fraction is due to changes in the total amount of $SiO_2(c)$ which has reacted with the vapor. Reaction 6.2.1 is important in this system and, as the pressure increases, causes more $SiO_2(c)$ to react which generates more H_2O.

The dominant silicon vapor specie present at the low end of the pressure range is SiO which is formed via the reaction

$$2SiO_2(c) + H_2 = 2SiO + H_2O \tag{6.2.9}$$

with the corresponding equilibrium relationship

$$K_3 = \frac{y_{SiO}^2 \, y_{H_2O} \, P_T^2}{y_{H_2}} \tag{6.2.10}$$

Thus, the observed minimum in the H_2O mole fraction is due to the interaction between the decreasing mole fraction of SiO with the increasing system pressure from reaction 6.2.7 along with the H_2O generation from reaction 6.2.1. Reaction 6.2.2 is not important in this situation.

The source zone which used solid GaAs as the Group III source material shows a strictly decreasing condensed phase silicon activity with increasing system pressure and is best described via reactions 6.2.1 and 6.2.2 in conjunction with the silicon activity model provided by equation 6.2.6. The decrease in silicon activity is due to the 3 order of magnitude increase in $SiCl_4$ mole fraction being offset by an order of magnitude increase in HCl mole fraction ($a_{Si} \propto y_{HCl}^4$) and the P_T^{-1} dependence of the silicon activity. Once again the activity of silicon in the system using solid GaAs as a source material is much less than the activity resulting from using liquid Ga_xAs_{1-x} as the Group III source material.

The mixing and deposition zones were studied using only the liquid Group III source material in the source zone. The mixing zone results were again essentially the same

as those of the source zone (operated at the same temperature) and therefore do not require further discussion.

The deposition zone, shown in Figures 6.8 and 6.9, exhibited a saturation ratio of approximately 2×10^{3} at a pressure of 1 kPa rising to approximately 2×10^{4} at 1000 kPa. Thus, the deposition zone was supersaturated over the entire pressure range investigated.

The maximum value of the condensed phase silicon activity observed for the source and mixing zones was not prevalent in the deposition zone since $SiO_2(c)$ was not included in the deposition zone model. Therefore, the silicon activity decreased with increasing pressure in accord with equation 6.2.5

The mole fraction of $AsCl_3$ present in the feed stream was varied from 0.1% to 10% in order to determine its effect on the condensed phase silicon activity. For the source zone utilizing a liquid Group III source material most of the chlorine atoms provided by the decomposition of $AsCl_3$ were used to generate GaCl. Therefore, the condensed phase silicon activity was not appreciably affected until large concentrations of $AsCl_3$ were reached. The silicon activity was found to decrease from 7×10^{-3} at 0.1% $AsCl_3$ to 6×10^{-3} at 1% $AsCl_3$ and finally to 7×10^{-4} at 10% $AsCl_3$. These results agree qualitatively with previous calculations [23,27] and observations [20,21,22,26].

A very marked effect on the silicon activity was observed as the $AsCl_3$ inlet concentration was varied in the system using solid GaAs as the Group III source material. Since less GaCl was generated in this system when compared to the system using a liquid Group III source, more HCl was available from the decomposition of $AsCl_3$ to react with the silicon vapor species. Thus, the condensed phase silicon activity was found to decrease uniformly from 9×10^{-5} at 0.1% $AsCl_3$ to 1.5×10^{-3} at 10% $AsCl_3$ inlet concentration.

The reason less GaCl was generated in the system using solid GaAs as the Group III source is explained by the following reactions.

Effect of pressure on the GaAs chloride system deposition zone

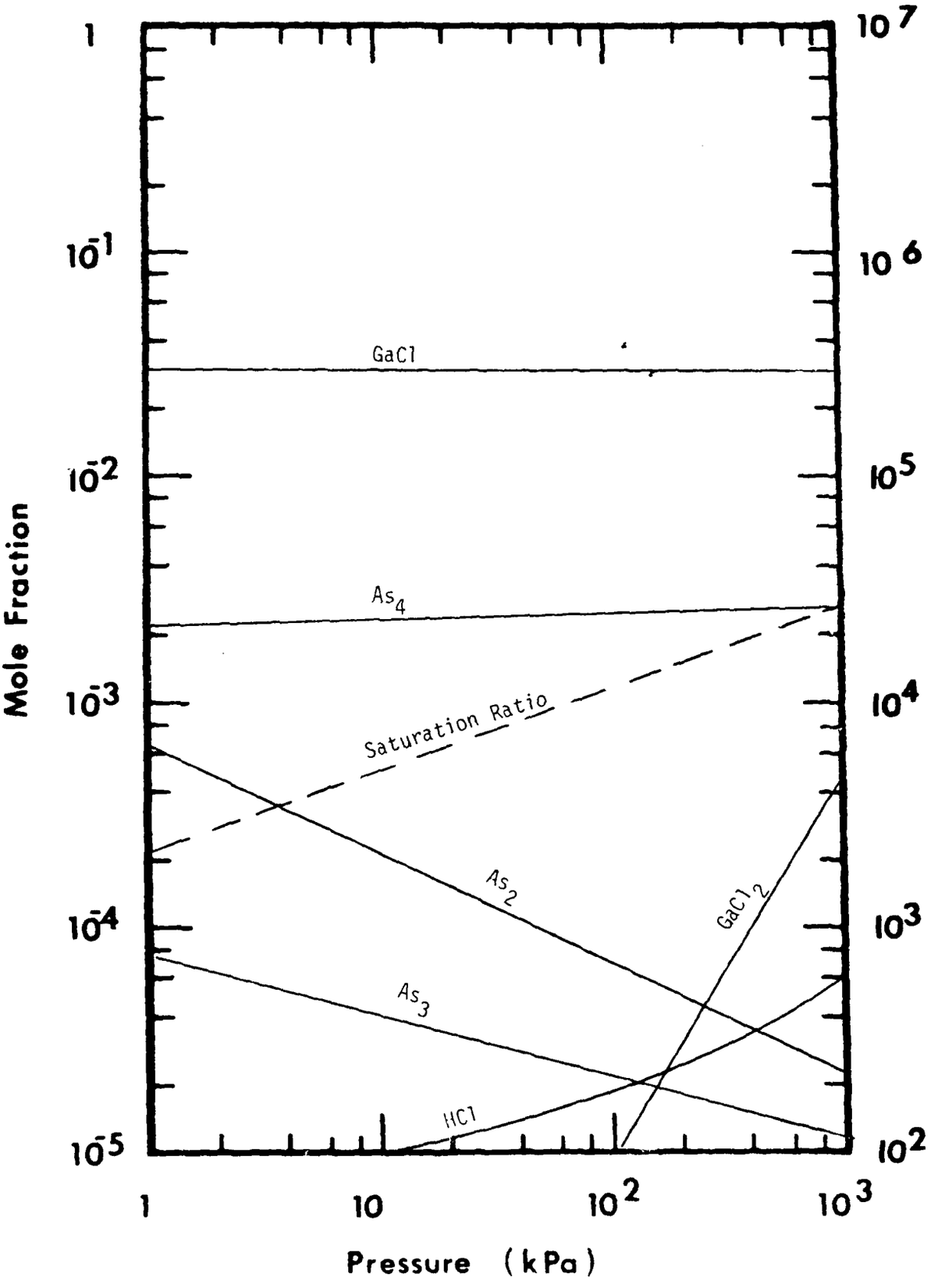
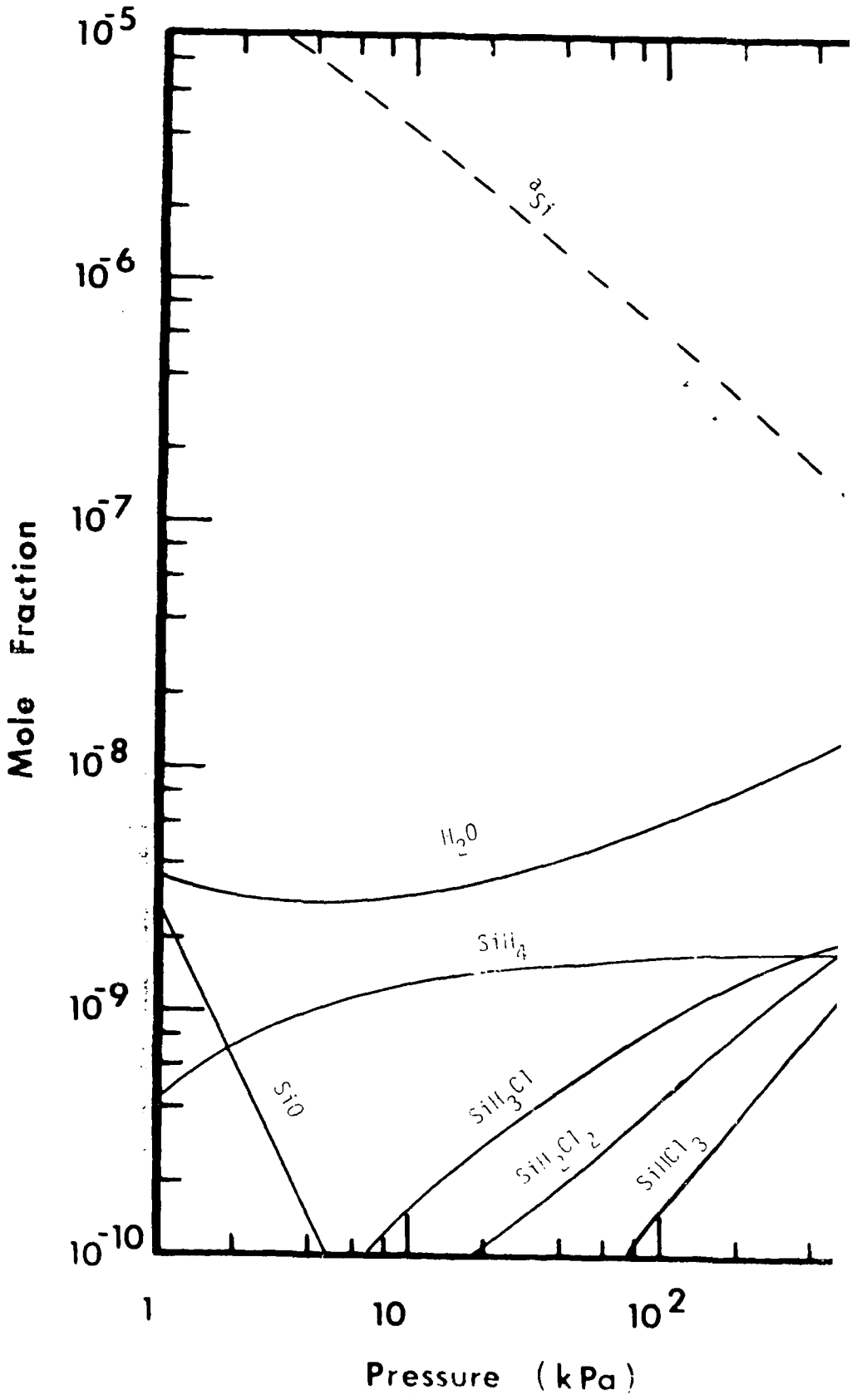


Figure ...

Effect of pressure on the GaAs chloride system deposition zor



$$GaAs(c) + HCl = GaCl + \frac{1}{4} As_4 + \frac{1}{2} H_2 \qquad (6.2.11)$$

$$Ga(l) + HCl = GaCl + \frac{1}{2} H_2 \qquad (6.2.12)$$

Reaction 6.2.11 refers to the system using the solid source and, at 973K, has a Gibbs energy change of 3.2 kcal mole^{-1} while reaction 6.2.12, representing the system with a liquid source, undergoes a Gibbs energy change of −9.5 kcal mole^{-1}. The negative Gibbs energy change of reaction 6.2.10 causes the products of the reaction to be favored.

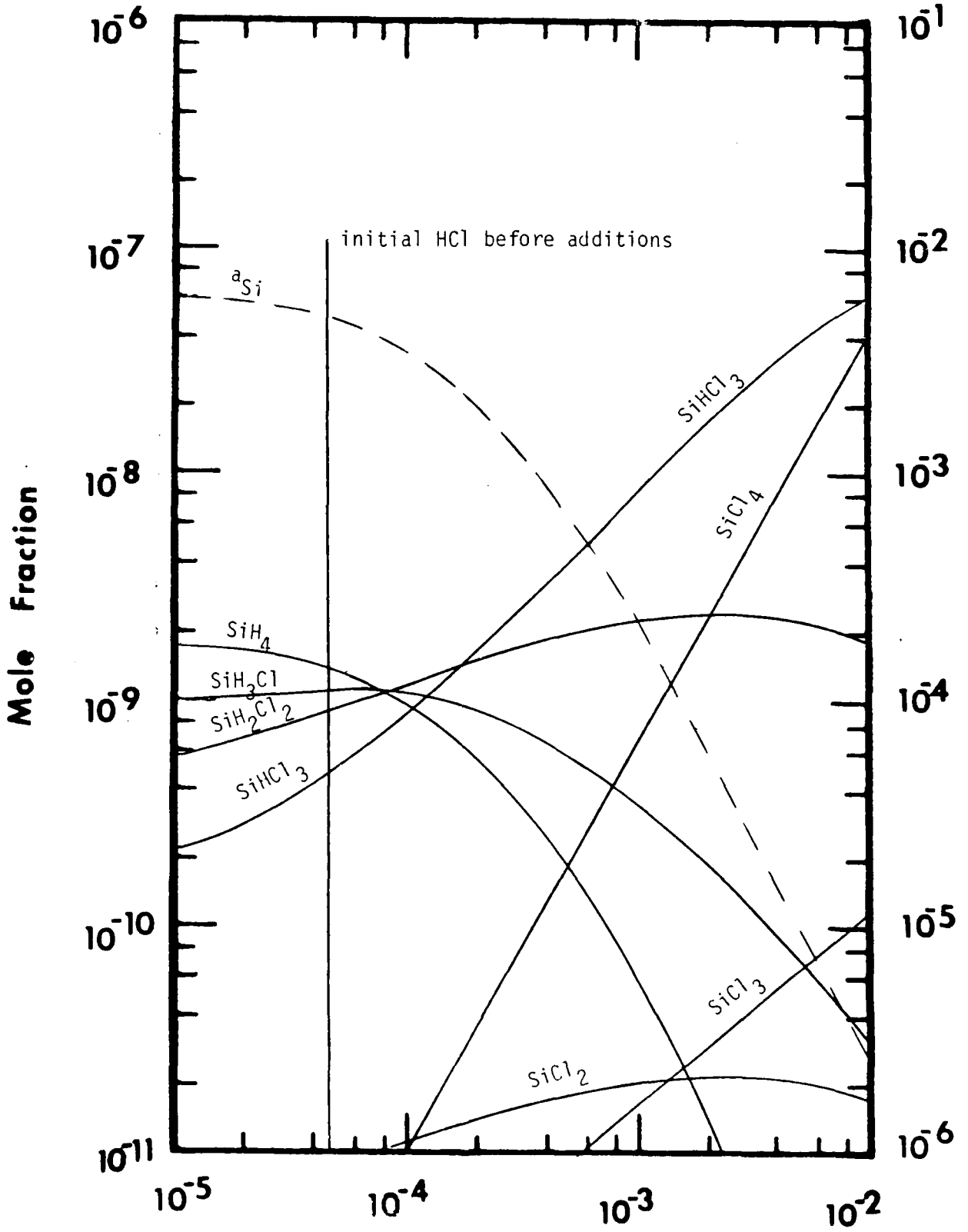
The source zone results were carried through the mixing zone and deposition zone for the system using a liquid Group III source. The mixing zone yielded the same results as the source zone (both zones operating at a temperature of 973K) and the deposition zone showed the same trends as were observed in the source and mixing zones with the values of silicon activity slightly higher due to the lower deposition zone temperature (873K).

A more effective way to reduce the silicon activity in systems using a liquid Group III source is to add HCl (or $AsCl_3$) downstream of the source zone. This allows the chlorine atoms to react with the silicon species instead of generating additional GaCl.

Figure 6.10 shows the effect of adding small quantities of HCl to the mixing zone on the condensed phase silicon activity in the deposition zone (basis: 1 mole of vapor in the mixing zone). The initial HCl mole fraction in the deposition zone prior to the addition of any HCl was 4.5×10^{-5}. In accord with reactions 6.2.1, 6.2.2, 6.2.5 and 6.2.6 the silicon compounds shift from being hydrogen rich to chlorine rich and the silicon activity decreases markedly. The addition of $AsCl_3$ has the same effect except that the activity decrease is slightly more pronounced since there are three chlorine atoms per molecule of $AsCl_3$ compared to one for HCl.

Another method of decreasing the condensed phase silicon activity is to add H_2O to the system. This causes a decrease in the total amount of silicon in the vapor by

Effect of adding HCl on the GaAs chloride system deposition zone



shifting reactions 6.2.1 and 6.2.2 in favor of $SiO_2(c)$. This effect is demonstrated in Figure 6.11 for small additions of H_2O to the mixing zone (basis: 1 mole of vapor in the mixing zone) where the mole fraction of H_2O prior to the additions was 5.5×10^{-9}. This effect was predicted by Rai-Choudhury [27] and observed by Palm [38].

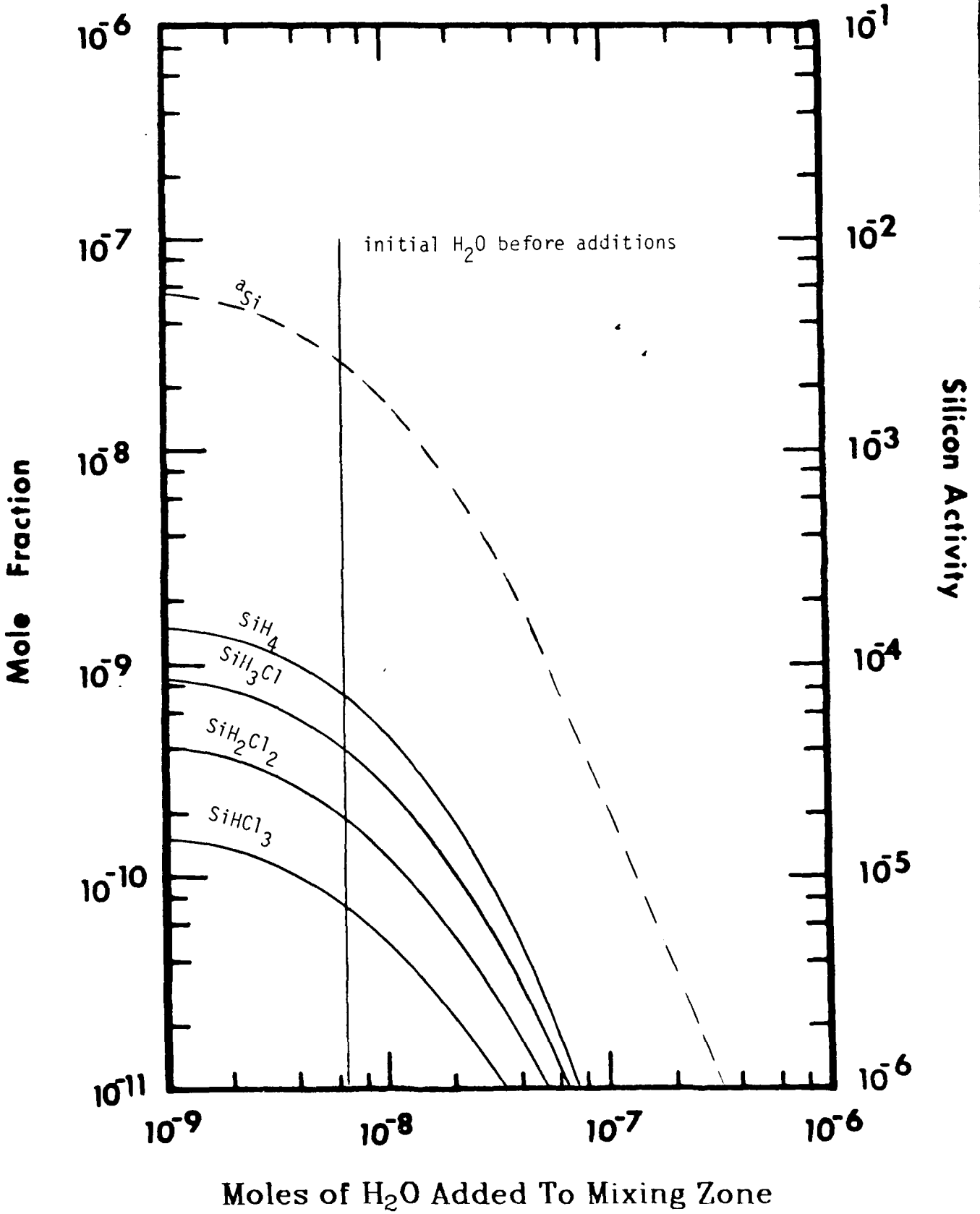
Replacing the hydrogen carrier gas with an inert gas is yet another method of reducing the condensed phase silicon activity. This method also reduces the total amount of silicon in the vapor by shifting reactions 6.2.1 and 6.2.2 in favor of $SiO_2(c)$ as shown in Figure 6.12. Reduction of silicon incorporation using an inert to replace H_2 was studied by Seki et al. [33] and observed by Ozeki et al. [34]. The curvature in the silicon activity is best understood by referring to reaction 6.2.5. As the hydrogen carrier gas is replaced by an inert the mole fractions of H_2 and SiH_4 decrease. The competing nature of these two mole fractions causes a maximum in the condensed phase silicon activity to occur at approximately 90% inerts after which the silane mole fraction rapidly goes to zero and the silicon activity decreases to a very small value. The silicon activity will never reach zero as predicted by 6.2.6 since reactions 6.2.1, 6.2.2, 6.2.5 and 6.2.6 are not valid models in systems devoid of hydrogen. Instead, small concentrations of Si(v), SiO(v) etc. will remain in the vapor to provide a nonzero but very small condensed phase silicon activity.

The use of solid GaAs as the Group III source material appears to offer an advantage over the liquid Group III source in that lower condensed phase silicon activities were predicted by these thermodynamic models. It must be emphasized, however, that the solid GaAs source was assumed to be pure (i.e. devoid of Si and other contaminants) and, from a thermodynamic point of view, that the purity of an epitaxial layer can be no better than that of the source material unless methods are employed to improve the purity (e.g. additions of HCl, H_2O, etc.) during the CVD process.

6.3 The GaAs Hydride System

The effect of temperature on the silicon species present in the Group III and Group

Effect of adding H_2O on the GaAs chloride system deposition zone



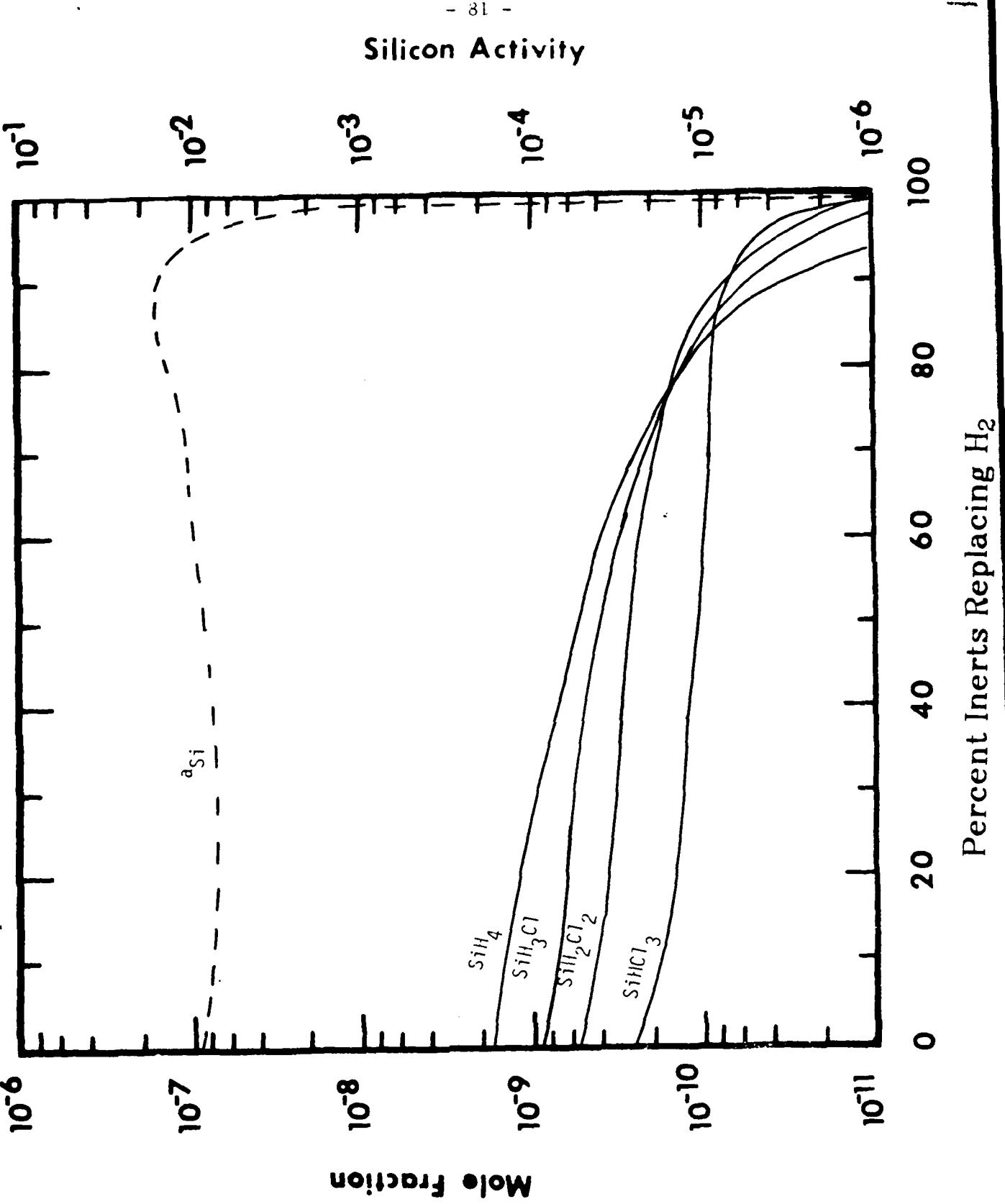
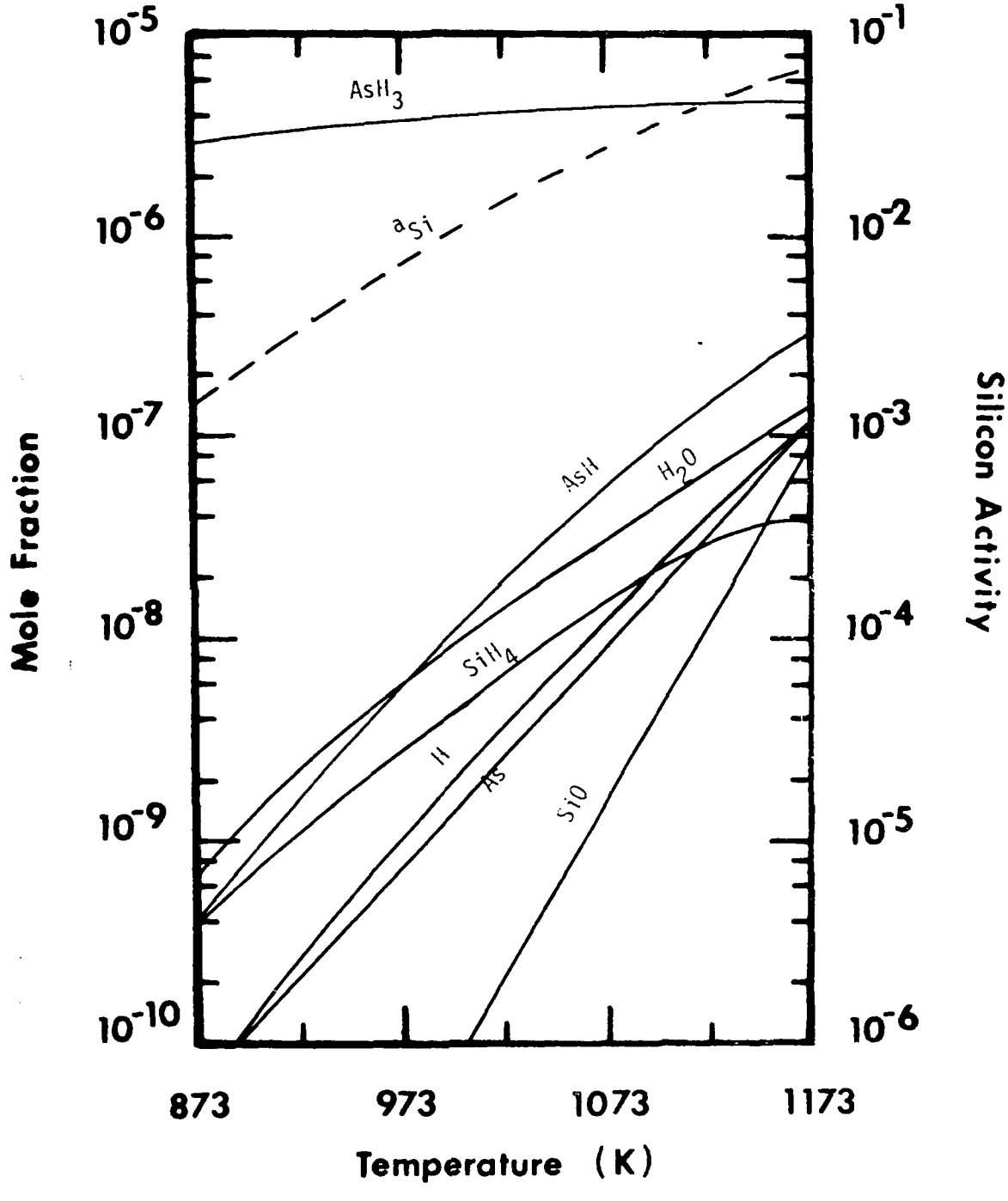

Silicon Activity
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Effect of replacing H_2 with inerts on the GaAs chloride system deposition zone
a_{Si}
SiH_4
SiH_3Cl
SiH_2Cl_2
$SiHCl_3$
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
Mole Fraction
0
20
40
60
80
100
Percent Inerts Replacing H_2

Figure 6.12

V source zones of the hydride system are shown in Figures 6.13 and 6.14. The condensed phase silicon activity for the Group V source zone was essentially the same as that which would be observed in the Group V pre-source zone (AsH_3 absent) since arsine did not compete with silicon for any atoms in the vapor other than hydrogen. The Group III source zone showed a much greater silicon activity than the Group V pre-source zone ($Ga(l)$ absent) shown in Figure 6.15 since the liquid gallium source reacted strongly with HCl to form GaCl. This forced the silicon species to be rich in hydrogen and therefore the condensed phase silicon activity was larger. As can be seen from Figures 6.13 and 6.14, the Group V source zone was primarily responsible for the silicon activity at low temperatures while at high temperatures the Group III source zone contribution to the silicon activity also became important. As was observed in the chloride system for the liquid Ga_xAs_{1-x} source, the dominant Group III vapor specie was GaCl with As_4 being the dominant Group V vapor specie at temperatures below 1073K and As_2 dominant above this temperature.

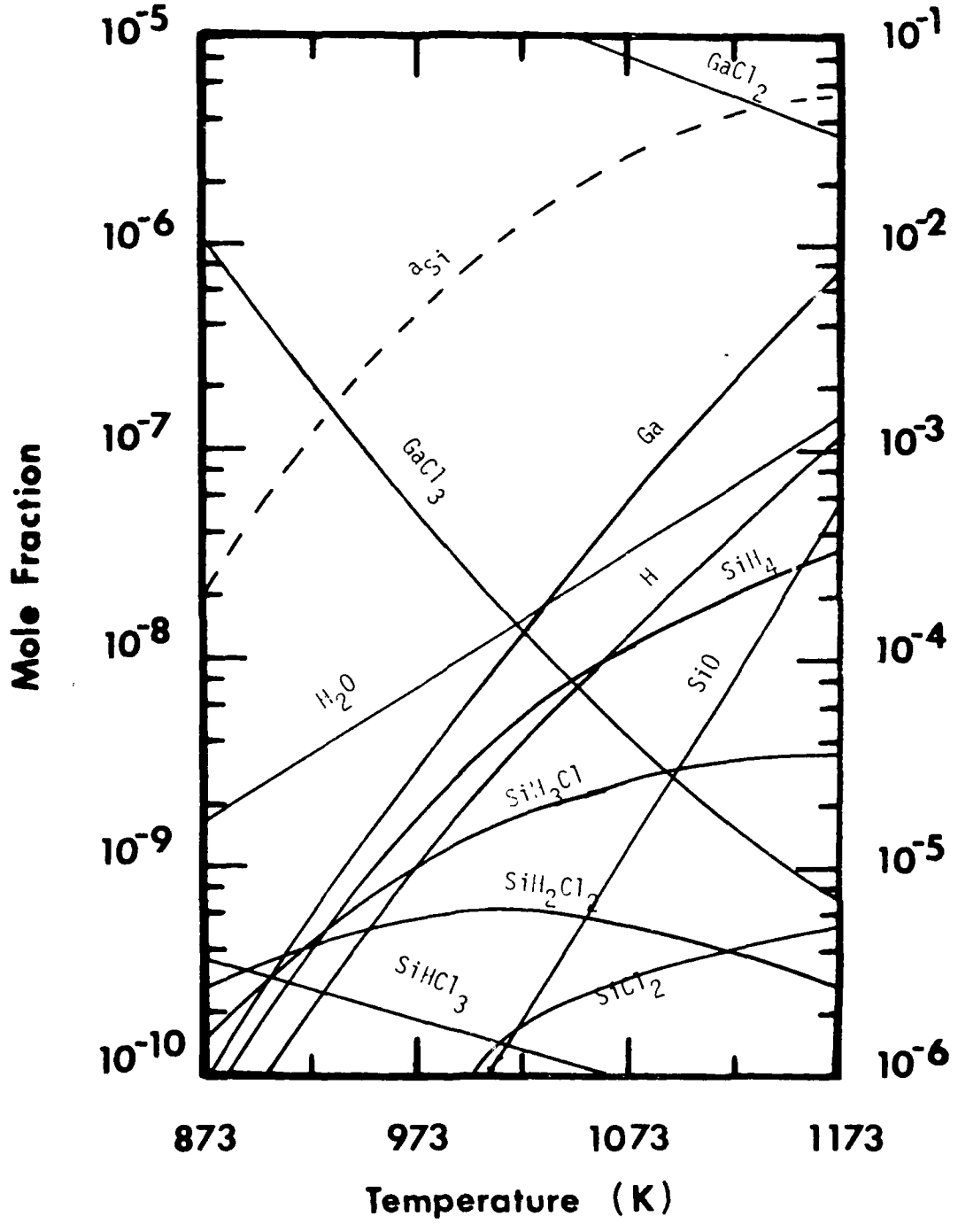
The results of these Group III and V source zone calculations at 973K were then combined and the effect of temperature in the mixing zone was investigated. Figure 6.16 shows this effect on the silicon activity and species in the lower five orders of magnitude in mole fraction. The silicon activity and silane mole fraction were found to be lower than the values for the Group V source zone alone at low temperatures due to the dilution effect of adding the two source zone streams together (equal molar flowrates were assumed in each source zone). Since the silane mole fraction and therefore the silicon activity in each source zone was approximately the same at 1173K, the resulting silicon activity in the mixing zone was the same as that at the outlet of either source zone.

Using the results from the mixing zone at 973K the deposition zone was studied in the absence of $SiO_2(c)$. The saturation ratio, as defined by equation 6.1.8, was found to decrease from 2×10^4 at 773K to 100 at 973K, indicating that the vapor was supersaturated over this entire deposition zone temperature range. The condensed phase



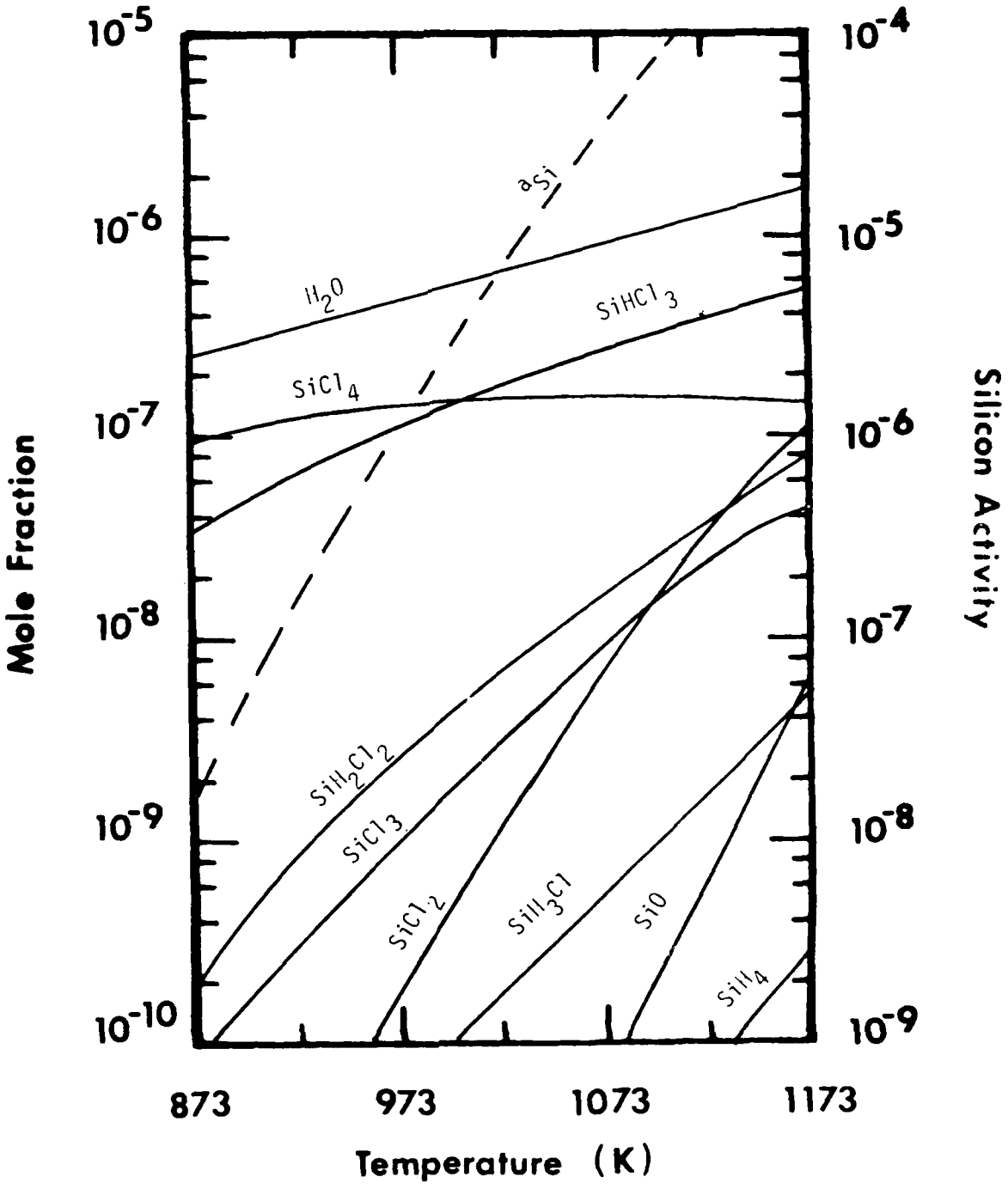
Effect of temperature on the Group V source zone of the GaAs hydride system

Figure 6.1



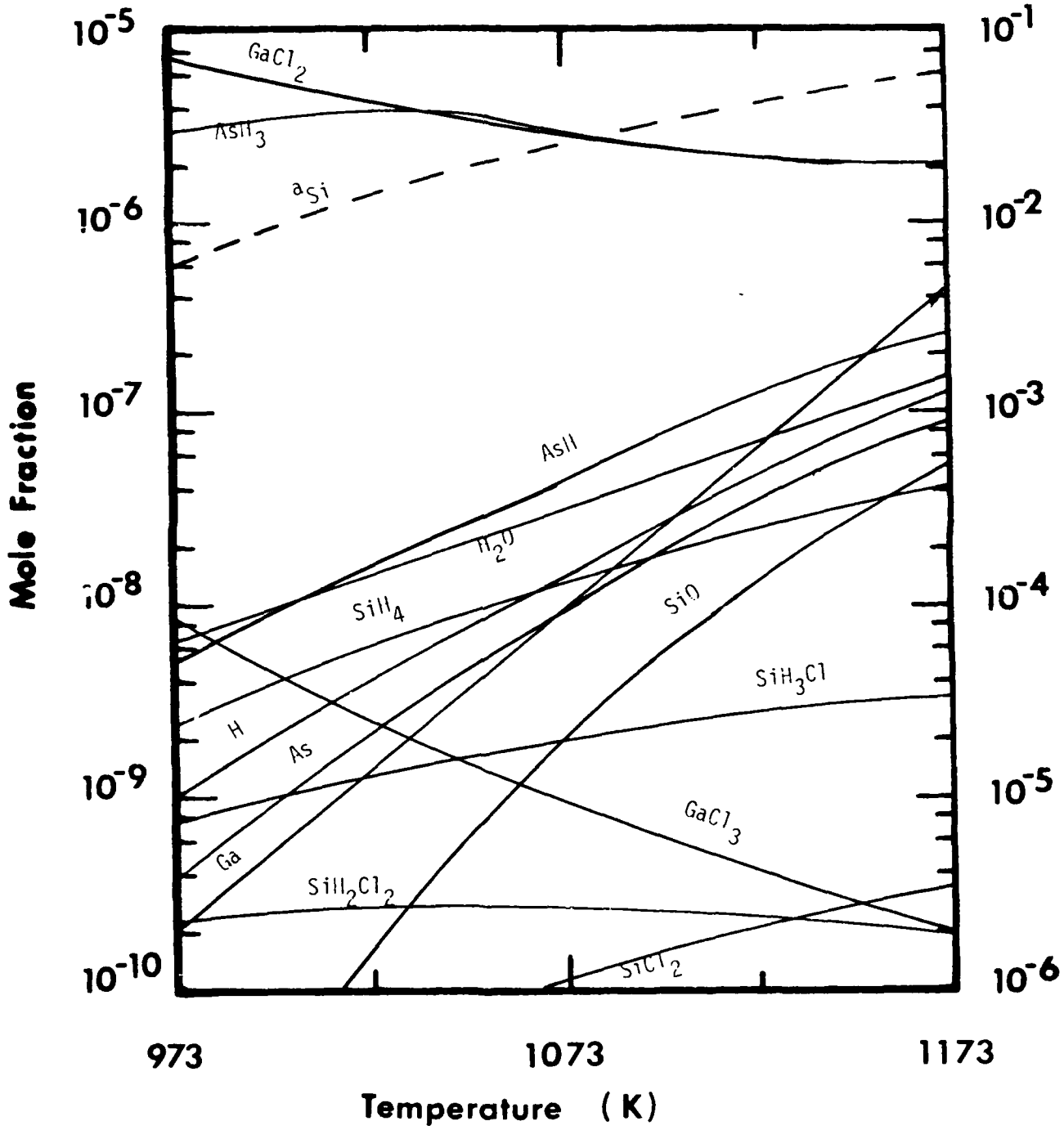
Effect of temperature on the Group III source zone of the GaAs hydride system

Figure 6.14



Effect of temperature on the Group III pre-source zone of the GaAs hydride system

Figure 6.13



Effect of temperature on the mixing zone of the GaAs hydride system

Figure 5.16

silicon activity varied only slightly, increasing from 2×10^{-3} at 773K to 5×10^{-3} at 973K, which is consistent with the effects observed in the chloride system using a liquid Ga_xAs_{1-x} Group III source. The lesser degree of supersaturation found for the hydride system when compared to the chloride system was due to the lesser amounts of Group III and V species present in the vapor. The dilution effect of adding the two source zone streams together causes the Group V vapor species to be one-half the mole fraction observed in the chloride system. The use of HCl coupled with this dilution effect reduces the rate of Group III specie transport to one-sixth of that in the chloride system.

The Group III and V source zones were investigated as functions of pressure at a temperature of 973K. The silicon activity in the Group III source zone was flat from 1 to 10 kPa then fell from a value of 3×10^{-2} to 4×10^{-4} at 1000 kPa. The Group V source zone exhibited a maximum in the condensed phase silicon activity at a pressure of 4 kPa, as did the chloride system source and mixing zones using a liquid Group III source. Upon combining the two hydride system source zones and performing the mixing zone equilibrium calculation the silicon activity in the mixing zone became a decreasing function of pressure.

The effect of pressure on the deposition zone of the hydride system very closely matched that of the chloride system. This result was expected since the source zones of the two systems are the only differences between the two and once downstream of the source zones the equilibrium chemistry of the hydride and chloride systems are the same.

The concentration of AsH_3 in the feed gas stream to the Group V source zone was found to have no effect on the condensed phase silicon activity. This was due to the silicon species being rich in hydrogen and, in the presence of a large fraction of hydrogen carrier gas (> 90%), the hydrogen atoms released from the decomposition of AsH_3 did not contribute significantly to the overall system hydrogen content. There-

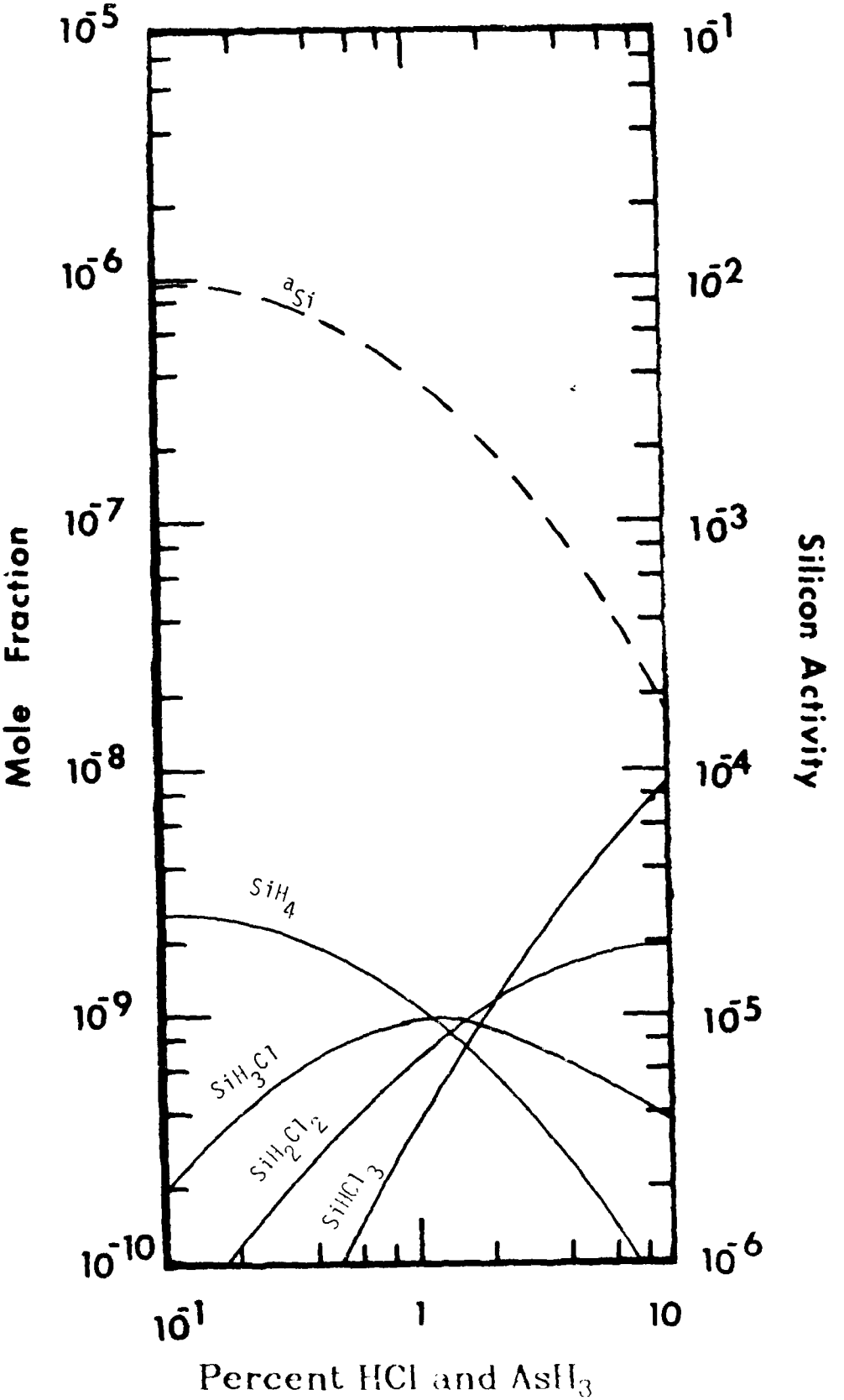
fore, the silane mole fraction was not significantly affected. In contrast Pogge and Kemlage [35] found that increased AsH_3 concentrations decreased the free carrier concentrations in epitaxial GaAs. They cited kinetic effects, however, not thermodynamic limitations as the reason for their observations.

Increasing the concentration of HCl in the feed stream to the Group III source considerably decreased the condensed phase silicon activity by forming chlorine rich, as opposed to hydrogen rich, silicon species. Thus, one method of decreasing the silicon activity while maintaining a constant vapor III/V ratio is to increase both the HCl and AsH_3 mole fractions in the feed streams to each source zone together. This effect is demonstrated for the deposition zone in Figure 6.17. Additionally, if various III/V ratios are desired it is advisable to operate the system with a large HCl concentration, in order to realize a low silicon activity, and vary the AsH_3 concentration until the appropriate III/V ratio is attained.

As was discussed for the chloride system, a very effective method for reducing the silicon activity is to make small additions to HCl or H_2O to the mixing zone. This preserves the system III/V ratio from the hydride system source zones and shifts reactions 6.2.1 and 6.2.2 in favor of $SiO_2(c)$. The results for the hydride system were essentially the same as those obtained for the chloride system and will not be discussed further.

Replacement of the hydrogen carrier gas by an inert gas was less effective in the hydride system than it was in the chloride system since hydrogen was provided by the decomposition of HCl and AsH_3. Figure 6.18 shows this effect for the deposition zone and although a very sharp bend is observed in the silicon activity, even when all of the hydrogen was replaced by inerts, the condensed phase silicon activity was approximately 4×10^{-5}. Therefore, replacing the hydrogen carrier gas by an inert gas was not an acceptable method to achieve low silicon activities. The addition of small amounts of HCl or H_2O to the mixing zone appears to be the most promising method of attain-

Effect of adding HCl on the GaAs hydride system deposition zone



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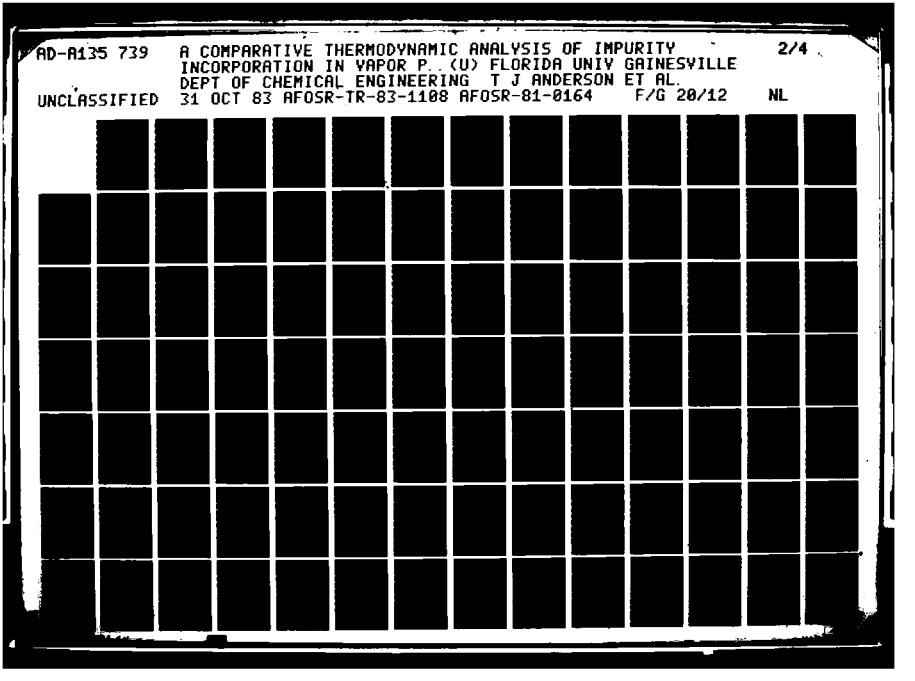

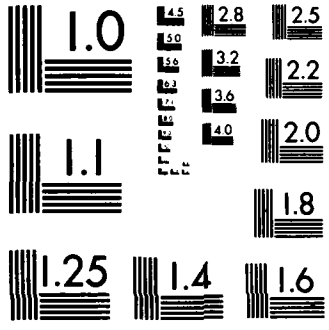

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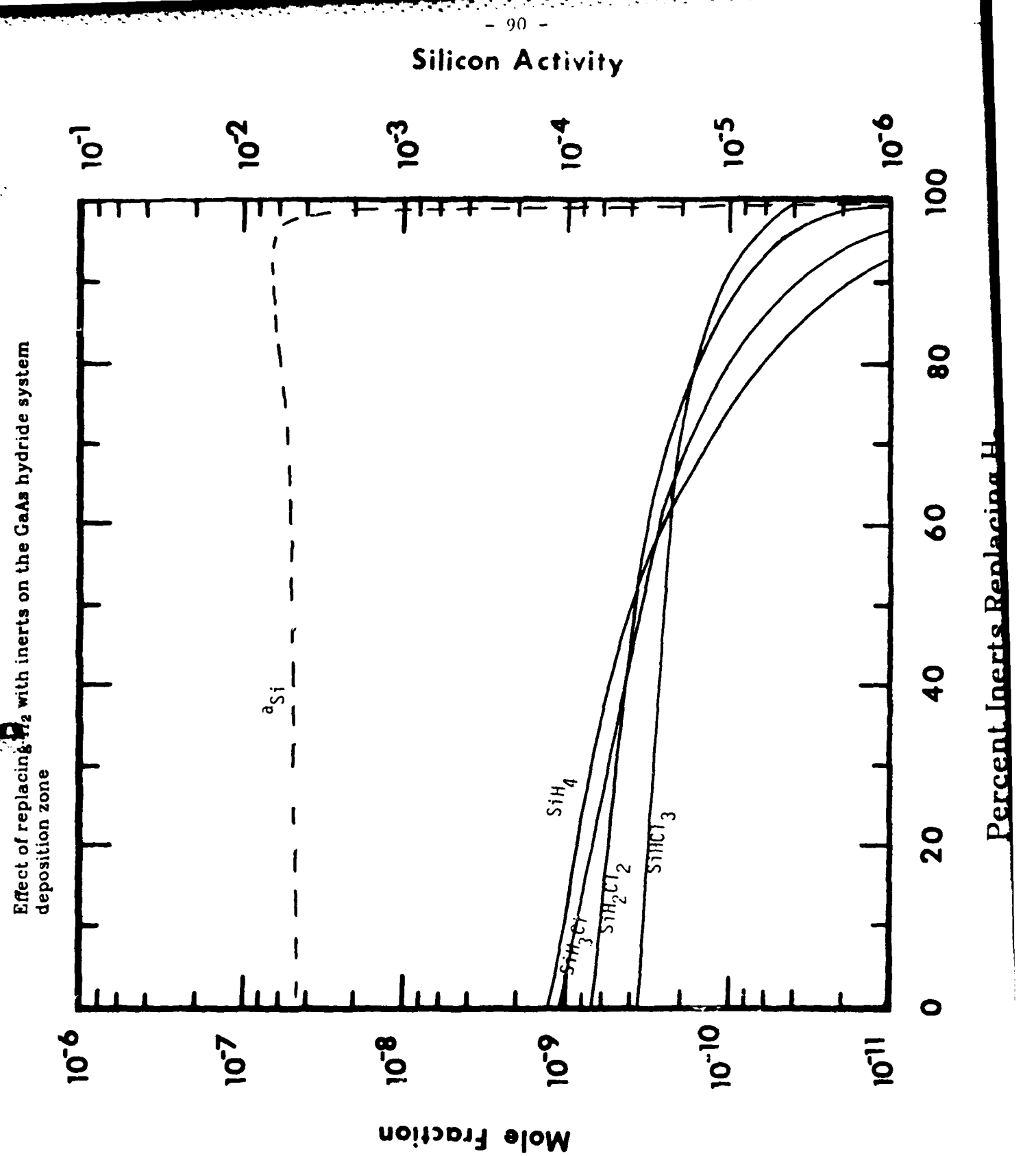


Effect of replacing H_2 with inerts on the GaAs hydride system deposition zone

Figure 6.13

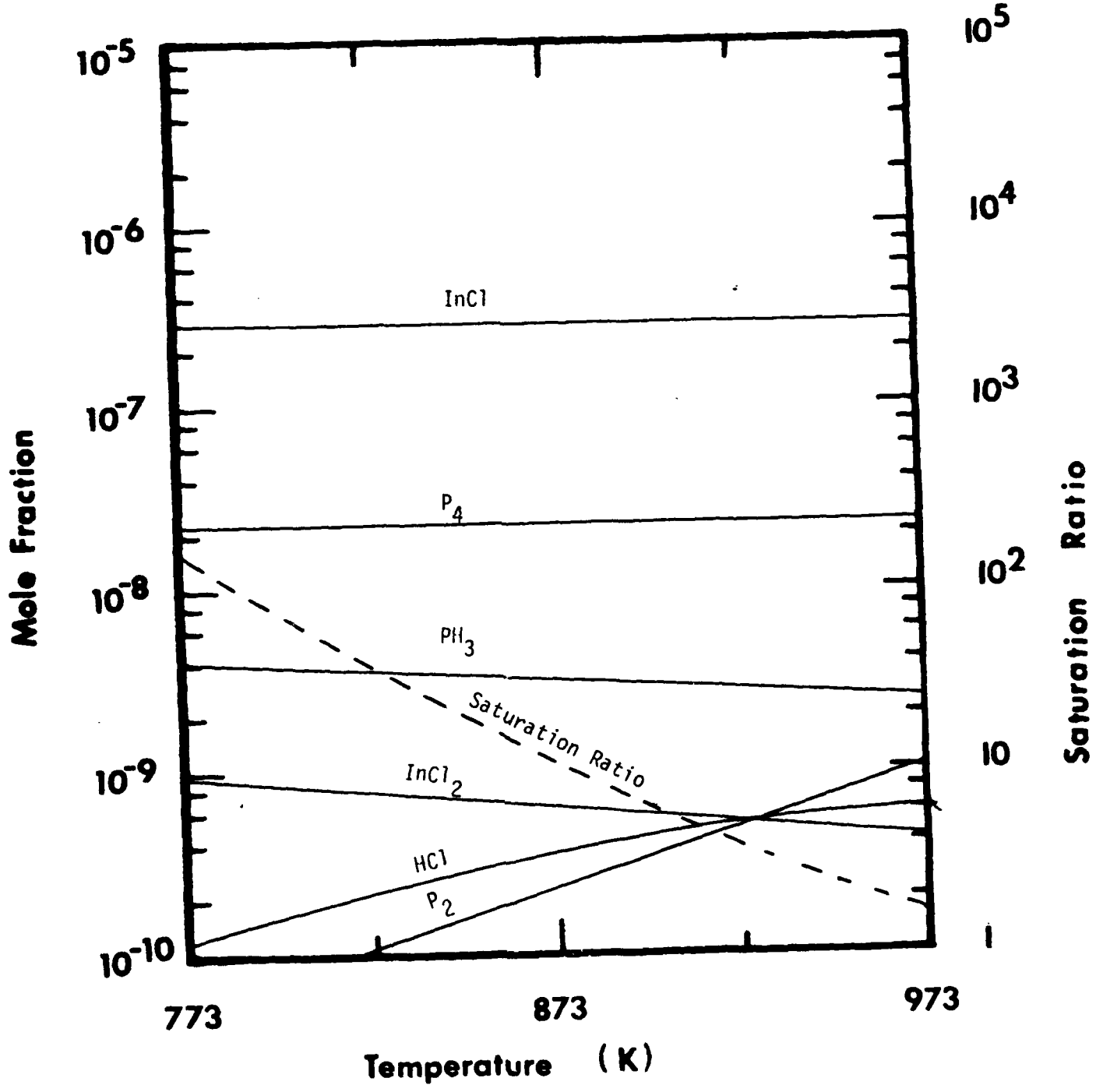
ing very low silicon activities in the hydride system.

6.4 The InP Chloride System

The InP chloride system was investigated under the same conditions as the GaAs chloride system and was found to behave similarly in many respects. The source zone using liquid In_xP_{1-x} as the Group III source material was quite similar to the GaAs system in that InCl and P_4 were the dominant Group III and V vapor species. One difference observed was that P_2 was not as important a specie in the InP system as As_2 was in the GaAs system. This may be due, however, to the equilibrium calculation being constrained as a result of the lack of a thermodynamic data set for the specie P_3. Condensed phase silicon activities for the GaAs and InP systems were found to be essentially the same. These same comments also apply to the mixing zone which was fed from this source zone.

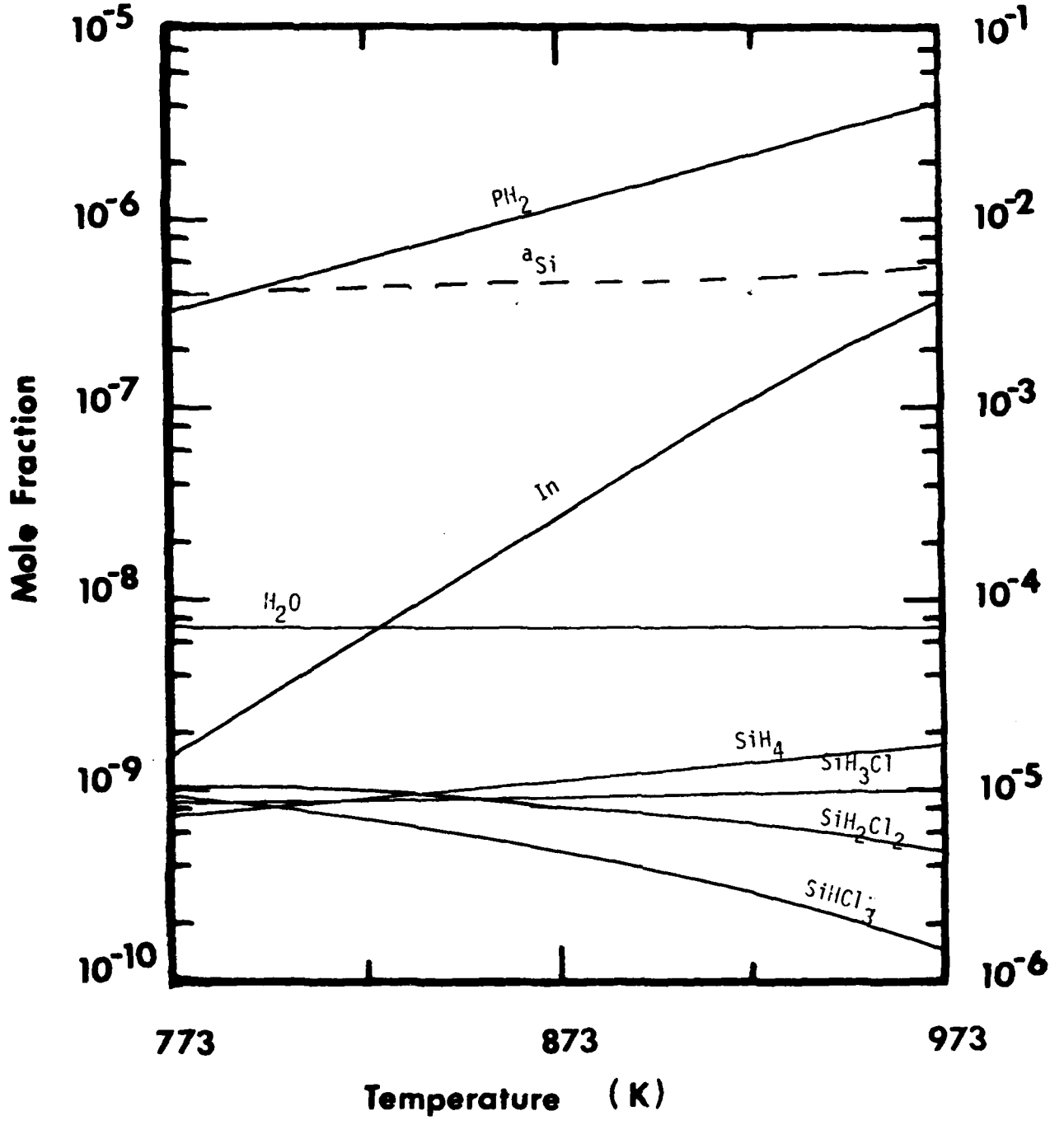
The deposition zone, shown in Figures 6.19 and 6.20 for the situation where $SiO_2(c)$ was not included in the calculation, demonstrates several differences between the GaAs and InP systems. First, the saturation ratio for the InP system defined in analogy with equations 6.1.7 and 6.1.8, was much smaller than that of the GaAs system. The Gibbs free energy change for reaction 6.1.7 at 873K is 95.2 kcal/g-mole while the free energy change of the analogous reaction in the InP system is only 69.5 kcal/g-mole. Thus, the value of the equilibrium constant for the InP system is much larger than that for the GaAs system and, therefore, larger gas phase In and P partial pressures must be present in order to attain equal degrees of supersaturation in the two systems.

The condensed phase silicon activity for the InP system was slightly lower than that of the GaAs system, due to the lower SiH_4 mole fraction, but increased slightly with temperature. Recall that the silicon activity in the GaAs system displayed a slight decrease in temperature when $SiO_2(c)$ was not included in the calculation.



Effect of temperature on the InP chloride system deposition zone

Figure 5.19



Effect of temperature on the InP chloride system deposition zone

Figure 6.20

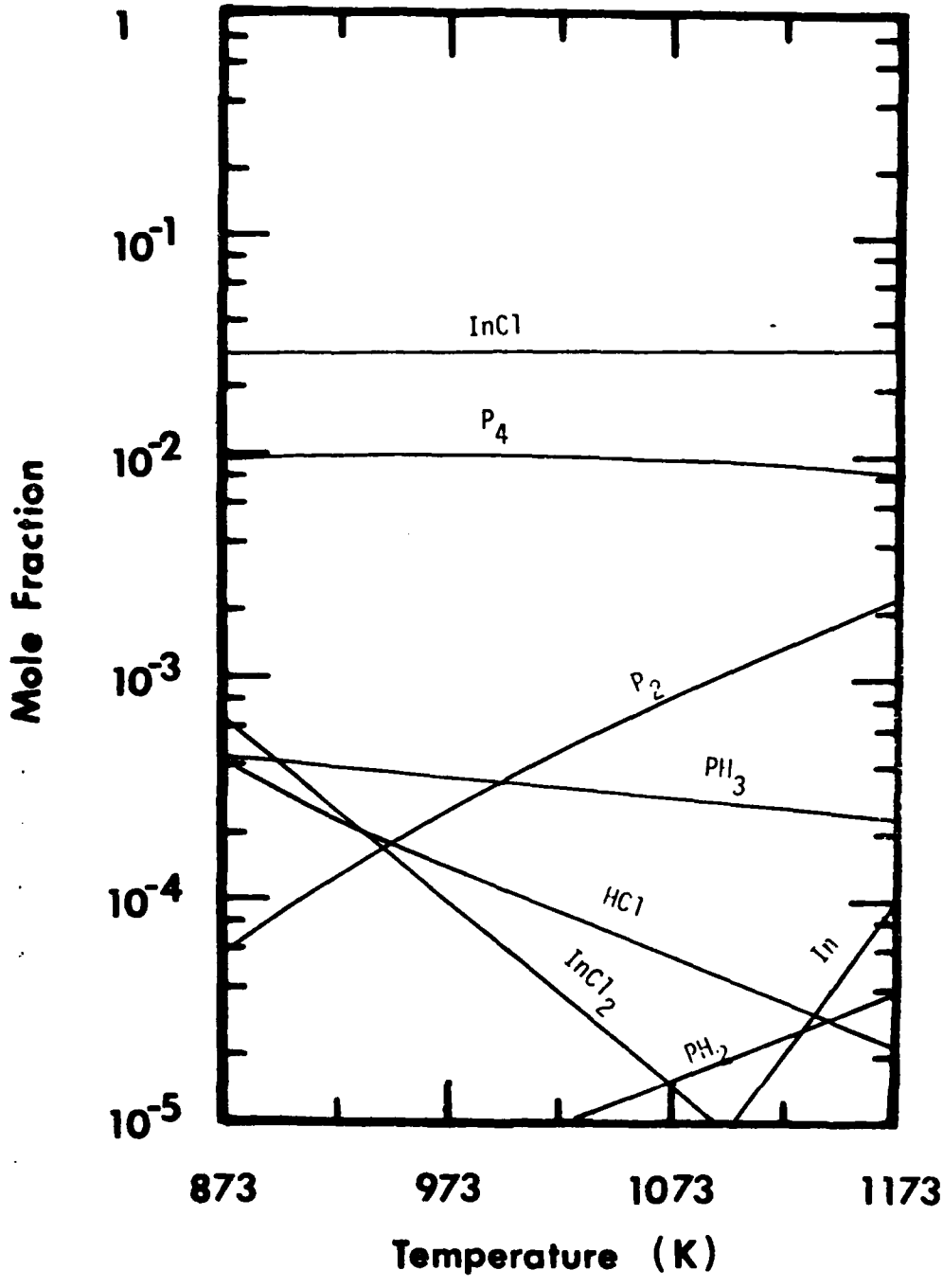
The InP source zone using solid InP as the Group III source material is shown in Figures 6.21 and 6.22. The behavior of this system was markedly different than that of the analogous GaAs system in that InCl was clearly the dominant Group III vapor specie due to the favorable Gibbs energy change (−8 kcal/g-mole at 973K) of the following reaction when compared to reaction 6.1.11 (3.2 kcal/g-mole at 973K).

$$InP(c) + HCl = InCl + \frac{1}{4} P_4 + \frac{1}{2} H_2 \qquad (6.4.1)$$

The formation of a larger amount of Group III monochloride consumed much of the HCl initially present in the system and caused the vapor phase silicon species to be higher in hydrogen content than those species in the analogous GaAs system. As a result, the condensed phase silicon activity in the InP chloride system using solid InP in the source zone was found to be much larger than that of the GaAs system. These same comments also apply to the mixing and deposition zones of the InP system which follow the source zone using solid InP as the Group III source material.

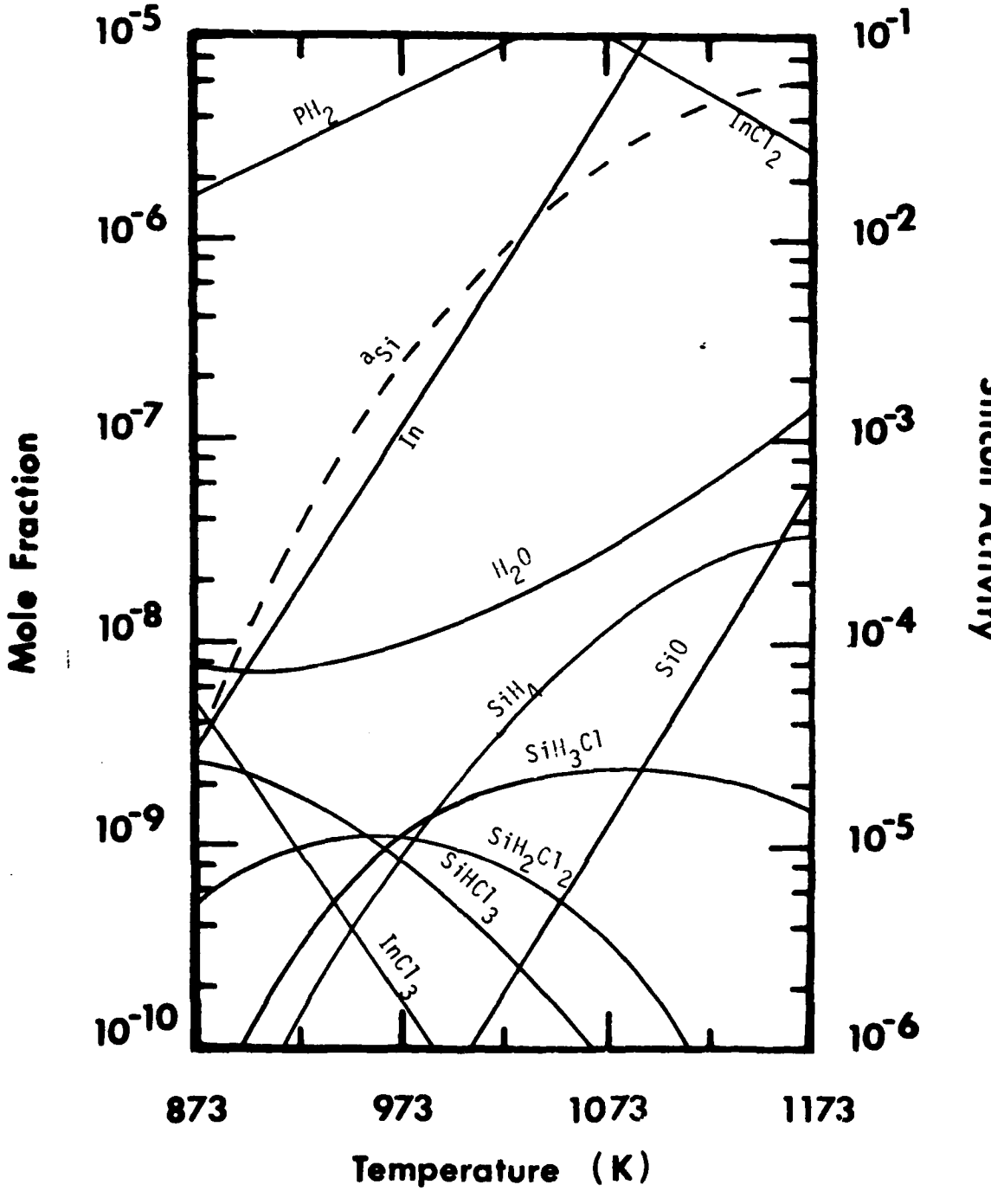
The effects of pressure on the InP chloride system follow closely those observed for the GaAs system relative to the previously discussed differences. Thus, for the system employing liquid $In_x P_{1-x}$ as the Group III source, the condensed phase silicon activity in each zone is slightly lower than that of the GaAs system and the InP saturation ratio in the deposition zone is much less than that of the GaAs system. As in the GaAs system, maxima are observed in the condensed phase silicon activities at 4 kPa in the source and mixing zones. The chloride system using solid InP as the Group III source also displayed a pressure dependent behavior which was similar to that of the analogous GaAs system except that InCl was clearly the dominant Group III specie and the condensed phase silicon activity was much higher in the InP system due to reasons previously discussed.

The influence of PCl_3 inlet concentration on the InP system was similar to that of $AsCl_3$ in the GaAs system with the following differences. When liquid $In_x P_{1-x}$ was used



Effect of temperature on the InP chloride system source zone (solid source)

Figure 6.21



Effect of temperature on the InP chloride system source zone (solid source)

Figure 6.22

as the Group III source material the condensed phase silicon activity was always 20% to 50% less than that of the corresponding GaAs system. This was due to $InCl_3$ being a less important specie in the InP system than $GaCl_3$ was in the GaAs system, which allowed more chlorine to react with the silicon vapor species. When solid InP was used as the Group III source material the silicon activity in the InP system was greater than that of the corresponding GaAs system due to the large amount of InCl formed.

Replacing the hydrogen carrier gas with an inert gas was also investigated in the InP system and the results followed the same trends as did the analogous GaAs system. The differences between the systems were consistent with the previous discussions, i.e. the condensed phase silicon activity for the InP system using solid InP for a source was larger than the GaAs system and the liquid source InP system showed a slightly reduced silicon activity in the deposition zone relative to the GaAs system.

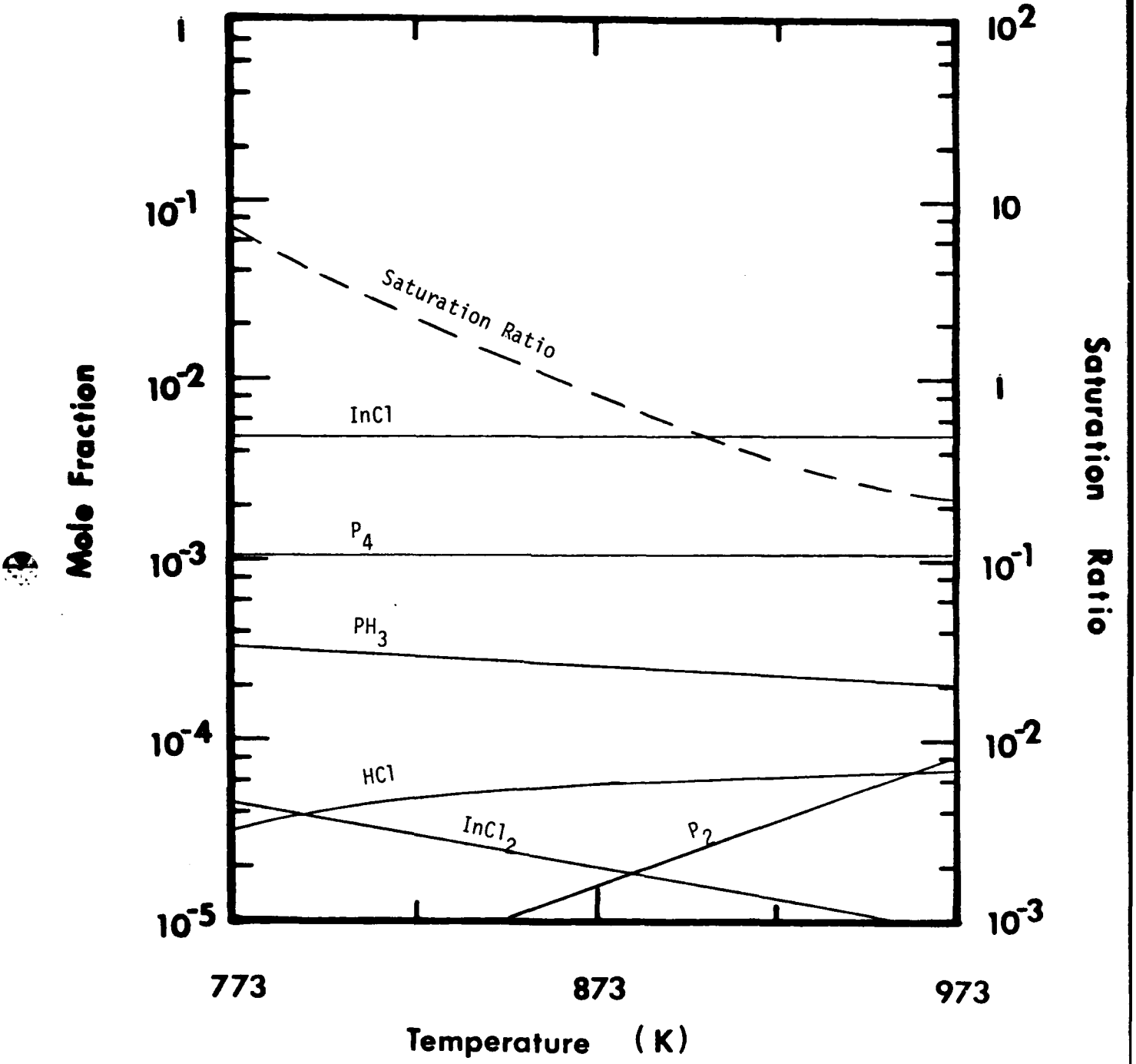
Additions of HCl, H_2O, and PCl_3 to the mixing zone of the InP system were also studied. The trends observed were the same as those in the GaAs system.

6.5 The InP Hydride System

The results of a parametric analysis of the InP chloride system were similar to those of the GaAs hydride system discussed previously. The condensed phase silicon activity in the InP system was found to be consistently less than that in the GaAs system under all analogous conditions. At very low inlet HCl concentrations (~ 0.1%) the silicon activities were nearly the same while at large inlet HCl concentrations (~ 10%) the InP system exhibited silicon activities which were half the value of those in the GaAs system. This was primarily due to the smaller (more negative) Gibbs energy of formation of GaCl (−41.5 kcal/mol^{-1} at 973K) which caused a greater production of GaCl via reaction 6.1.12 than InCl in the analogous reaction where In is the Group III specie. The differences in the Gibbs energies of formation at 973K for $Ga(l)$ and $In(l)$ were not significant. Thus, more HCl was available in the InP system to form chlorine rich silicon vapor species via reaction 6.1.1 which in turn lowered the condensed

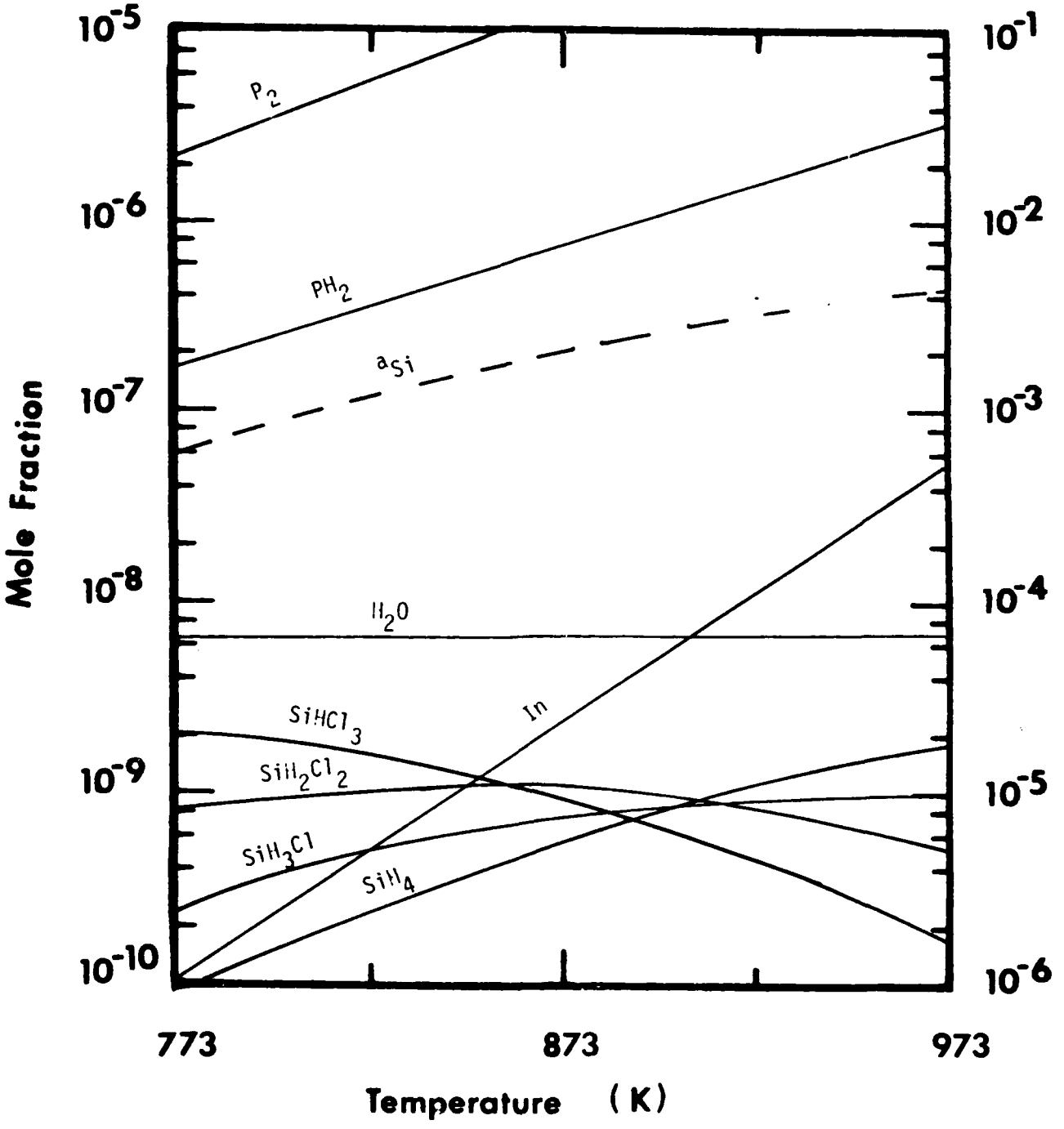
phase silicon activity relative to the GaAs system.

Figures 6.23 and 6.24 show the effect of temperature on the deposition zone of the InP system. As observed in the chloride systems, the saturation ratio for InP was much smaller than that for GaAs. The hydride system showed that, for the source zone conditions shown in the figures, the InP system did not become supersaturated until the temperature was below 860K. Alternatively, supersaturation at 873K can be achieved by increasing the system pressure from 100 kPa to 200 kPa or by increasing the PH_3 and HCl inlet compositions. These results are in contrast to those observed in the InP chloride system and both GaAs systems which displayed supersaturated conditions in the deposition zone under all situations studied.



Effect of temperature on the InP hydride system deposition zone

Figure 6.23



Effect of temperature on the InP hydride system deposition zone

Figure 6.

7. CONCLUSIONS

Parametric analyses of the chemical reaction thermodynamics pertaining to the chemical vapor deposition of GaAs and InP in the chloride and hydride systems have revealed some of the dissimilarities between these systems. Within the chloride system the condensed phase silicon activity resulting from the use of solid III-V material as the Group III source was shown to be much smaller than that obtained when a liquid Group III source was used. This difference was more pronounced for the GaAs system than it was for the InP system. The silicon activity for the InP system using a liquid source was slightly less than that of the analogous GaAs system while the GaAs system using the solid source exhibited a much smaller silicon activity than did the InP system using a solid source. Small additions of HCl, H_2O or VCl_3 to the mixing zones of these chloride systems were very effective in reducing the silicon activity. Replacing the hydrogen carrier gas with an inert gas was found to be an effective method of reducing the silicon activity only if greater than 98% of the hydrogen was replaced. The degree of supersaturation in the deposition zone was much larger for the GaAs system than for the InP system. Also, the use of a liquid Group III source material led to greater supersaturations than the use of a solid III-V compound as the Group III source.

The hydride system was found to be substantially less supersaturated than the chloride system under typical operating conditions and the condensed phase silicon activity was less by approximately one order of magnitude for the hydride system when compared to the chloride system. Replacement of the hydrogen carrier gas with an inert was not as effective a method of reducing the silicon activity in the hydride system as it was in the chloride system due to the H_2 liberated from the decomposition of HCl and VH_3. The condensed phase silicon activity was found to decrease with increasing pressure in the deposition zones while maxima in the silicon activity were found in the source and mixing zones at approximately 4 kPa pressure for systems using liquid source materials. Increasing the temperature was found to strongly

increase the silicon activity in the source and growth zones. The influence of inlet composition on silicon activity was not as strong as that of temperature, pressure, replacement of H_2 by inerts or the addition of species downstream of the source zone. Reduced silicon activities occurred as the inlet composition of chlorine containing species was increased.

In general it was found that shifting the vapor phase silicon species from those which are hydrogen rich to chlorine rich species markedly reduced the condensed phase silicon activity. This effect was so pronounced that even in systems where the total amount of silicon in the vapor phase as chlorinated species was much greater than that of hydrogen rich species in other systems, the condensed phase silicon activity was still sharply reduced.

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9. Appendix A. MCMPEC.RAND: A Computer Code For Calculating Chemical Equilibrium Using A Nonstoichiometric Algorithm

Appendix A

MCMPEC.RAND: A Computer Code for Calculating Chemical Equilibrium Using a Nonstoichiometric Algorithm

A.1 Introduction

The calculation of chemical equilibrium using a nonstoichiometric algorithm (the Rand algorithm) is based on the work of Clasen [1]. A nonstoichiometric algorithm adjusts the amount of each specie present in the system without referring to a specific set of chemical reaction equations. The overall system mass is conserved by constraining the amount of each element present to a constant value. Equilibrium is attained when the free energy of the system is minimized. A developement of the Rand algorithm, extended to include a solution phase and pure condensed phases in addition to a vapor phase, is presented in section A.5. Since CVD systems are operated at constant pressure the Gibbs Free Energy was chosen as the appropriate free energy function.

The algorithm consists of a set of linearized finite difference equations which are formed from the overall system free energy function and the elemental abundance constraints. These equations are solved to predict changes in the amount of each specie which will yield a decrease in the overall system free energy. The vapor phase is assumed to be ideal although activity coefficients (which are set to unity) are included in the equations. The solution phase includes options for ideal behavior, a binary system simple solution theory model or inclusion of a Henry's Law constant. An inert specie in the vapor phase is also available as an option.

The use of linear algebra techniques to solve the system of linear equations results in three complications. First, a vapor phase must always be present in order to prevent the coefficient matrix from becoming singular. Therefore, systems consisting of only pure condensed phases and a solution phase cannot be solved using this algorithm. Second, pure condensed phases which have compositions that vanish must be removed from the calculation in order to prevent the coefficient matrix from becoming singular. This results in the addition of some rather intricate logic and a considerable amount of "book keeping" in order to remove the phase, shift the equation order and then perform tests to determine whether the phase needs to be reinserted later in the calculation. Finally, a considerable amount of computer storage is required (about 111 k-bytes on an IBM 370 for 50 species) in order to execute the code.

The code includes options to allow temperature, pressure and inlet composition loops in order to generate the data required for parametric analyses.

Currently there is evidence which suggests that the liquid solution in the source zone of the CVD halide system is at steady state [2]. Therefore, an option has been included to model this situation in the Ga/As and In/P systems. Several data output options and debugging aids have also been included. The reader is referred to subsection A.2.2 for a discussion of these options.

The structure of the main program along with data input and output are discussed in section A.2. A description of the major variables used in the code is presented in section A.3 and each subroutine is discussed separately in Section A.4. As was previously mentioned, the theoretical development of this extended version of the Rand algorithm is presented in section A.5 and an example calculation is located in section A.6.

A.2 The Main Program

A flowsheet for MCMPEC.RAND is shown in Figure A1. The primary functions of the main program are to set array dimensions, provide a framework for calling the subroutines and to take care of data input and output. Thus the actual looping parameters for the temperature, pressure and composition options are located in the main program as are the loop and convergence test for determining the equilibrium compositions. All of the data input and output are performed in the main program. Subroutines DEBUG and PRINTAB write out information useful for debugging purposes and execution diagnostics pertaining to the various subroutines are written out directly from the appropriate subroutine. Also, subroutine WRAPUP writes out a concise wrapup file when the option is active.

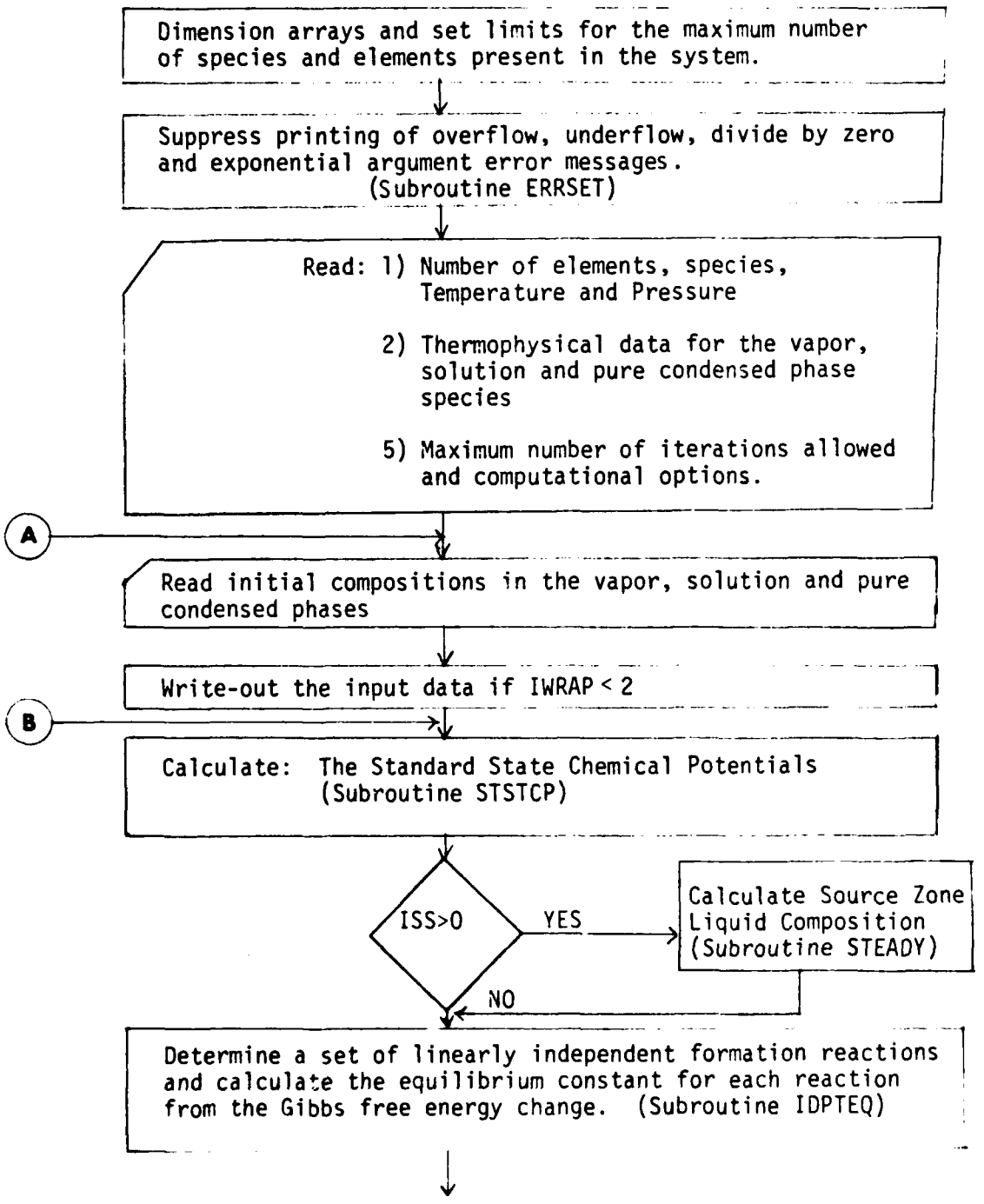
A listing of the main program is located in subsection A.2.6.

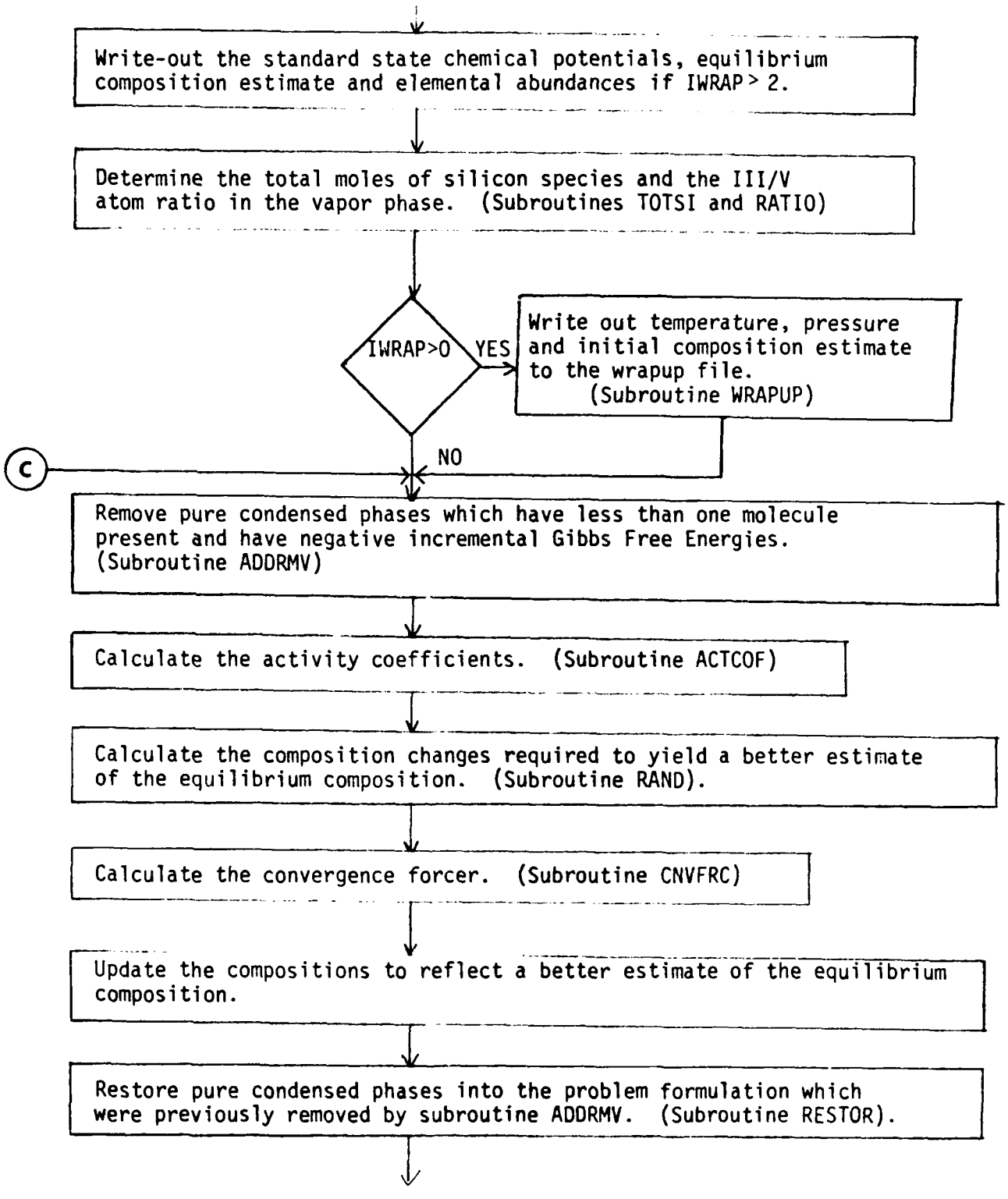
A.2.1 Array Dimensions, Expandability and Initialization

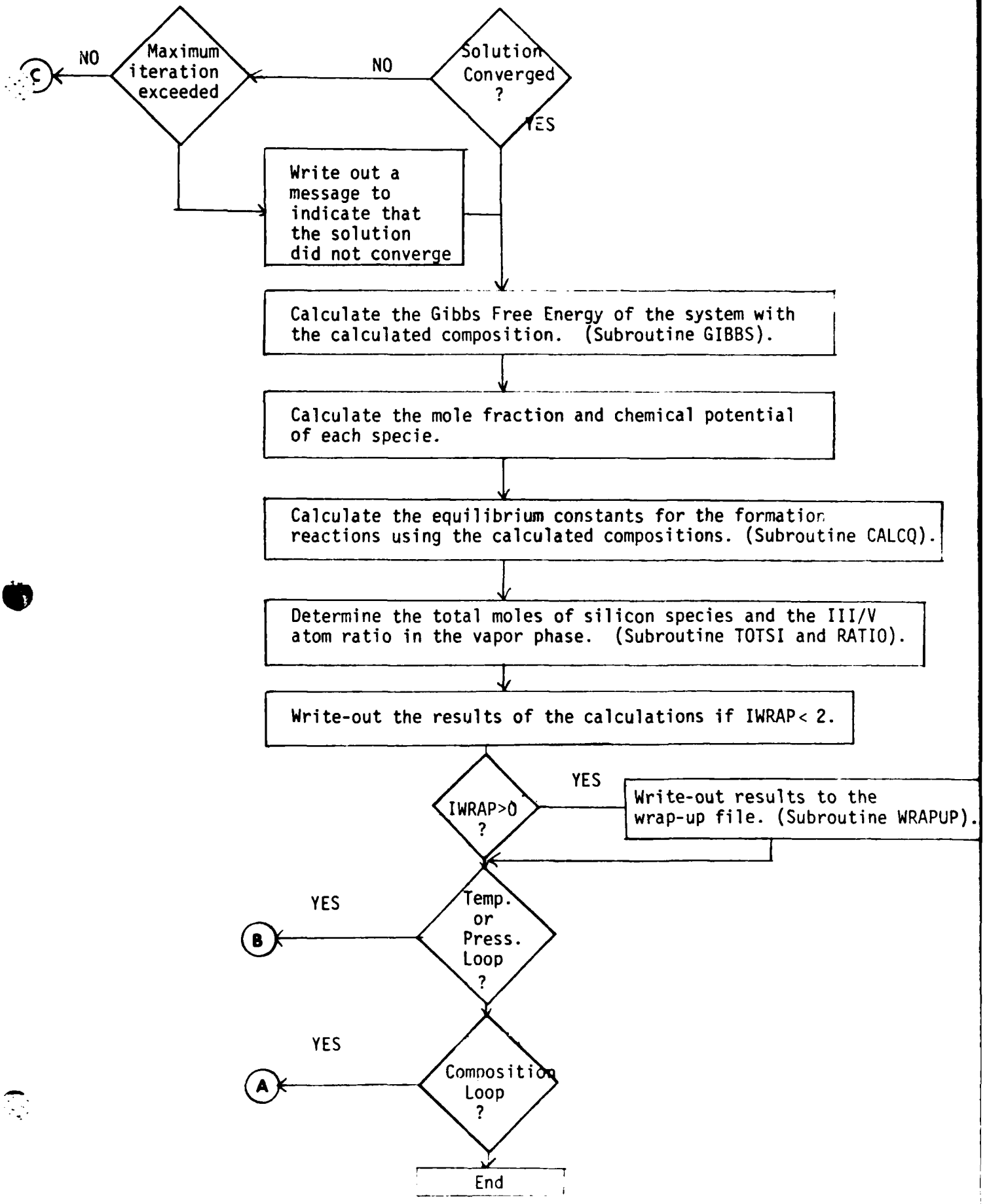
The arrays used in MCMPEC.RAND are dimensioned in lines 5 through 17. Currently these arrays are dimensioned to accommodate systems containing up to 50 different species comprised of a maximum of 13 different elements. The variables IDIM1, IDIM2 and IDIM3, which are initialized in lines 36, 37 and 38, are used to set the array dimensions in the subroutines. Therefore, the code can be expanded to accommodate larger systems simply by changing the array dimensions and the values of IDIM1 and IDIM2 in the main program. The double precision arrays ALEQ,

Figure A1

Main Program Flowsheet for MCMPEC.RAND




Write-out the standard state chemical potentials, equilibrium composition estimate and elemental abundances if IWRAP > 2.
Determine the total moles of silicon species and the III/V atom ratio in the vapor phase. (Subroutines TOTSI and RATIO)
IWRAP>0
YES
Write out temperature, pressure and initial composition estimate to the wrapup file. (Subroutine WRAPUP)
NO
C
Remove pure condensed phases which have less than one molecule present and have negative incremental Gibbs Free Energies. (Subroutine ADDRMV)
Calculate the activity coefficients. (Subroutine ACTCOF)
Calculate the composition changes required to yield a better estimate of the equilibrium composition. (Subroutine RAND).
Calculate the convergence forcer. (Subroutine CNVFRC)
Update the compositions to reflect a better estimate of the equilibrium composition.
Restore pure condensed phases into the problem formulation which were previously removed by subroutine ADDRMV. (Subroutine RESTOR).


Solution Converged ?
NO
YES
Maximum iteration exceeded
NO
C
Write out a message to indicate that the solution did not converge
Calculate the Gibbs Free Energy of the system with the calculated composition. (Subroutine GIBBS).
Calculate the mole fraction and chemical potential of each specie.
Calculate the equilibrium constants for the formation reactions using the calculated compositions. (Subroutine CALCQ).
Determine the total moles of silicon species and the III/V atom ratio in the vapor phase. (Subroutine TOTSI and RATIO).
Write-out the results of the calculations if IWRAP< 2.
IWRAP>0 ?
YES
Write-out results to the wrap-up file. (Subroutine WRAPUP).
Temp. or Press. Loop ?
YES
B
Composition Loop ?
YES
A
End

BLEQ and WKA are dimensioned IDIM1 + IDIM2 and therefore must be modified accordingly. It is suggested that the element dimension IDIM2 not be increased beyond 13 as this will cause output line lengths in excess of 132 characters which will either be lost or difficult to read as a result of printer "wrap around". There are no restrictions (other than available computer memory) to the number of species which the code may be expanded to accomodate.

Character strings used to build the output for the reaction formation equations are initialized at lines 11 through 16. The vapor, solution and condensed phase identifying character strings are also initialized here.

The logical unit designators for the input file, printed output and the wrap-up file are initialized at 5, 6 and 2 respectively in lines 33 through 36.

Lines 43 and 44 call the system subroutine ERRSET to supress the printing of overflow, underflow, divide by zero and exponential argument error messages. These errors occur commonly in the IMSL matrix routine LEQT1F and since this routine internally tests for the number of significant figures in the results it is unnecessary to receive these system warnings. The exponential argument error message occurs quite frequently in the calculation of equilibrium constants from composition (subroutine CALCQ). This is a result of species having very small concentrations being included in the formation reactions. The equilibrium constants are calculated for comparison purposes only and therefore do not effect the calculated compositions. Discrepancies between the equilibrium

constants as calculated from composition and Gibbs Free Energy usually result from exceeding the numerical range of the computer.

A.2.2 Data Input

Data input is accomplished in lines 45 through 146. A summary of the input data set is shown in Table A.1 and a description of each input variable is located in Table A.2.

The first input record consists of a data set title which may be up to 80 characters in length. The second record consists of the number of elements in the system, the number of species in the vapor (V > 0), solution and pure condensed phases, followed by the system temperature and pressure. The last two pieces of information on this record are the reference temperature and pressure for the enthalpies and entropies of formation. The symbols for each element are on the third record. Two characters are allowed for each element symbol.

The next 3V records contain information regarding the species present in the vapor phase. The first record contains a 12 character specie name and the enthalpy and entropy of formation at temperature TO and pressure PO for this specie. Heat capacity correlation information is contained on the second record and the number of atoms of each element which are present in a single molecule of the specie are on the third record. Records 3V + 1 to 3V + 3 contain this same information for an inert specie in the vapor phase. The inert specie information must always be present in the data set. When it is desired to perform a calculation without the inert, its initial concentration is simply set to zero. This same information must also be provided for each specie in the solution phase and each pure condensed phase.

Table A.1
Input Data Set for MCMPEC.RAND

Record	Comments	Format
Title (1),.... TITLE (20)	80 Character Title	20A4
E, V, S, C, T, P, T_O, P_O		4I5, 4F10.0
ELMNT (1), ELMNT (2) .... ELMNT (E)	Element Symbols	13 (1X, A2)
SPECIE (I,K), DMO(I), DSO(I)		3A4, 2E12.5
AO(I), AI(I), A2(I), A3(I), ICP(I)	Each vapor phase specie	4E12.5, I2
A(I,1), A(I,2).... A(I,E)		13(F5.0, 1X)
Inert(K), DHOZ, DSOZ		3A4, 12E12.5
AOZ, AIZ, A2Z, A3Z, ICPZ	Inert vapor phase specie	4E12.5, I2
IDUMMY		13(F5.0, 1X)
SPECIE(I, K), DHO(I), DSO(I)		3A4, 12E12.5
AO(I), AI(I), A2(I), A3(I), ICP(I)	Each solution phase specie	4E12.5, I2
A(I,1), A(I,2),...A(I,E)		13(F5.0,1X)
SPECIE(I,K), A2(I), A3(I), ICP(I)		3A4, 12E12.5
AO(I), AI(I), A2(I), A3(I), ICP(I)	Each pure condensed phase	4E12.5, I2
A(I,1), A(I,2)...A(I,E)		13(F5.0,1X)
IDEBUG, IOPT, ISS, IWRAP, MAXIT, NMAX CNVG, TINC, PINC		6I5, 3F10.0
TOTMV		E12.5
FRAC(1), FRAC(2).... FRAC(V), FRACZ		6E12.5
TOTMS		E12.5
FRAC(V+1), FRAC(V+2)... FRAC(V+S)		6E12.5
IXSCOR, AXS, BXS		I5, 2E12.5
TOTMC(V+S+1)...TOTMC(V+S+C)		6E12.5

Table A.2

Description of Input Variables

Variable	Description
TITLE (20)	80 Character data set title
E	Number of elements (E ≤13)
V	Number of vapor species excluding the inert
S	Number of solution species
C	Number of pure condensed phases
T	System Temperature (K)
P	System Pressure (Pa)
TO	Reference Temperature for ΔH and ΔS formation
PO	Reference Pressure for ΔH and ΔS formation
ELMNT (13)	2 character symbol for each element (right justified)
SPECIE (50, 3)	12 character symbol for each specie
A (50, 13)	Elemental abundance matrix
DHO (50)	Enthalpy of formation (kcal/g-mole) for each specie at Temperature TO and Pressure PO.
DSO (50)	Entropy of formation (kcal/g-mole-K) for each specie at Temperature TO and Pressure PO.
AO (50)	Heat capacity correlation parameter (kcal/g-mole-K)
A1 (50)	Heat capacity correlation parameter (kcal/g-mole-K^2)
A2 (50)	Heat capacity correlation parameter (see Table)
A3 (50)	Heat capacity correlation parameter (see Table)
ICP (50)	Heat capacity correlation parameter (see Table)

Heat Capacity Correlations

ICP (I)	A2 (I)	A3 (I)	Correlation
0	kcal-K/g-mole	kcal/g-mole-K-ℓn(k)	$AO+A1*T+A2/T^2+A3*\ell n(T)$
1	kcal/g-mole-K^3	kcal/g-mole-K^4	$AO+A1*T+A2*T^2+A3*T^3$

INERT (3) 12 character name for inert vapor specie

DHOZ Inert specie enthalpy of formation

DSOZ Inert specie entropy of formation

AOZ, A1Z, A2Z, A3Z, ICPZ — Inert specie heat capacity correlation parameters

IDEBUG Debugging output parameter

IDEBUG	FUNCTION
0	warning messages are printed when problems are encountered in the IMSL subroutines
1	Prints IDEBUG = 0 option plus composition changes and Gibbs Free Energy for each iteration.
2	Prints IDEBUG = 1 option plus matricies and vectors ALEQ, BLEQ and X for each iteration.

IOPT Looping option parameter

IOPT	FUNCTION
0	One pass through routine
1	Temperature loop
2	Pressure loop
3	Composition loop

ISS Source zone steady state option parameter

ISS	FUNCTION
0	Steady state option is inactive
1	Ga/As liquid composition is at steady state with GaAs solid
2	In/P liquid composition is at steady state with InP solid.

IWRAP — Data output option parameter

IWRAP	FUCTION
0	Write-out input data, execution diagnostics and results to printer
1	IWRAP=0 function plus writes-out a concise wrap-up file.
2	No printer output just a wrap-up file
3	Write a wrap-up to the printer

MAXIT — maximum number of iterations allowed for the equilibrium composition to converge

NMAX — maximum number of loops allowed for the IOPT parameter

CNVG — convergence criterion

TINC — temperature increment for each loop if IOPT=1

PINC — pressure increment for each loop if IOPT=2

TOTMV — total moles in the vapor phase

TOTMS — total moles in the solution phase

TOTMC (I) — total moles in each pure condensed phase

FRAC (I) — $1<I<V$ mole fraction of specie i in vapor
$V+1<I<V+s$ mole fraction of specie i in solution

FRACZ — mole fraction of inert in vapor

IXSCOR — activity coefficient correlation parameter for the solution phase

IXSCOR	Correlation
0	ideal solution
1	binary simple solution
2	Henry's Law

AXS, BXS — activity coefficient correlation coefficients for the solution phase

IXSCOR	Correlation
0	ideal solution
1	$G^E = (AXS + BXS * T) * X1 * X2$
2	H = AXS * EXP (BXS/T)

Following the data for each individual specie is a record describing the various options available and numerical methods information. Parameter IDEBUG should be set to zero for production type jobs but may be set to 1 or 2 to provide information which allows the calculations to be examined in a step by step fashion.

Parameter IOPT allows the code to be looped in order to generate temperature, pressure or composition parametric curves. NMAX sets the number of loops to be carried out while TINC and PINC are the temperature and pressure increments per loop. If a composition loop is desired a new initial composition data set must be provided for each loop.

Parameter ISS is used to activate the steady state liquid source option. If ISS is set to 1 the composition of a liquid containing Ga and As in equilibrium with GaAs solid is calculated. This liquid is inserted as the last pure condensed phase in the system. Thus when the value of C (number of pure condensed phases) is specified it must include a steady state phase if ISS > 0 otherwise the last pure condensed phase in the system will be replaced with the steady state liquid. Setting ISS = 2 will model a liquid of In and P in equilibrium with InP solid.

The parameter IWRAP is used to choose the amount of data output desired. When IWRAP = 0 the input data is written out in tabulated form along with a description of the options chosen, execution diagnostics, equilibrium compositions, reaction formation equations and a comparison between the equilibrium constants for these equations as calculated from the free energy changes and the compositions. With IWRAP = 1 a concise wrap-up file is written to logical unit designator IFILE (IFILE = 2)

in addition to the IWRAP = 0 option. These two output options are quite useful when one is becoming acquainted with the code as they provide an echo of the input data set and a verification of the results. Options IWRAP = 2 and IWRAP = 3 provide only wrapup file output to IFILE and IWRT respectively.

MAXIT sets the maximum number of iterations to be performed for calculating the equilibrium compositions. Typically MAXIT is set to 1000.

The equilibrium compositions are considered converged when, after two successive iterations, the largest fractional change in any significant specie concentration is less than CNVG. A significant specie is one which is present in a concentration of $1 \cdot 10^{-50}$ moles or greater. A typical value for CNVG is 10^{-4}.

The inlet compositions for the vapor, solution and pure condensed phases are next in the input data set. The total moles in the vapor are on one record and the following records contain the mole fractions of each component in the vapor, the last value being the mole fraction of the inert. The solution phase inlet compositions are done the same way except that there is no inert. Following the solution phase mole fractions is a record which determines the activity coefficient model to be used in the solution phase. For IXSCOR = 0 the solution is considered to be ideal. Setting IXSCOR = 1 yields a binary simple solution model for the excess Gibbs Free Energy. A Henry's Law constant for the first component in the solution phase is activated by setting IXSCOR = 2. The parameters AXS and BXS are used in the activity coefficient models as shown in Table A.2.

The final records of the input data set contain the number of moles in each pure condensed phase.

A.2.3. Preparation for the Iterative solution

The limits for the temperature, pressure and composition loops are set in lines 126 through 129. The composition loop (IOPT = 3) starts at line 130.

The input specie order is saved so that the results may be output in this order. This step is necessary since pure condensed phases may be removed and reinstated during the calculational procedure and it is convenient to compare the equilibrium results to the input concentrations in the original sequence.

The specie names along with their associated enthapy of formation, entropy of formation and heat capacity correlation data are then written to IWRT if IWRAP <2. Also, the temperature and pressure of the reference state, maximum number of iterations, convergence criterion and the debug, steady-state and solution phase excess free energy correlation options are identified.

The temperature and pressure loops (IOPT = 1 or IOPT = 2) start at line 205. Subroutine STSTCP is called to calculate the standard state chemical potential of each specie. Subroutine ESTMTE is then called to provide an estimate to the equilibrium composition during the first pass through the temperature/pressure loop. Succeeding passes through this loop utilize the equilibrium composition of the preceding pass as an estimate of the current equilibrium composition when ISS = 0.

If the steady state option is activated (ISS> 0) subroutine STEADY inserts as the last pure condensed phase a liquid phase composed of group III and V elements which has a composition determined by the liquidus line of the III-V system at the specified temperature. The total moles of each element present are then calculated based on the initial estimate of the equilibrium composition.

Subroutine IDPTEQ calculates a set of independent reaction formation equations and the equilibrium constants for each of these equations based on the Gibbs Free Energy change associated with each reaction. This result is later compared with equilibrium constants calculated using the "converged" equilibrium compositions to assure that convergence has been attained.

The initial composition estimate, standard chemical potential and elemental abundance vector for each specie along with the amount of each element present in the system are written out if IWRAP < 2. This occurs in lines 244 through 287. Headings for a page containing execution diagnostics are set up in lines 289 through 293 and the standard state chemical potentials are divided by R and T in accord with the derivation in section A.5.

During the first pass through the temperature or pressure loop the total moles of silicon compounds and the group III to group V atom ratio in the vapor phase are calculated in subroutine TOTSI and RATIO. The specie initial concentration along with the total silicon and III-V atom ratio in the vapor are then written to a wrap-up file if IWRAP > 0.

A.2.4 Iterative Solution for Equilibrium Composition

The iteration scheme for determining equilibrium compositions is located in lines 313 through 362. Before entering the loop RELMAX and IACFF are initialized to prevent calculation of activity coefficients during the first iteration. If a nonideal solution option is chosen activity coefficients are calculated only after RELMAX has reached a value of less than 0.1. This greatly reduces the chance that the numerical solution will diverge.

At the top of the loop subroutine ADDRMV is called to remove pure condensed phases from the calculation which have compositions of less than 1.65×10^{-25} g-moles. ADDRMV then reinserts one molecule of the pure condensed phase which has the smallest negative incremental Gibbs Free Energy of those which have been removed. Subroutine ACTCOF is called to calculate activity coefficients for each of the species followed by RAND which calculates the change in composition for each specie which will yield a closer approximation to the system equilibrium composition.

A convergence forcer is calculated in subroutine CNVFRC. The purpose of the convergence forcer is to assure that negative compositions do not occur and, if IALG = 1, to provide a correction to the predicted composition changes which will help eliminate numerical instabilities. Lines 338 through 341 apply the convergence forcer to update the current estimate of the equilibrium composition. The minimum composition any specie in the vapor or solution phases may attain is set to 10^{-50} g-moles in line 340.

Subroutine RESTOR is called to replace any pure condensed phases which were removed by ADDRMV back into the problem in the original sequence. Subroutines GIBBS and DEBUG provide diagnostic information if IDEBUG > 1.

Lines 352 through 360 test for convergence of the solution. The maximum fractional change of all species with compositions greater than 10^{-50} g-moles over two successive iterations is compared with CNVG. The solution is considered converged if the largest fractional change is less than CNVG.

The iteration process will also be terminated if the maximum number of iterations, MAXIT, is exceeded or if ISTOP = 1. The parameter ISTOP is set to unity if the coefficient matrix in subroutine RAND is found to be algorithmically singular which prohibits the solution of the set of linear equations. A message is printed in line 363 if the numerical solution does not converge.

A.2.5 Output of Results

Following the loop for determining the equilibrium compositions subroutine GIBBS is called to calculate the final system Gibbs Free Energy. Lines 369 through 409 then determine mole fractions and chemical potentials for each of the species. Subroutine CALCQ is called to calculate equilibrium constants for the reaction formation equations using the compositions determined by the RAND algorithm. Subroutines TOTSI and RATIO then determine the total silicon concentrations and the group III-V atom ratio in the vapor phase.

The results of the equilibrium calculations are written out in lines 422 through 470 if IWRAP <2. A wrap-up file is written at line 472 if IWRAP >0. If a temperature, pressure or composition loop option has been chosen (IOPT >0) the program jumps to the bottom of this loop at line 553. Otherwise the set of independent formation reaction equations are written out followed by a comparison of the equilibrium constants for these reactions as calculated by the free energy change and the equilibrium compositions.

A.2.6 Listing of The Main Program

```
C  MCMPEC.RAND .... MULTICOMPONENT MULTIPHASE EQUILIBRIUM CODE
C                   RAND ALGORITHUM
C
C
      DOUBLE PRECISION ALEQ(63,63),BLEQ(63),D(13,13),DPRMF(13,13),
     &                 DINV(13,13),WKA1(13),WKA(63)
      DIMENSION A(50,13),A0(50),A1(50),A2(50),A3(50),ACOEF(50),B(13),
     &          BCALC(50),CHMPT(50),COEFF(6),DELN(50),DG(50),
     &          DTST(50),DH0(50),DS0(50),FRAC(50),FRACIN(50),GNU(50,13
     &          ICP(50),IDXBAS(50),INERT(3),Q(50),STDCP(50),TOTMC(50)
      INTEGER ISPCE(50,3),PHASE(50,3),SPECIE(50,3),STRING(6,4),
     &        TITLE(20),V,S,C,E,VP1,VPS,VPSP1,VSC,VSCE,EPCP2,
     &        ELMNT(13)/13*'  '/,VAPOR(3)/'  V','APO','R  '/,
     &        SOLN(3)/'SOL','UTI','ON '/,COND(3)/'CON','DEN','SED'/,
     &        RPSPS/') + '/,RPAS/')<= '/,RPBL/')   '/,SSPS/'  + '/,
     &        BLNKS/'    '/,LP/'('/
      REAL N(50),KEQ(50),NV,NS,LAMBDA
C
C  A(I,J)    : ELEMENTAL ABUNDANCE MATRIX
C  B(J)      : TOTAL NUMBER OF GRAM-MOLES OF ELEMENT J
C  DH0(I)    : ENTHALPY OF FORMATION OF SPECIES I
C  DS0(I)    : ENTROPY OF FORMATION OF SPECIES I
C  STDCP(I)  : STANDARD CHEMICAL POTENTIAL OF SPECIES I
C
C  **********  HEAT CAPACITY CORRELATIONS  **********
C  ICP(I)=0 : CP(I) = A0(I) + A1(I)*T + A2(I)/T**2 + A3(I)*ALOG(T)
C  ICP(I)=1 : CP(I) = A0(I) + A1(I)*T + A2(I)*T**2 + A3(I)*T**3
C
C  ***************************************************************
C  *  DOUBLE PRECISION IS USED IN THE MATRIX ROUTINE LEQT1F  *
C  ***************************************************************
C
      IRD=5
      IWRT=6
      IFILE=2
      IDIM1=50
      IDIM2=13
      IDIM3=IDIM1+IDIM2
C
C SUPRESS PRINTING OF OVERFLOW, UNDERFLOW, DIVIDE BY ZERO
C AND EXPONENTIAL ARGUMENT ERROR MESSAGES
C
      CALL ERRSET(207,0,-1,0,0,209)
      CALL ERRSET(252,0,-1,0,0,253)
C
C READ TITLE
C
      READ(IRD,5) (TITLE(K),K=1,20)
    5 FORMAT(20A4)
C
C NUMBER OF ELEMENTS, VAPOR SPECIES, SOLUTION SPECIES,
C CONDENSED PURE PHASES, SYSTEM TEMPERATURE (K) AND PRESSURE (PA)
C
      READ(IRD,10) E,V,S,C,T,P,T0,P0
```

```
   10 FORMAT(4I5,4F10.0)
      IF(V.EQ.0) WRITE(IWRT,11) V
   11 FORMAT('0',50('*'),/,1X,'PROBLEM CANNOT BE SOLVED USING THE ',
     &'RAND ALGORITHUM',/,1X,'NUMBER OF VAPOR PHASE SPECIES = ',I2,
     &/,1X,50('*'))
      IF(V.EQ.0) GO TO 3000
      VP1=V+1
      VPS=V+S
      VPSP1=V+S+1
      VSC=V+S+C
      VSCE=V+S+C+E
      EPCP2=E+C+2
      IF(S.EQ.0) EPCP2=E+C+1
C
C  READ ELEMENTS
C
      READ(IRD,15) (ELMNT(J),J=1,E)
   15 FORMAT(13(1X,A2))
C
C  VAPOR SPECIES INFORMATION
C
      DO 110 I=1,V
      READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
      READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
      READ(IRD,22) (A(I,J),J=1,E)
   20 FORMAT(3A4,2E12.5)
   21 FORMAT(4E12.5,I2)
   22 FORMAT(13(F5.0,1X))
      DO 110 J=1,3
      PHASE(I,J)=VAPOR(J)
  110 CONTINUE
C
C  INERT VAPOR SPECIE DATA
C
      READ(IRD,20) (INERT(K),K=1,3),DH0Z,DS0Z
      READ(IRD,21) A0Z,A1Z,A2Z,A3Z,ICPZ
      READ(IRD,22) IDUMMY
C
C  SOLUTION SPECIES INFORMATION
C
      IF(S.EQ.0) GO TO 125
      DO 120 I=VP1,VPS
      READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
      READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
      READ(IRD,22) (A(I,J),J=1,E)
      DO 120 J=1,3
      PHASE(I,J)=SOLN(J)
  120 CONTINUE
  125 CONTINUE
C
C  CONDENSED PHASE DATA
C
      IF(C.EQ.0) GO TO 135
      DO 130 I=VPSP1,VSC
```

```
      READ(IRD,20) (SPECIE(I,K),K=1,3),DHO(I),DSO(I)
      READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
      READ(IRD,22) (A(I,J),J=1,E)
      DO 130 J=1,3
      PHASE(I,J)=COND(J)
  130 CONTINUE
  135 CONTINUE
C
C  MAXIMUM NUMBER OF ITERATIONS, CONVERGENCE CRITERION AND OPTIONS
C
      READ(IRD,136) IDEBUG,IOPT,ISS,IWRAP,MAXIT,NMAX,CNVG,TINC,PINC
  136 FORMAT(6I5,3F10.0)
      IF(IWRAP.EQ.3) IFILE=IWRT
C
C  SET THE LOOP LIMITS FOR THE TEMPERATURE, PRESSURE AND COMPOSITION
C  LOOPS.  THE COMPOSITION LOOP STARTS HERE
C
      NCMP=1
      NTP=1
      IF(IOPT.EQ.1.OR.IOPT.EQ.2) NTP=NMAX
      IF(IOPT.EQ.3) NCMP=NMAX
      DO 2000 ICMP=1,NCMP
C
C  TOTAL NUMBER OF MOLES OF VAPOR AND MOLE FRACTIONS
C
      READ(IRD,137) TOTMV
      READ(IRD,137) (FRACIN(I),I=1,V),FRCZIN
  137 FORMAT(6E12.5)
C
C  TOTAL NUMBER OF MOLES OF SOLUTION SPECIES, MOLE FRACTIONS
C  AND EXCESS FREE ENERGY CORRELATION PARAMETERS
C
      IF(S.EQ.0) GO TO 139
      READ(IRD,137) TOTMS
      READ(IRD,137) (FRACIN(I),I=VP1,VPS)
      READ(IRD,138) IXSCOR,AXS,BXS
  138 FORMAT(I5,2E12.5)
  139 CONTINUE
C
C  TOTAL NUMBER OF MOLES IN PURE CONDENSED PHASES
C
      IF(C.EQ.0) GO TO 140
      READ(IRD,137) (TOTMC(I),I=VPSP1,VSC)
  140 CONTINUE
C
C  SAVE THE ORIGINAL SPECIE ORDER SO THAT THE PROBLEM CAN BE PLACED
C  IN THIS ORDER IF ANY PURE CONDENSED PHASES ARE REMOVED OR SHIFTED
C
      DO 165 I=1,VSC
      DO 165 K=1,3
      ISPCE(I,K)=SPECIE(I,K)
  165 CONTINUE
      IF(ICMP.GT.1.OR.IWRAP.EQ.3) GO TO 187
C
```

```
C  WRITE-OUT SOME OF THE INPUT DATA
C
      IPAGE=1
      WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
      WRITE(IWRT,410) T,P
      IF(IWRAP.GT.1) GO TO 187
      WRITE(IWRT,170)
  170 FORMAT('0',/,1X,T55,'HEAT CAPACITY CORRELATION COEFFICIENTS',
     &/,1X,T16,'ENTHALPY OF',T33,'ENTROPY OF',T58,'ICP=0:  CP = A0',
     &' + A1*T + A2/T**2 + A3*LN(T)',/,1X,T17,'FORMATION',T33,'FORMAT',
     &'ION',T58,'ICP=1:  CP = A0 + A1*T + A2*T**2 + A3*T**3',/,1X,T4,
     &'SPECIE',T20,'DH0',T37,'DS0',T54,'A0',T73,'A1',T93,'A2',T113,
     &'A3',T122,'ICP',/,1X,T4,'SYMBOL',T15,'(KCAL/G-MOLE)',T30,
     &'(KCAL/G-MOLE-K)',T47,'(KCAL/G-MOLE-K)',T65,'(KCAL/G-MOLE-K**2)',
     &T86,'(..............)',T106,'(..............)',T122,'(-)',
     &/,'+',12('_'),T15,13('_'),T30,15('_'),T47,15('_'),
     &T65,18('_'),T86,15('_'),T106,15('_'),T122,3('_'))
      DO 180 I=1,VSC
      WRITE(IWRT,175) (SPECIE(I,K),K=1,3),DH0(I),DS0(I),A0(I),A1(I),
     &                A2(I),A3(I),ICP(I)
  175 FORMAT(1X,3A4,T17,F9.3,T33,F9.6,T50,F9.6,T68,E12.5,T88,E12.5,
     &T108,E12.5,T123,I1)
      IF(I.EQ.V) WRITE(IWRT,175) (INERT(K),K=1,3),DH0Z,DS0Z,A0Z,A1Z,
     &                           A2Z,A3Z,ICPZ
  180 CONTINUE
      WRITE(IWRT,184) T0,P0,MAXIT,CNVG,IDEBUG
  184 FORMAT('0',/,'0',T10,'THE ENTHALPY AND ENTROPY OF FORMATION ',
     &'REFERENCE TEMPERATURE AND PRESSURE ARE:',5X,'T0 = ',F6.1,' K',
     &5X,'P0 = ',F9.1,' PA',/,'0',T35,'MAXIMUM NUMBER OF ITERATIONS ',
     &'ALLOWED = ',I5,/,'0',T50,'CONVERGENCE CRITERION = ',E12.4,
     &/,'0',T48,'OUTPUT PARAMETER IDEBUG = ',I2)
      IF(S.GT.1) WRITE(IWRT,185) IXSCOR,AXS,BXS
  185 FORMAT('0','EXCESS FREE ENERGY CORRELATION :',2X,'IXSCOR = ',
     &      I5,5X,'AXS = ',E12.5,5X,'BXS = ',E12.5)
      IF(ISS.GT.0) WRITE(IWRT,186) ISS
  186 FORMAT('0',T24,'ISS= ',I2,'  THE III-V LIQUID SOLUTION IS AT ',
     &      'EQUILIBRIUM WITH THE III-V STOICHIOMETRIC SOLID')
  187 CONTINUE
C
C  CALCULATE THE STANDARD STATE CHEMICAL POTENTIALS
C  AND AN INITIAL ESTIMATE OF THE EQUILIBRIUM COMPOSITION
C
      DO 2000 ITP=1,NTP
      IF(IOPT.EQ.1.AND.ITP.GT.1) T=T+TINC
      IF(IOPT.EQ.2.AND.ITP.GT.1) P=P+PINC
      CALL STSTCP(A0,A1,A2,A3,A0Z,A1Z,A2Z,A3Z,DH0,DS0,DH0Z,DS0Z,
     &            STDCP,STDCPZ,ICP,ICPZ,T0,T,IDIM1,V,S,C)
      IF(ITP.GT.1.AND.ISS.EQ.0) GO TO 195
      DO 190 I=1,VPS
      FRAC(I)=FRACIN(I)
  190 CONTINUE
      FRACZ=FRCZIN
      CALL ESTMTE(TOTMV,TOTMS,TOTMC,FRAC,N,FRACZ,ZV,
     &                              IDIM1,V,S,C)
```

```
  195 CONTINUE
C
C  SOURCE ZONE STEADY-STATE LIQUID COMPOSITION MODEL
C
      IF(ISS.GT.0) CALL STEADY(SPECIE,A,STDCP,ELMNT,XIII,T,T0,V,S,C,
     &             IDIM1,IDIM2,ISS,IWRT)
C
C  CALCULATE THE TOTAL GRAM-MOLES OF EACH ELEMENT
C  BASED ON THE INITIAL COMPOSITION ESTIMATES IN THE PHASES
C
      DO 200 J=1,E
      BCALC(J)=0.
      DO 200 I=1,VSC
      BCALC(J)=A(I,J)*N(I)+BCALC(J)
      B(J)=BCALC(J)
  200 CONTINUE
C
C  DETERMINE A SET OF INDEPENDENT REACTION EQUATIONS,
C  THE GIBBS FREE ENERGY CHANGE FOR THESE REACTIONS
C  AND THE REACTION EQUILIBRIUM CONSTANTS
C
      RT=0.0019872*T
      CALL IDPTEQ(A,D,DPRME,DINV,STDCP,GNU,IDXBAS,KEQ,WKA1,DG,
     &             RT,IDIM1,IDIM2,V,S,C,E,IWRT)
      IF(IWRAP.GT.1) GO TO 476
      IF(ITP.GT.1) GO TO 472
C
C  WRITE-OUT THE INITIAL COMPOSITION ESTIMATES, STANDARD STATE
C  CHEMICAL POTENTIALS AND THE ELEMENTAL ABUNDANCE MATRIX
C
      IPAGE=IPAGE+1
      WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
  400 FORMAT('1',/,'0',T38,'RAND ALGORITHUM FOR DETERMINING ',
     &       'EQUILIBRIUM COMPOSITIONS',/,'0',T30,20A4,T120,
     &       'PAGE ',I2)
      WRITE(IWRT,410) T,P
  410 FORMAT('0',T43,'TEMPERATURE = ',F6.1,' K',5X,'PRESSURE = ',F12.5,
     &       ' PA')
      WRITE(IWRT,420) (ELMNT(K),K=1,13)
  420 FORMAT('0',/,T48,'INPUT DATA AND INITIAL COMPOSITION ESTIMATES',
     &/,'0',T29,'INITIAL',T43,'STANDARD',/,1X,T27,'COMPOSITION',
     &T43,'CHEMICAL',/,1X,T4,'SPECIE',T29,'ESTIMATE',T42,'POTENTIAL',
     &T72,'ELEMENTAL ABUNDANCE MATRIX',/,1X,T4,'SYMBOL',T17,'PHASE',
     &T28,'(G-MOLES)',T40,'(KCAL/G-MOLE)',T55,13(A2,4X),/,'+',
     &12('_'),T15,9('_'),T25,14('_'),T40,13('_'),T55,78('_'))
      DO 440 I=1,VSC
      WRITE(IWRT,430) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),N(I),
     &                STDCP(I),(A(I,J),J=1,E)
  430 FORMAT(1X,3A4,T15,3A3,T25,E14.7,T42,F9.3,T55,13(F5.3,1X))
      IF(I.EQ.V) WRITE(IWRT,430) (INERT(K),K=1,3),
     &                           (PHASE(I,K),K=1,3),ZV,STDCPZ
  440 CONTINUE
      IF(ISS.GT.0) WRITE(IWRT,445) XIII
  445 FORMAT(4X,'X=',F6.4)
```

```
      WRITE(IWRT,450)
  450 FORMAT('0',/,'0',T44,'TOTAL GRAM-MOLES OF EACH ELEMENT FROM IN',
     &       'PUT DATA',/,1X,T40,'AND AS CALCULATED FROM THE INITIAL',
     &       ' COMPOSITION ESTIMATES',/,'0',4(4X,'INPUT DATA',3X,
     &       'CALCULATED',5X))
      NPRT=E/4
      NCHK=NPRT*4
      IF(NCHK.NE.E) NPRT=NPRT+1
      ISTRT=1
      DO 470 K=1,NPRT
      NEND=ISTRT+3
      IF(NEND.GT.E) NEND=E
      WRITE(IWRT,460) (ELMNT(J),B(J),BCALC(J),J=ISTRT,NEND)
  460 FORMAT(1X,4(A2,1X,E12.5,1X,E12.5,4X))
      ISTRT=NEND+1
  470 CONTINUE
  472 CONTINUE
      IPAGE=IPAGE+1
      WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
      WRITE(IWRT,410) T,P
      WRITE(IWRT,475)
  475 FORMAT('0',T58,'EXECUTION DIAGNOSTICS',/,'+',T58,9('_'),1X,
     &       11('_'),/,'0')
  476 CONTINUE
C
C  DIVIDE THE STANDARD STATE CHEMICAL POTENTIALS BY RT
C
      DO 480 I=1,VSC
      STDCP(I)=STDCP(I)/RT
  480 CONTINUE
      STDCPZ=STDCPZ/RT
C
C  CALCULATE THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR
C  AND WRITE-OUT THE INITIAL RESULTS TO THE WRAPUP FILE
C
      IF(ITP.GT.1) GO TO 485
      CALL TOTSI(A,ELMNT,FRAC,N,SITOT,SIMF,IDIM1,IDIM2,V,E)
      CALL RATIO(A,ELMNT,FRAC,RIIIV,IDIM1,IDIM2,V,E)
      IF(IWRAP.GT.0) CALL WRAPUP(TITLE,SPECIE,INERT,N,FRAC,ZV,FRACZ,
     &                           SITOT,SIMF,RIIIV,CNVG,CNVG,ISS,XIII,
     &                           T,P,IDATA,IDIM1,IFILE,V,VSC)
  485 CONTINUE
C
C  ITERATIVE SOLUTION FOR THE EQUILIBRIUM COMPOSITIONS
C
      RELMAX=100.0
      IACFF=0
      DO 600 I=1,MAXIT
      ITER=I
C
C  REMOVE OR ADD PURE CONDENSED PHASES INTO THE CALCULATION
C  BASED ON THEIR INCREMENTAL GIBBS FREE ENERGIES
C
      CALL ADDRMV(A,N,DGTST,STDCP,BLEO,SPECIE,DELN,VPSP1,VSC,E,C,
```

```
      &              EPCP2,IOUT,IDIM1,IDIM2,IDIM3)
       CALL ACTCOF(N,ACOEF,ZACT,IDIM1,IXSCOR,AXS,BXS,T,V,S,C,IACFF,
      &              RELMAX)
       CALL RAND(A,S,BCALC,N,DELN,STDCP,ALEQ,BLEQ,WKA,ACOEF,
      &           ZACT,V,S,C,E,VSC,EPCP2,IDIM1,IDIM2,IDIM3,ITER,P0,P,ZV,
      &           ISTOP,IWRT,IDEBUG,IWRAP)
C
C  CALCULATE THE CONVERGENCE FORCER
C  AND THE NEW ESTIMATE TO THE EQUILIBRIUM COMPOSITION
C
       IALG=1
       CALL CNVFRC(STDCP,N,DELN,ACOEF,V,S,C,IDIM1,IALG,ZV,
      &              P,P0,RT,LAMBDA,ITER,IWRT)
       DO 510 II=1,VSC
       N(II)=N(II)+LAMBDA*DELN(II)
       IF(II.LT.VPS.AND.N(II).LE.1.0E-50) N(II)=1.0E-50
  510 CONTINUE
C
C  RESTORE THE CONSTANTS AND ARRAYS TO THE ORIGINAL PROBLEM FORMULATION
C  (THIS UNDOES THE SHIFTING DONE IN SUBROUTINE ADDRMV)
C
       CALL RESTOR(A,SPECIE,ISPCE,STDCP,N,DELN,IDIM1,IDIM2,VSC,
      &              EPCP2,C,VPSP1,E,IOUT)
       IF(IDEBUG.GE.1) CALL GIBBS(N,STDCP,STDCPZ,ACOEF,ZACT,ZV,T,P,P0,
      &                           IDIM1,V,S,C,GFE)
       IF(IDEBUG.GE.1) CALL DEBUG(N,DELN,DGTST,VSC,IDIM1,ITER,LAMBDA,
      &                           GFE,RELMAX,IWRT)
C
C  CHECK FOR CONVERGENCE OF THE EQUILIBRIUM COMPOSITIONS
C
       RELMAX=0.
       DO 520 II=1,VSC
       IF(N(II).GT.0.0) RELERR=DELN(II)/N(II)
       IF(ABS(RELERR).GT.RELMAX.AND.N(II).GT.1.0E-50)
      &                            RELMAX=ABS(RELERR)
  520 CONTINUE
       IF(RELMAX.LT.CNVG.OR.ISTOP.EQ.1) GO TO 610
  600 CONTINUE
       IF(IWRAP.LT.3) WRITE(IWRT,605) MAXIT
  605 FORMAT('0',' ***** AFTER ',I5,' ITERATIONS THE EQUILIBRIUM ',
     &'COMPOSITION DID NOT CONVERGE')
  610 CONTINUE
       CALL GIBBS(N,STDCP,STDCPZ,ACOEF,ZACT,ZV,T,P,P0,IDIM1,V,S,C,GFE)
C
C  CALCULATE NV, NS, MOLE FRACTIONS, AND THE CHEMICAL POTENTIALS
C
       NV=ZV
       DO 800 I=1,V
       NV=NV+N(I)
  800 CONTINUE
       NS=0.
       IF(S.EQ.0) GO TO 815
       DO 810 I=VP1,VPS
       NS=NS+N(I)
```

```
      810 CONTINUE
      815 CONTINUE
          DO 820 I=1,V
          CHMPT(I)=0.
          FRAC(I)=N(I)/NV
          ARG=ACOEF(I)*FRAC(I)
          IF(ARG.LT.1.0E-50) ARG=1.0E-50
          CHMPT(I)=RT*(STDCP(I)+ALOG(ARG))
      820 CONTINUE
          IF(S.EQ.0) GO TO 835
          DO 830 I=VP1,VPS
          CHMPT(I)=0.
          FRAC(I)=N(I)/NS
          ARG=ACOEF(I)*FRAC(I)
          IF(ARG.LT.1.0E-50) ARG=1.0E-50
          CHMPT(I)=RT*(STDCP(I)+ALOG(ARG))
      830 CONTINUE
      835 CONTINUE
          IF(C.EQ.0) GO TO 845
          DO 840 I=VPSP1,VSC
          FRAC(I)=1.
          IF(N(I).LT.1.0E-50) FRAC(I)=0.0
          CHMPT(I)=STDCP(I)*RT
      840 CONTINUE
      845 CONTINUE
          FRACZ=ZV/NV
          DZV=0.
          CHMPTZ=0.
          IF(FRACZ.LE.0.0) GO TO 850
          CHMPTZ=(STDCPZ+ALOG(ZACT*FRACZ))*RT
      850 CONTINUE
C
C  CALCULATE THE EQUILIBRIUM CONSTANTS FROM COMPOSITION
C
          CALL CALCQ(GNU,N,ACOEF,FRAC,IDXBAS,Q,
     &              P,P0,V,S,C,E,IDIM1,IDIM2)
C
C  CALCULATE THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR
C
          CALL TOTSI(A,ELMNT,FRAC,N,SITOT,SIMF,IDIM1,IDIM2,V,E)
          CALL RATIO(A,ELMNT,FRAC,RIIIV,IDIM1,IDIM2,V,E)
          IF(IWRAP.GT.1) GO TO 971
C
C  WRITE-OUT THE RESULTS
C
           IPAGE=IPAGE+1
          WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
          WRITE(IWRT,410) T,P
          WRITE(IWRT,900) ITER,GFE,RELMAX,CNVG,LAMBDA
      900 FORMAT('0',/,1X,T45,'EQUILIBRIUM COMPOSITIONS AFTER ',I5,
     &' ITERATIONS',/,'0',T42,'SYSTEM GIBBS FREE ENERGY = ',E14.7,
     &' (KCAL)',
     & /,'0','RELATIVE ERROR = ',E12.5,5X,'CONVERGENCE CRITERION = ',
     & E12.5,5X,'RELAXATION PARAMETER AT LAST ITERATION = ',F12.5,
```

```
      & /,'0',T57,'ESTIMATED',/,1X,T25,'EQUILIBRIUM',T39,'EQUILIBRIUM',
      & T56,'COMPOSITION',T92,'CHEMICAL',
      & /,1X,T4,'SPECIE',T29,'MOLE',T39,'COMPOSITION',T56,
      & 'UNCERTAINTY',T91,'POTENTIAL',T109,'ACTIVITY',
      & /,1X,T4,'SYMBOL',T17,'PHASE',T27,'FRACTION',T40,'(G-MOLES)',
      & T57,'(G-MOLES)',T90,'(KCAL/G-MOLE)',T107,'COEFFICIENT',
      & /,'+',12('_'),T15,9('_'),T25,12('_'),T37,14('_'),T54,
      & 14('_'),T89,14('_'),T106,12('_'))
       DO 920 I=1,VSC
       WRITE(IWRT,910) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),FRAC(I),
      &                N(I),DELN(I),CHMPT(I),ACOEF(I)
  910 FORMAT(1X,3A4,T15,3A3,T24,E12.5,T37,E14.7,T54,E14.7,T92,F9.3,
     &T106,E12.5)
       IF(I.EQ.V) WRITE(IWRT,910) (INERT(K),K=1,3),(PHASE(I,K),K=1,3),
      &                           FRACZ,ZV,DZV,CHMPTZ,ZACT
  920 CONTINUE
       IF(ISS.GT.0) WRITE(IWRT,445) XIII
       WRITE(IWRT,930) SIMF
  930 FORMAT('0',T35,'MOLE FRACTION OF SILICON SPECIES IN ',
     &       'VAPOR PHASE = ',E12.5)
       WRITE(IWRT,940) RIIIV
  940 FORMAT('0',T50,'III/V RATIO IN THE VAPOR PHASE = ',F9.4)
       WRITE(IWRT,950)
  950 FORMAT('0',/,'0',T44,'TOTAL GRAM-MOLES OF EACH ELEMENT FROM IN',
     &'PUT DATA',/,1X,T42,'AND AS CALCULATED FROM THE EQUILIBRIUM',
     &      ' COMPOSITIONS',/,'0',4(4X,'INPUT DATA',3X,
     &      'CALCULATED',5X))
       NPRT=E/4
       NCHK=NPRT*4
       IF(NCHK.NE.E) NPRT=NPRT+1
       ISTRT=1
       DO 970 K=1,NPRT
       NEND=ISTRT+3
       IF(NEND.GT.E) NEND=E
       WRITE(IWRT,960) (ELMNT(J),B(J),BCALC(J),J=ISTRT,NEND)
  960 FORMAT(1X,4(A2,1X,E12.5,1X,E12.5,4X))
       ISTRT=NEND+1
  970 CONTINUE
  971 CONTINUE
       IF(IWRAP.GT.0) CALL WRAPUP(TITLE,SPECIE,INERT,N,FRAC,ZV,FRACZ,
      &SITOT,SIMF,RIIIV,RELMAX,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE,
      &V,VSC)
       IF(ITP.GT.1.OR.ICMP.GT.1.OR.IWRAP.GT.1) GO TO 1900
C
C  WRITE-OUT THE INDEPENDENT EQUATIONS
C
       IPAGE=IPAGE+1
       WRITE(IWRT,400) (TITLE(K),K=1,20), IPAGE
       WRITE(IWRT,410) T,P
       WRITE(IWRT,980)
  980 FORMAT('0',T38,'A SET OF INDEPENDENT REACTION EQUATIONS FOR ',
     &       'THIS SYSTEM IS AS FOLLOWS:',/,'0')
       DO 1100 I=1,VSC
C
```

```
C  DETERMINE THE NUMBER OF BASIS SPECIES IN EACH FORMATION REACTION
C
      NSPEC=0
      DO 990 K=1,E
      IF(I.EQ.IDXBAS(K)) GO TO 1100
      IF(ABS(GNU(I,K)).LT.1.0E-6) GO TO 990
      NSPEC=NSPEC+1
  990 CONTINUE
C
C  FILL THE CHARACTER ARRAY "STRING" WITH THE FORMATION REACTION SPECIE
C
      NLOOP=1
      IF(NSPEC.GT.4) NLOOP=FLOAT(NSPEC)/4.0+0.9
      DO 1000 K=1,3
      STRING(1,K)=SPECIE(I,K)
 1000 CONTINUE
      STRING(1,4)=RPAS
      COEFF(1)=1.0
      IST=1
      ICNT=0
      DO 1060 ILOOP=1,NLOOP
      NCNT=NSPEC-ICNT+1
      IF(NCNT.GT.5) NCNT=5
      DO 1020 IDX=2,NCNT
      ICNT=ICNT+1
      DO 1015 IBASE=IST,E
      IF(ABS(GNU(I,IBASE)).LT.1.0E-6) GO TO 1015
      IDXB=IDXBAS(IBASE)
      DO 1010 K=1,3
      STRING(IDX,K)=SPECIE(IDXB,K)
 1010 CONTINUE
      COEFF(IDX)=GNU(I,IBASE)
      STRING(IDX,4)=RPSPS
      GO TO 1018
 1015 CONTINUE
 1018 IST=IBASE+1
 1020 CONTINUE
      STRING(NCNT,4)=RPBL
      IF(ILOOP.EQ.1) WRITE(IWRT,1040)(LP,COEFF(IJK),
     &                                (STRING(IJK,K),K=1,4),IJK=1,NCNT)
 1040 FORMAT('0',A1,F5.2,4A4,4(A1,E10.3,4A4))
      IF(ILOOP.GT.1) WRITE(IWRT,1050) SSPS,(LP,COEFF(IJK),
     &                                (STRING(IJK,K),K=1,4),IJK=2,NCNT)
 1050 FORMAT(1X,T20,A4,4(A1,E10.3,4A4))
 1060 CONTINUE
 1100 CONTINUE
C
C  WRITE-OUT A COMPARISON BETWEEN THE EQUILIBRIUM CONSTANTS
C  AS CALCULATED BY THE GIBBS FREE ENERGY CHANGE AND BY COMPOSITION
C
      IPAGE=IPAGE+1
      WRITE(IWRT,400) (TITLE(K),K=1,20), IPAGE
      WRITE(IWRT,410) T,P
      WRITE(IWRT,1110)
```

```
541   1110 FORMAT('0',/,1X,T40,'EQUILIBRIUM CONSTANTS FOR THE INDEPENDENT',
542          &' REACTIONS',/,'0',T20,'GIBBS FREE ENERGY CHANGE',T47,
543          &'EQUILIBRIUM CONSTANT',T73,'EQUILIBRIUM CONSTANT',/,1X,
544          &'REACTION PRODUCT',T25,'(KCAL/G-MOLE)',T46,'FROM GIBBS FREE ',
545          &'ENERGY',T70,'FROM PREDICTED COMPOSITION',/,'+',16('_'),T20,
546          &24('_'),T46,22('_'),T70,26('_'))
547           DO 1200 I=1,VSC
548           WRITE(IWRT,1120) (SPECIE(I,K),K=1,3),DG(I),KEQ(I),Q(I)
549   1120 FORMAT(1X,3A4,T28,F8.3,T51,E12.5,T77,E12.5)
550   1200 CONTINUE
551           IF(ISS.GT.0) WRITE(IWRT,445) XIII
552   1900 IF(ISTOP.EQ.1) GO TO 3000
553   2000 CONTINUE
554   3000 STOP
555           END
```

A.3 A Description of the Major Variables in MCMPEC.RAND

Variables which are used in the IMSL subroutines LINV1F, LEQT1F, LUDAT F and LUELMF are not included in this list. FORTRAN default typing applies unless otherwise specified.

Variable	Description	Units
A (I,J)	elemental abundance matrix	$\frac{\text{atoms of element j}}{\text{molecule of specie i}}$
ACOEF (I)	activity coefficient of specie i	-
ALEQ (I, J)	matrix containing coefficients in the RAND algorithm	variable
AMAX	maximum value the convergence forcer may attain	-
AMIN	minimum value the convergence forcer may attain	-
AXS	activity coefficient correlation parameter	variable
A0 (I)	heat capacity correlation parameter	kcal/g-mole-K
A1 (I)	heat capacity correlation parameter	kcal/g-mole-K^2
A2 (I)	heat capacity correlation parameter	variable
A3 (I)	heat capacity correlation parameter	variable
A0Z	inert specie heat capacity correlation parameter	kcal/g-mole-K
A1Z	inert specie heat capacity correlation parameter	kcal/g-mole-K^2
A2Z	inert specie heat capacity correlation parameter	variable
A3Z	inert specie heat capacity correlation parameter	variable

Variable	Description	Units
B (J)	moles of element J specified in the system	g-moles
BCALC (J)	moles of element J as calculated by algorithm	g-moles
BK (J)	same as BCALC (J)	g-moles
BLEQ (I)	vector containing the right-hand-side of the RAND algorithm	variable
BXS	activity coefficient correlation parameter	variable
C	number of pure condensed phases (integer)	-
CHMPT (I)	chemical potential of specie i	kcal/g-mole
CHMPTZ	chemical potential of the inert	kcal/g-mole
CNVG	composition convergence criterion	-
COND (3)	vector containing the character string 'CONDENSED'	-
D (I, J)	matrix of basis species	$\frac{\text{atoms of j}}{\text{molecule of i}}$
DELH	total enthalpy change	kcal/g-mole
DELN (I)	change in moles of specie i	g-mole
DELS	total entropy change	kcal/g-mole-K
DG (I)	Gibbs Free Energy change of reaction i	kcal/g-mole
DGDL	change in system Gibbs Free Energy with respect to the convergence forcer	kcal/g-mole

Variable	Description	Units
DGTST (I)	incremental change in Gibbs free energy for specie i	kcal/g-mole
DHO (I)	enthalpy of formation of specie i	kcal/g-mole
DHOZ	enthalpy of formation of the inert specie	kcal/g-mole
DINV (I, J)	inverse of matrix D	-
DPRME (I, J)	Gram-Schmidt orthogonalization of matrix D	-
DSO (I)	entropy of formation of specie i	kcal/g-mole-K
DSOZ	entropy of formation of the inert specie	kcal/g-mole-K
E	number of elements in the system (integer)	-
ELIII (K)	vector containing character string of group III elements	-
ELMNT (J)	vector containing character strings of the elements present in the system	-
ELV (K)	vector containing character strings of group V element	-
EPCP2	E + C + 2 (integer)	-
EP3	E + 3 (integer)	-
EP3PC	E + 3 + C (integer)	-
FRAC (I)	mole fraction of specie i in its phase	-
FRACZ	mole fraction of inert in the vapor	-

Variable	Description	Units
GNU (I, J)	formation reaction coefficient matrix	g-mole
GFE	Gibbs Free Energy of the system	kcal/g-mole
GSTAR	GFE divided by RT	-
IACFF	activity coefficient switch	-
IALG	convergence forcer algorithm switch	-
ICMP	index for the composition loop	-
ICP (I)	heat capacity correlation parameter	-
IDATA	switch used with the wrap-up file	-
IDGT	number of significant figures in each matrix element	-
IDIM1	maximum number of species allowed in system	-
IDIM2	maximum number of elements allowed in system	-
IDIM3	IDIM1 + IDIM2	-
IDEBUG	option to aid in trouble-shooting	-
IDXBAS (J)	vector containing the index of each basis specie	-
IFILE	logical unit designator of the wrap-up file	-
INERT (3)	vector containing the inert specie name	-

Variable	Description	Units
IOPT	parameter to allow various computational options	-
IOUT	number of pure condensed phases removed by subroutine ADDRMV	-
IRD	logical unit designator for data input	-
ISPCE (I, J)	array containing the original specie order	-
ISS	steady state option parameter	-
ISTOP	switch which halts the computation if problems develope	-
ITER	current iteration number in the equilibrium calculation	-
ITP	index for the temperature and pressure loop	-
ITST	parameter which indicates linear dependence in the basis specie matrix	-
IWRAP	switch used with the wrap-up file	-
IWRT	logical unit designator for data output	-
IXSCOR	parameter which chooses the solution phase activity coefficient model	-
KEQ (I)	equilibrium constant for formation reaction i as calculated from the Gibbs Free Energy change (real)	-
LAMBDA	convergence forcer (real)	-
MAXIT	maximum number of iterations to be used	-
N (I)	moles of specie i (real)	g-moles
NMAX	total number of loops to be made in the composition or temperature and pressure loops	-

Variable	Description	Units
NS	total moles in solution (real)	g-moles
NSPEC	number of species in the formation reaction	-
NV	total moles in the vapor (real)	g-moles
P	system pressure	Pa
PHASE (I, 3)	matrix containing a character string to denote the phase of each specie	-
PINC	pressure increment for each loop	Pa
PO	formation data reference pressure	Pa
Q (I)	equilibrium constant for formation reaction i as calculated from composition	-
RELERR	fractional change in composition resulting from one iteration	-
RELMAX	maximum fractional change in composition of all species resulting from one iteration	-
RIIIV	vapor phase III/V atomic ratio	-
RT	product of the ideal gas constant and the temperature	kcal/g-mole
S	total number of species in the solution phase	-
SIMF	mole fraction of silicon species in the vapor	-
SITOT	moles of silicon species in the vapor	g-moles
SOLN (3)	vector containing the character string 'SOLUTION'	-

Variable	Description	Units
SPECIE (I, 3)	matrix of character strings containing the names of each specie	-
STDCP (I)	standard chemical potential of specie i	kcal/g-mole
STDCPZ	standard chemical potential of the inert	kcal/g-mole
SUMIII	total moles of group III atoms in the vapor	g-mole
SUMV	total moles of group V atoms in the vapor	g-mole
T	system temperature	K
TITLE (K)	vector containing an 80 character title	-
TINC	temperature increment for each loop	K
TOTMC (I)	total moles of pure condensed phase i as input	g-moles
TOTMOL	total moles in a single phase	g-moles
TOTMS	total moles in the solution phase	g-moles
TOTMV	total moles in the vapor phase	g-moles
TO	formation data reference temperature	K
US	coefficient for the solution species	-
UV	coefficient for the vapor species	-
V	total number of species in the vapor (integer)	-
VAPOR (3)	vector containing the character string 'VAPOR'	-

Variable	Description	Units
WKA	work area for LEQT1F	
WKA1	work area for LINV1F	
XIII	group III specie fraction in the steady state liquid "pure" condensed phase	-
ZV	moles of inert in the system	g-moles
ZACT	activity coefficient of the inert	-

A.4 A Description of the Subroutines

The subroutine calling sequence is shown in Figure A2. All of the subroutines in MCMPEC.RAND are discussed separately in the following sections with the exception of subroutine ERRSET and the IMSL subroutines LINV1F and LEQT1F. Subroutine ERRSET is a system subroutine which is used to suppress printing of certain execution time error messages. This subroutine may not be available at all computer installations and therefore the two calls to ERRSET may have to be removed if this code is to be implemented on other systems. The IMSL subroutines are briefly described in section A.4.18.

A.4.1 STSTCP

A listing of subroutine STSTCP is shown in Figure A3. STSTCP calculates the standard state chemical potentials for each specie in the system. The reference state is the system temperature T, the formation pressure P0, and pure component in the phase in which the specie is present.

The pure component Gibbs Free Energy (standard chemical potential) of specie i at temperature To and pressure Po is:

$$\mu_i^\circ (T_o, P_o) = \underline{G}_i^\circ = \Delta \underline{H}_f^\circ - T_o \Delta \underline{S}_f^\circ \qquad (1)$$

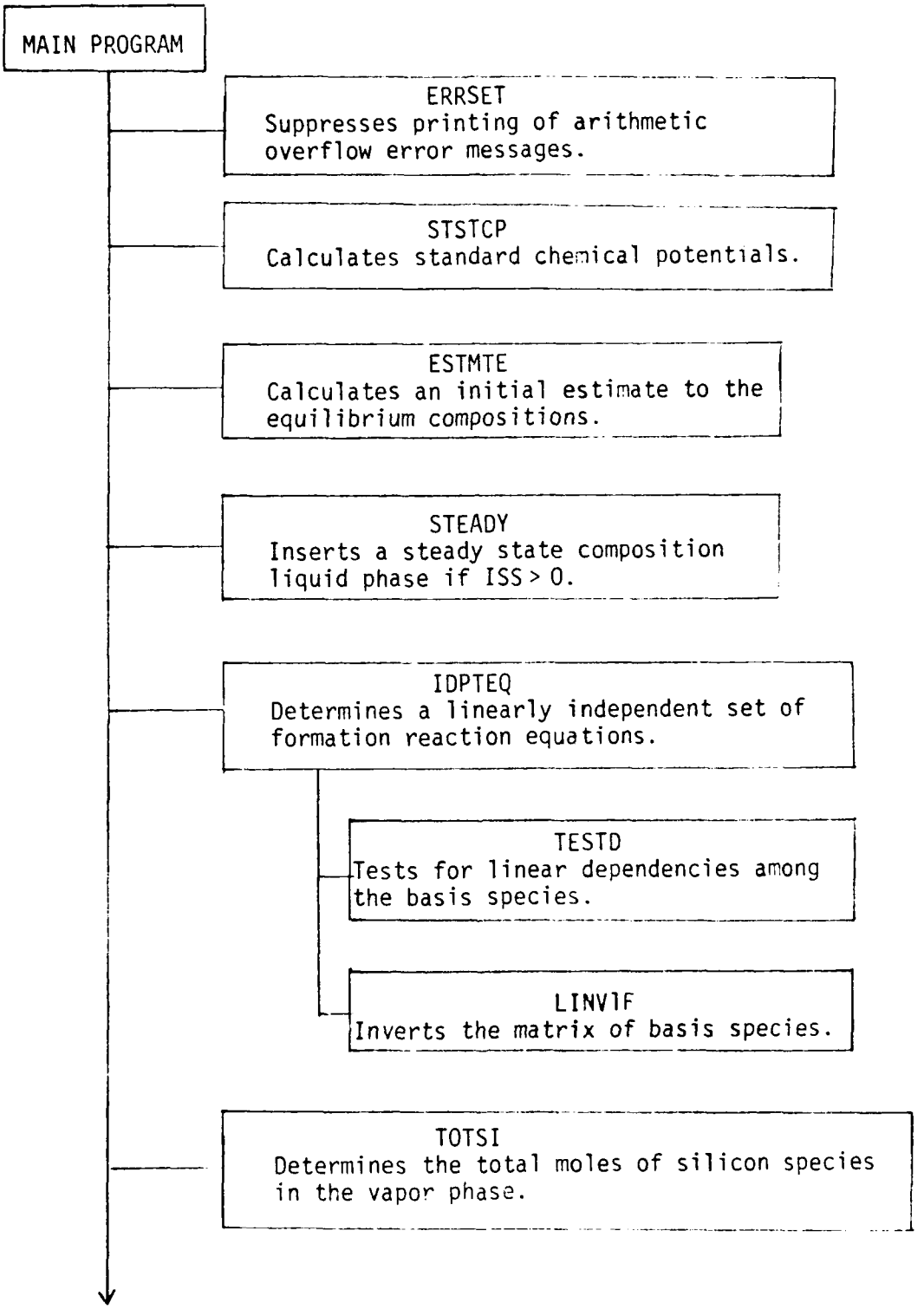
For a system temperature T the standard chemical potential of specie i is given by:

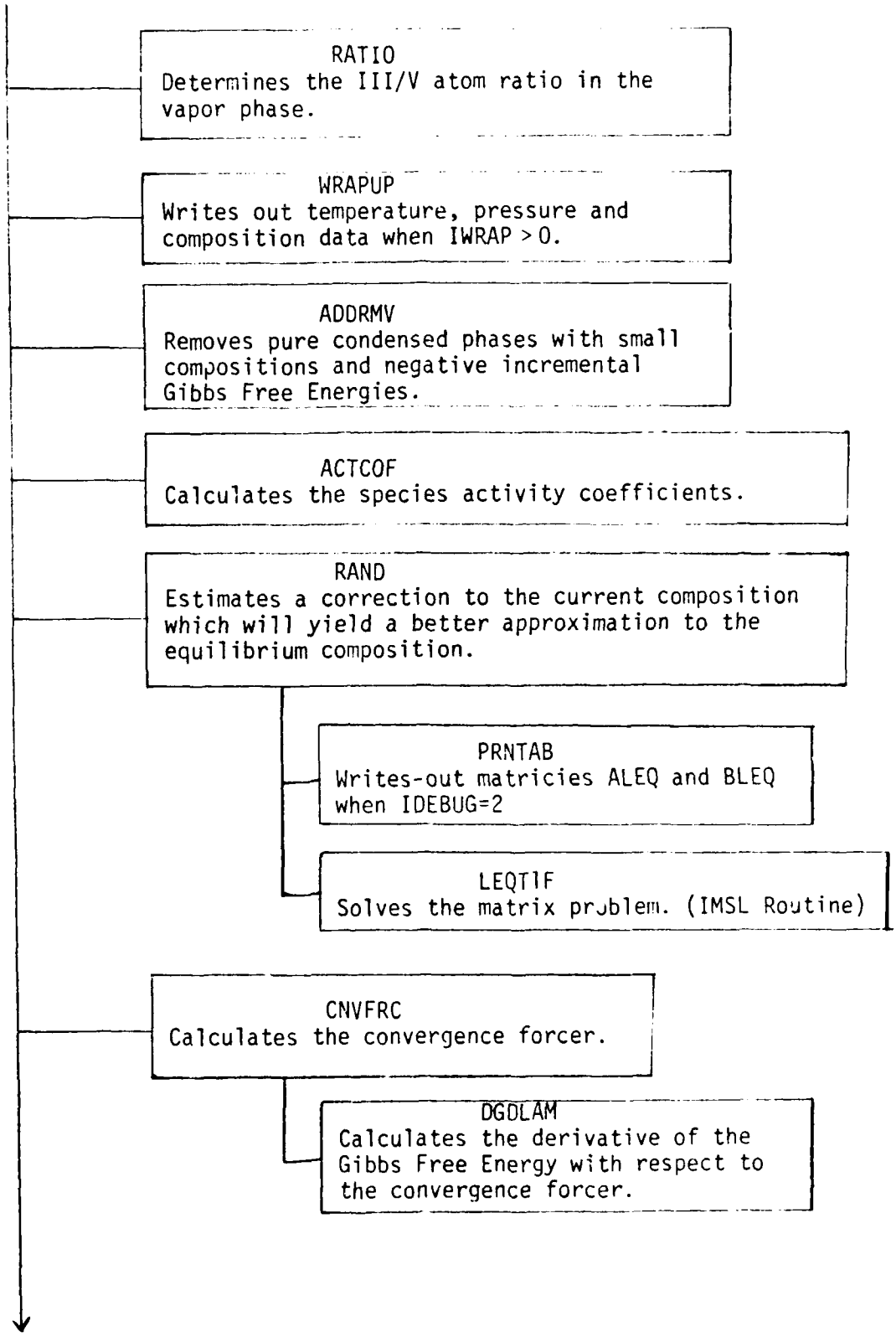
$$\mu_i^\circ (T, P_o) = \Delta \underline{H}_f^i (T_o) + \int_{T_o}^{T} C_p^i \, dT - T \left[\Delta \underline{S}_f^i (T_o) + \int_{T_o}^{T} \frac{C_p^i}{T} \, dT \right] \qquad (2)$$

Two heat capacity correlations are available and are chosen by the

Figure A2

Subprogram Structure of MCMPEC.RAND




RATIO
Determines the III/V atom ratio in the vapor phase.
WRAPUP
Writes out temperature, pressure and composition data when IWRAP > 0.
ADDRMV
Removes pure condensed phases with small compositions and negative incremental Gibbs Free Energies.
ACTCOF
Calculates the species activity coefficients.
RAND
Estimates a correction to the current composition which will yield a better approximation to the equilibrium composition.
PRNTAB
Writes-out matricies ALEQ and BLEQ when IDEBUG=2
LEQT1F
Solves the matrix problem. (IMSL Routine)
CNVFRC
Calculates the convergence forcer.
DGDLAM
Calculates the derivative of the Gibbs Free Energy with respect to the convergence forcer.

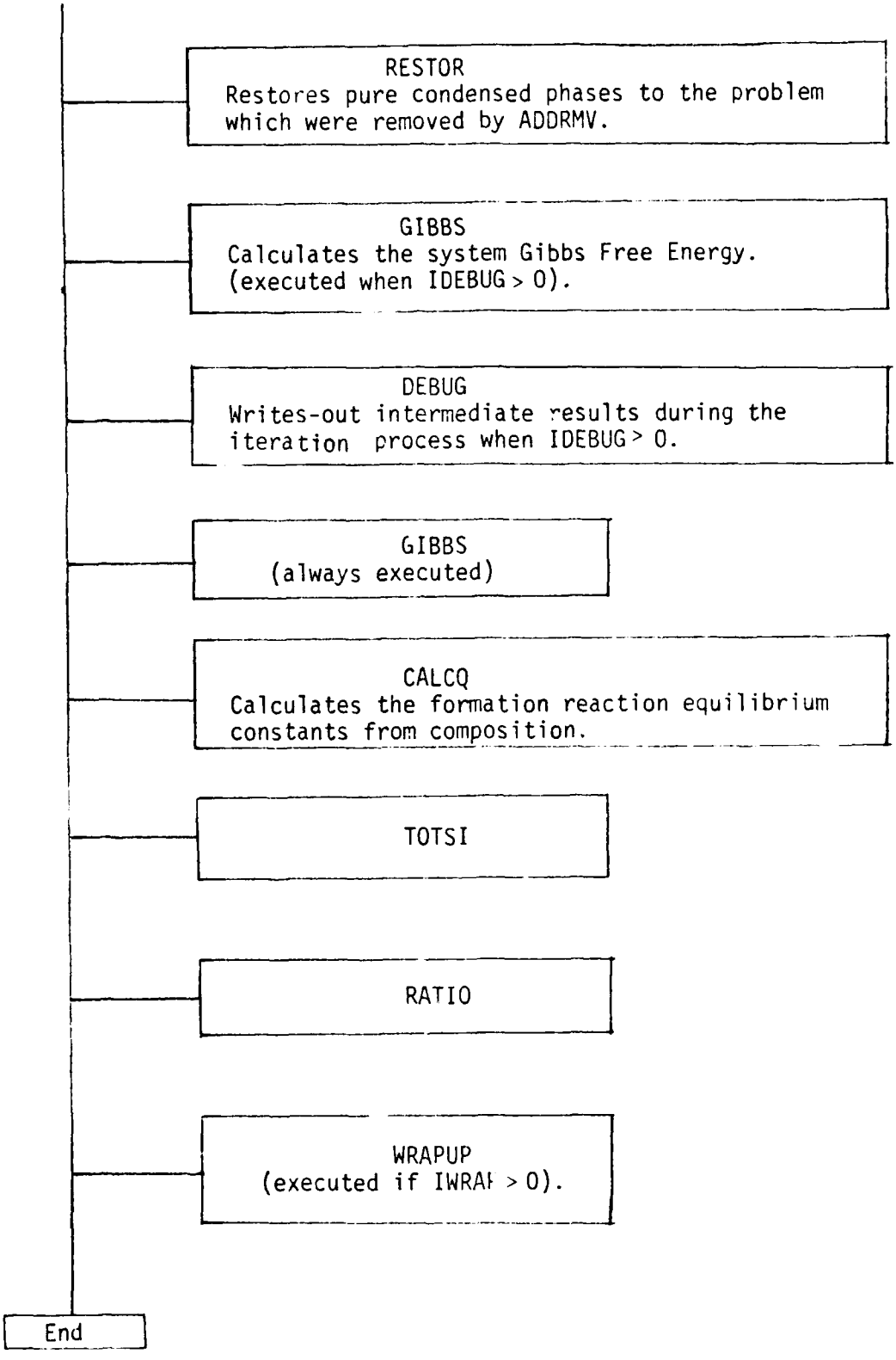

RESTOR
Restores pure condensed phases to the problem which were removed by ADDRMV.
GIBBS
Calculates the system Gibbs Free Energy. (executed when IDEBUG > 0).
DEBUG
Writes-out intermediate results during the iteration process when IDEBUG > 0.
GIBBS
(always executed)
CALCQ
Calculates the formation reaction equilibrium constants from composition.
TOTSI
RATIO
WRAPUP
(executed if IWRAP > 0).
End

Figure A3. Subroutine STSTCP

```
      SUBROUTINE STSTCP(A0,A1,A2,A3,A0Z,A1Z,A2Z,A3Z,DH0,DS0,DH0Z,DS0Z,
     &                  STDCP,STDCPZ,ICP,ICPZ,T0,T,IDIM1,V,S,C)
C
C  THIS SUBROUTINE CALCULATES THE STANDARD STATE CHEMICAL POTENTIALS
C  REFERENCE STATE: PURE COMPONENT (APPROPRIATE PHASE)
C                   AT TEMPERATURE T.
C
      DIMENSION A0(IDIM1),A1(IDIM1),A2(IDIM1),A3(IDIM1),DH0(IDIM1),
     &          DS0(IDIM1),STDCP(IDIM1),ICP(IDIM1)
      INTEGER V,S,C,VSC
      VSC=V+S+C
      DT=T-T0
      DT2=T**2-T0**2
      DT3=T**3-T0**3
      DT4=T**4-T0**4
      DTM1=1.0/T-1.0/T0
      DTM2=1.0/T/T-1.0/T0/T0
      DLNT=ALOG(T)-ALOG(T0)
      DLNT2=ALOG(T)**2-ALOG(T0)**2
      DTLNT=T*ALOG(T)-T0*ALOG(T0)
C
C CHEMICAL POTENTIALS FOR THE VAPOR, SOLUTION AND CONDENSED PHASES
C
      DO 100 I=1,VSC
      DELH=A0(I)*DT+A1(I)*DT2/2.-A2(I)*DTM1+A3(I)*(DTLNT-DT)
      DELS=A0(I)*DLNT+A1(I)*DT-A2(I)*DTM2/2.+A3(I)*DLNT2/2.
      IF(ICP(I).EQ.1) DELH=A0(I)*DT+A1(I)*DT2/2.+A2(I)*DT3/3.
     &                     +A3(I)*DT4/4.
      IF(ICP(I).EQ.1) DELS=A0(I)*DLNT+A1(I)*DT+A2(I)*DT2/2.
     &                     +A3(I)*DT3/3.
      STDCP(I)=DH0(I)+DELH-T*(DS0(I)+DELS)
  100 CONTINUE
C
C  CHEMICAL POTENTIAL FOR THE INERT COMPONENT IN THE VAPOR PHASE
C
      DELH=A0Z*DT+A1Z*DT2/2.-A2Z*DTM1+A3Z*(DTLNT-DT)
      DELS=A0Z*DLNT+A1Z*DT-A2Z*DTM2/2.+A3Z*DLNT2/2.
      IF(ICPZ.EQ.1) DELH=A0Z*DT+A1Z*DT2/2.+A2Z*DT3/3.
     &                   +A3Z*DT4/4.
      IF(ICPZ.EQ.1) DELS=A0Z*DLNT+A1Z*DT+A2Z*DT2/2.
     &                   +A3Z*DT3/3.
      STDCPZ=DH0Z+DELH-T*(DS0Z+DELS)
      RETURN
      END
```

parameter ICP. These correlations are:

ICP	Heat Capacity Correlation	
0	$C_p(T) = a_0 + a_1 T + a_2 T^{-2} + a_3 \ell n(T)$	(3)
1	$C_p(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3$	(4)

Obviously various other correlations (constant, linear, quadratic, etc.) may be generated from these two functions by simply setting the appropriate coefficients to zero.

Lines 12 through 20 calculate the necessary limit differentials which result from performing the indicated integrations in Equation 2 using the heat capacity correlations in Equations 3 and 4. The integrals are evaluated as DELH and DELS and the standard chemical potential for each specie, STDCP(I)is then calculated.

A.4.2 ESTMTE

A listing of subroutine ESTMTE is provided in Figure A4. ESTMTE simply calculates the number of moles of each specie from the specie mole fraction and the total number of moles in the phase. ESTMTE is provided as a subroutine to allow the inclusion of an algorithm which will yield an estimate to the equilibrium composition and therefore reduce the number of iterations required to obtain convergence. Currently the inlet composition is used as this initial estimate.

A.4.3 STEADY

Subroutine STEADY inserts a pure condensed phase into the system in order to model a III-V liquid solution with a steady state composition. The composition of this liquid is that which would exist at equilibrium

FIGURE A4. Subroutine ESTMTE

```
      SUBROUTINE ESTMTE(TOTMV,TOTMS,TOTMC,FRAC,N,FRACZ,ZV,IDIM1,
     &                  V,S,C)
C
C  THIS SUBROUTINE CALCULATES AN INITIAL ESTIMATE
C  TO THE SYSTEM EQUILIBRIUM COMPOSITIONS
C
      DIMENSION TOTMC(IDIM1),FRAC(IDIM1)
      INTEGER V,S,C,VS,VS1,VSC
      REAL N(IDIM1)
      VS=V+S
      VS1=VS+1
      VSC=V+S+C
      TOTMOL=TOTMV
      DO 50 I=1,VS
      IF(I.GT.V) TOTMOL=TOTMS
      N(I)=TOTMOL*FRAC(I)
   50 CONTINUE
      ZV=FRACZ*TOTMV
      IF(C.EQ.0) RETURN
      DO 60 I=VS1,VSC
      N(I)=TOTMC(I)
   60 CONTINUE
      RETURN
      END
```

with the stoichiometric III-V solid at the system temperature. This subroutine is invoked when ISS > 0, a Ga/As liquid phase being inserted for ISS = 1 and an In/P liquid phase for ISS = 2. This phase is inserted as the last pure condensed phase in the system (specie V+S+C).

A solid liquid equilibrium model for a binary liquid with the mole fraction of group V specie designated as X in obtained by writing the following reactions.

$$(1-x)\mathrm{III}(s) \doteq (1-x)\mathrm{III}(\ell) \quad (1)$$

$$x\mathrm{V}\ (s) = x\ \mathrm{V}\ (\ell) \quad (2)$$

$$(1-x)\mathrm{III}(\ell) + x\ \mathrm{V}\ (\ell) = \mathrm{III}_{1-x}\ \mathrm{V}_x\ (\ell) \quad (3)$$

$$(1-x)\mathrm{III}(s) + x\ \mathrm{V}\ (s) = \mathrm{III}_{1-x}\ \mathrm{V}_x\ (\ell) \quad (4)$$

Reaction 4, which is the sum of the previous three reactions, represents the formation of a liquid solution having a composition (1-X)III and x V.

The Gibbs Free Energies of reactions 1 and 2 are simply those due to melting at Tm corrected for the temperature, T, of the solution.

$$\Delta G_1 = (1-x)\left[\Delta S_m^{III}\ (T_m^{III} - T) + \Delta C_p^{III}\ (T - T_m^{III} - T\ \ln \frac{T_m^{III}}{T})\right] \quad (5)$$

$$\Delta G_2 = x\left[\Delta S_m^{V}\ (T_m^{V} - T) + \Delta C_p^{V}\ (T - T_m^{V} - T\ \ln \frac{T_m^{V}}{T})\right] \quad (6)$$

where it has been assumed that ΔC_p, the difference between the liquid and solid heat capacities, may be approximated as a constant.

The Gibbs Free Energy of reaction 3 is that due to the mixing of the group III and V liquids. This free energy consists of an ideal free energy of mixing (comprised of a configurational entropy term) and an excess Gibbs Free Energy term due to nonidealities. Applying a simple solution theory model for the excess Gibbs Free Energy yields [4]:

$$\Delta G_3 = RT [x \ln x + (1-x) \ln (1-x)] + (A_{xs} + B_{xs} T) x (1-x) \quad (7)$$

The Gibbs Free Energy of the liquid solution represented by reaction 4 is therefore given by:

$$\Delta G_4 = \Delta G_1 + \Delta G_2 + \Delta G_3 \quad (8)$$

Determination of the mole fraction of group V atoms in the melt, X, is accomplished by solving the implicit equation developed by Veiland [10] modified to include a simple solution rather than a regular solution model.

$$T = \frac{T_m^{III V} \Delta S_m^{III V} - A_{xs} (2x - 2x^2 - 0.5)}{\Delta S_m^{III V} - R \ln 4x(1-x) + B_{xs} (2x-2x^2-0.5)} \quad (9)$$

The thermodynamic constants necessary for the evalution of equations 8 and 9 are listed in Table A.3. Figures A5 and A6 demonstrate how well the theory predicts the liquidus temperature in the Ga/As and In/P systems.

Table A.3

Thermodynamic Data for the Ga/As and In/P Systems.

	ΔS_m (cal/g-mole-k)	T_m (K)	ΔC_p (cal/g-mole-K)	A_{xs} (cal/g-mole)	B_{xs} (cal/g-mole-K)
Ga	4.411	302.9	-0.05		
As	4.7	1090	1.0	4666	-8.741
GaAs	16.64	1511	0		
In	1.815	429.8	-0.2		
P	0.5011	313.3	0.47	32750	-23.95
InP	10.81	1332.2	0		

Figure A5
The Ga/As System Liquidus Line
(Data refs. 3, 14, 15)

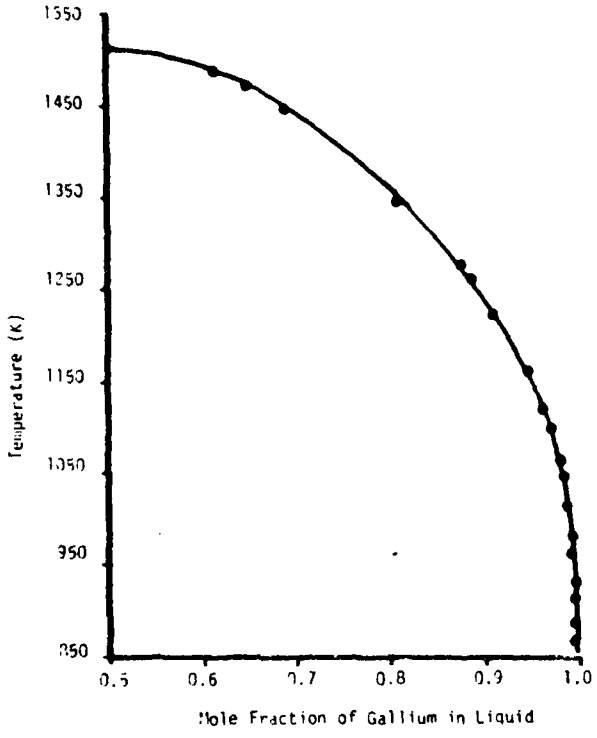
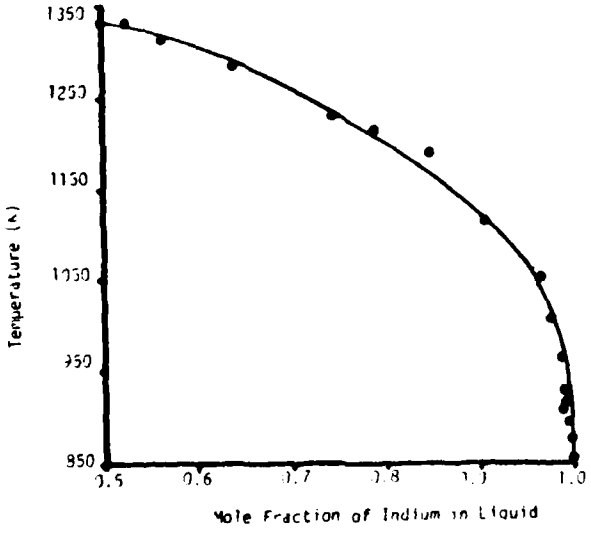


Figure A6
The In/P System Liquidus Line
(Data refs. 5, 11, 12, 13)



A listing of subroutine STEADY is shown in Figure A7. Lines 16 and 17 define a statement function which corresponds to the right hand side of Equation 9. Hollerith strings are assigned to the specie identifier matrix in lines 19 through 21. The melting temperature, entropies and excess Gibbs Free Energy correlation parameters for the Ga/As and In/P systems are assigned in lines 29 through 54.

An "interval halving" root finding algorithm for solving the implicit equation is located at lines 57 through 80. The iteration is considered to have converged when the two sides of the equation differ by less than 0.01%.

The standard state chemical potential of the liquid solution is calculated in lines 86 through 91. Finally, the elemental abundance matrix is assigned the appropriate values which reflect the elemental composition of the liquid solution in lines 93 through 107.

A.4.4 IDPTEQ

Subroutine IDPTEQ constructs a set of linearly independent formation reaction equations for the species in the system and then calculates the equilibrium constants for each of these reactions from the Gibbs Free Energy change of each reaction. A flowsheet and a listing of this subroutine are shown in Figures A8 and A9 respectively.

Lines 15 through 33 construct a matrix D which contains a linearly independent set of basis species using an algorithm similar to that of Cruise [6]. A matrix GNU, which contains the stoichiometric coefficients of all of the formation reactions, is then calculated in lines 39 through 57 using the relation

$$GNU = A\ D^{-1} \qquad (1)$$

Figure A7. Subroutine STEADY

```
      SUBROUTINE STEADY(SPECIE,A,STDCP,ELMNT,XIII,T,T0,V,S,C,IDIM1,
     &                  IDIM2,ISS,IWRT)
C
C  SUBROUTINE TO CALCULATE THE SOLID-LIQUID EQUILIBRIUM COMPOSITIONS
C  FOR USE IN THE STEADY-STATE APPROXIMATION IN THE SOURCE ZONE
C
C     ISS      SYSTEM
C       1      GA(L)-AS(L)/GA-AS (S)
C       2      IN(L)-P(L)/IN-P (S)
C
      DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1)
      INTEGER SPECIE(IDIM1,3),ELMNT(IDIM2),IIIEL(2),VEL(2),V,S,C,VSC,
     &        LAST/'1-X)'/,GA/'GA'/,AS/'AS'/,IN/'IN'/,P/' P'/
      DATA IIIEL(1)/' GAX'/,IIIEL(2)/' INX'/,
     &     VEL(1)/'-AS('/,VEL(2)/'- P('/
      THETA2(XV)=(TMIIIV*DSIIIV-AXS*(0.5-XV**2-(1.-XV)**2))/
     &       (DSIIIV-R*ALOG(4.*XV*(1.-XV))+BXS*(0.5-XV**2-(1.-XV)**2))
      VSC=V+S+C
      SPECIE(VSC,1)=IIIEL(ISS)
      SPECIE(VSC,2)=VEL(ISS)
      SPECIE(VSC,3)=LAST
      DT=T-T0
      DT2=T**2-T0**2
      DTM1=1.0/T-1.0/T0
      DTM2=1.0/T**2-1.0/T0**2
      DLNT=ALOG(T/T0)
      IF(ISS.EQ.2) GO TO 50
C
C  GA-AS SYSTEM
C
      TMIII=302.9
      TMV=1090.
      TMIIIV=1511.
      DSIII=0.004411
      DSV=0.0047
      DSIIIV=0.01664
      DCIII=-0.00005
      DCV=0.001
      AXS=4.666
      BXS=-0.008741
      GO TO 60
C
C  IN-P SYSTEM
C
   50 TMIII=429.8
      TMV=317.3
      TMIIIV=1343.2
      DSIII=0.00185
      DSV=0.000498
      DSIIIV=0.0152
      DCIII=-0.0024
      DCV=0.000592
      AXS=0.0
      BXS=0.0
```

```
 55     60 CONTINUE
 56 C
 57 C  BINARY ROOT FINDING ROUTINE FOR THE GROUP III AND V COMPOSITIONS
 58 C
 59        XV=0.5
 60        XMIN=0.0
 61        XMAX=1.0
 62        R=0.0019872
 63        THETA1=T
 64        XOLD=0.4
 65        THTOLD=THETA2(XOLD)
 66        DO 100 I=1,50
 67        THET2=THETA2(XV)
 68        ERR=(THET2-THETA1)/THETA1
 69        IF(ABS(ERR).LT.0.0001) GO TO 200
 70        SWTCH=(THET2-THTOLD)/(XV-XOLD)
 71        THTOLD=THET2
 72        XOLD=XV
 73        IF(SWTCH.GT.0.AND.THET2.LT.THETA1) GO TO 80
 74        IF(SWTCH.LT.0.AND.THET2.GT.THETA1) GO TO 80
 75        XMAX=XV
 76        XV=0.5*(XMIN+XV)
 77        GO TO 100
 78     80 XMIN=XV
 79        XV=0.5*(XMAX+XV)
 80    100 CONTINUE
 81        WRITE(IWRT,120)
 82    120 FORMAT('0','***** SUBROUTINE STEADY: ITERATION FOR SOURCE '.
 83       &       'COMPOSITION DID NOT CONVERGE')
 84    200 CONTINUE
 85 C
 86 C  CALCULATE THE STANDARD CHEMICAL POTENTIAL OF THE SOURCE SOLUTION
 87 C
 88        DGA=(1.0-XV)*(DSIII*(TMIII-T)+DCIII*(T-TMIII-T*ALOG(T/TMIII)))
 89        DGB=XV*(DSV*(TMV-T)+DCV*(T-TMV-T*ALOG(T/TMV)))
 90        DGC=(AXS+BXS*T)*XV*(1.-XV)+R*T*(XV*ALOG(XV)+(1.-XV)*ALOG(1.-XV))
 91        STOCP(VSC)=DGA+DGB+DGC
 92 C
 93 C  LOCATE THE GROUP III AND V ELEMENTS IN THE ELEMENTAL ABUNDANCE ARRAY
 94 C  AND INSERT THE CALCUALATED ABUNDANCES INTO THIS ARRAY
 95 C
 96        IDX3=0
 97        IDX5=0
 98        DO 300 I=1,IDIM2
 99        IF(ISS.EQ.2) GO TO 250
100        IF(ELMNT(I).EQ.GA) IDX3=I
101        IF(ELMNT(I).EQ.AS) IDX5=I
102        GO TO 300
103    250 IF(ELMNT(I).EQ.IN) IDX3=I
104        IF(ELMNT(I).EQ.P) IDX5=I
105    300 CONTINUE
106        A(VSC,IDX3)=1.0-XV
107        A(VSC,IDX5)=XV
108        XIII=1.0-XV
109        RETURN
110        END
```

Figure A8

Flowsheet for Subroutine IDPTEQ

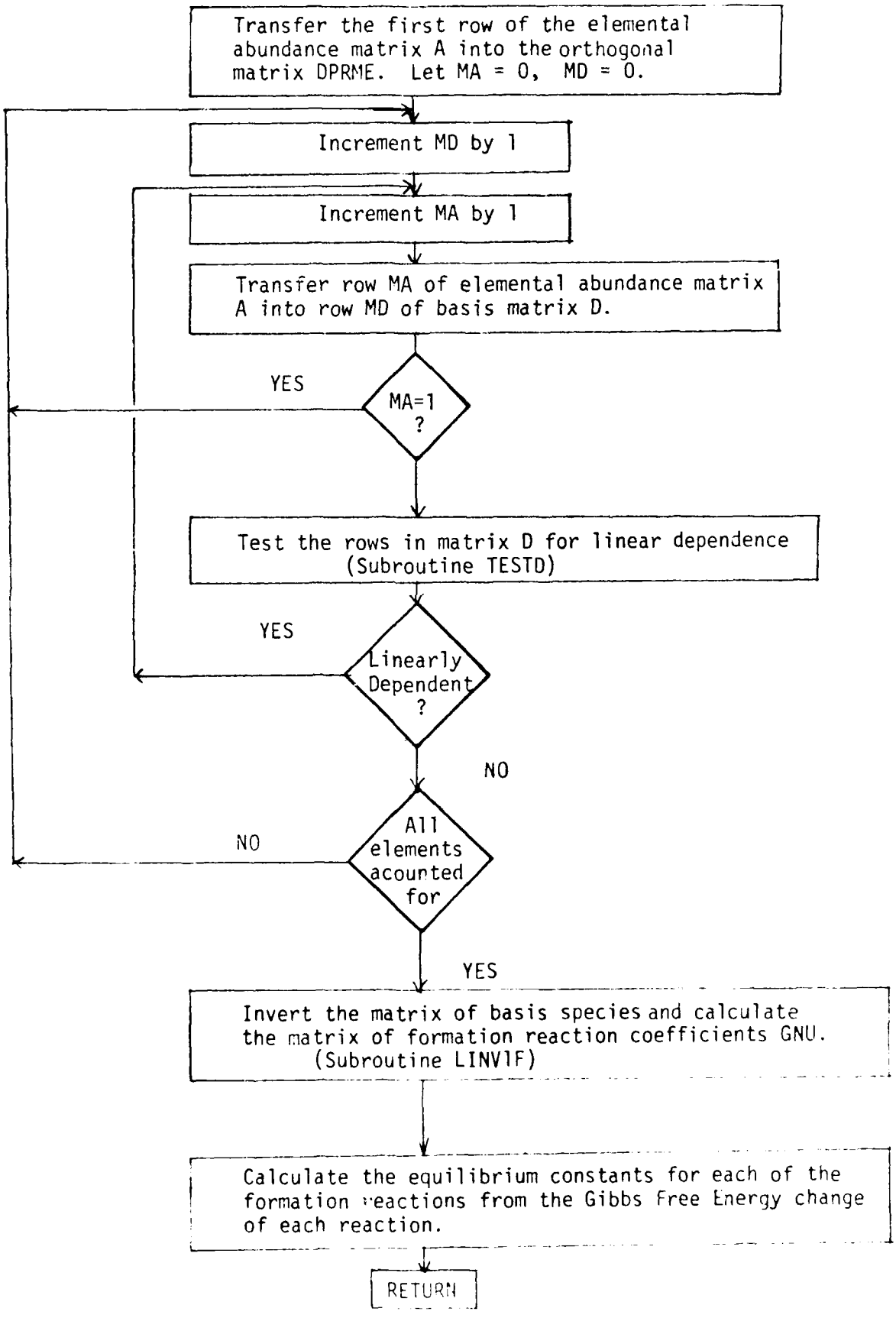


Figure A9. Subroutine IDPTEQ

```
      SUBROUTINE IDPTEQ(A,D,DPRME,DINV,STDCP,GNU,IDXBAS,KEQ,WKA,DG,
     &                  RT,IDIM1,IDIM2,V,S,C,E,IWRT)
C
C  THIS SUBROUTINE DETERMINES A SET OF LINEARLY INDEPENDENT REACTION EQ
C  AND CALCULATES THE EQUILIBRIUM CONSTANTS FOR THESE REACTIONS FROM TH
C  GIBBS FREE ENERGY CHANGE OF EACH REACTION.
C
      DOUBLE PRECISION D,DPRME,DINV,WKA
      DIMENSION D(IDIM2,IDIM2),DPRME(IDIM2,IDIM2),DINV(IDIM2,IDIM2),
     & WKA(IDIM2),IDXBAS(IDIM2),STDCP(IDIM1),DG(IDIM1),GNU(IDIM1,IDIM2)
     & A(IDIM1,IDIM2)
      REAL KEQ(IDIM1)
      INTEGER V,S,C,E,VSC
      VSC=V+S+C
C
C  BUILD THE D MATRIX WHICH WILL CONTAIN THE LINEARLY INDEPENDENT BASIS
C
      DO 100 J=1,E
      DPRME(1,J)=A(1,J)
  100 CONTINUE
      MA=0
      DO 200 MD=1,E
  140 MA=MA+1
      IF(MA.GT.VSC) GO TO 250
      DO 150 J=1,E
      D(MD,J)=A(MA,J)
  150 CONTINUE
      IDXBAS(MD)=MA
      IF(MD.EQ.1) GO TO 200
      CALL TESTD(D,DPRME,MD,E,IDIM2,ITST)
      IF(ITST.EQ.0) GO TO 140
  200 CONTINUE
      GO TO 280
  250 WRITE(IWRT,260)
  260 FORMAT('0','***** A COMPLETE SET OF BASIS SPECIES COULD NOT BE ',
     &       'FOUND IN SUBROUTINE IDPTEQ')
  280 CONTINUE
C
C  INVERT MATRIX D USING IMSL SUBROUTINE LINVIF
C  AND CALCULATE THE REACTION COEFFICIENT MATRIX GNU
C
      IDGT=4
      CALL LINV1F(D,E,IDIM2,DINV,IDGT,WKA,IER)
      IF(IER.EQ.34) WRITE(IWRT,310) IDGT
  310 FORMAT('0','***** ACCURACY TEST FAILED DURING MATRIX INVERSION ',
     &       'IN SUBROUTINE IDPTEQ.... IDGT=',I2)
      IF(IER.EQ.129) WRITE(IWRT,320)
  320 FORMAT('0','***** MATRIX D IS SINGULAR IN SUBROUTINE IDPTEQ')
      DO 400 I=1,VSC
      DO 400 J=1,E
      TEMP=0.0
      DO 350 JJ=1,E
      TEMP=TEMP+A(I,JJ)*DINV(JJ,J)
  350 CONTINUE
```

```
55          GNU(I,J)=TEMP
56      400 CONTINUE
57  C
58  C   CALCULATE THE EQUILIBRIUM CONSTANTS FOR THE FORMATION REACTIONS
59  C
60          DO 500 I=1,VSC
61          ARG=(-1.0)*STDCP(I)
62          DO 450 K=1,E
63          IDXB=IDXBAS(K)
64          ARG=ARG+GNU(I,K)*STDCP(IDXB)
65      450 CONTINUE
66          DG(I)=(-1.0)*ARG
67          ARG=ARG/RT
68          KEQ(I)=EXP(ARG)
69      500 CONTINUE
70          RETURN
71          END
```

The equilibrium constants for each reaction are then calculated in lines 58 through 70 by

$$K_{eqi} = EXP\left[\left(\sum_{j=1}^{E} \nu_{ij} \mu_j^\circ - \mu_i^\circ \right) / RT \right] \qquad (2)$$

Where μ_j° is the standard chemical potential of basis specie j and ν_{ij} is the stoichiometric coefficient of basis specie j in formation reaction i.

A.4.5 TESTD

Subroutine TESTD tests the rows of the D matrix for linear independence by building a Gram-Schmidt orthogonalized matrix DPRME from D. The Gram-Schmidt orthogonalization procedure essentially subtracts away the projection of all the rows in the matrix which are above the row being orthogonalized. If the resulting orthogonalized row is composed of all zeros then this row was linearly dependent upon at least one of the above rows in the matrix. The equations used to construct matrix DPRME from matrix D are [7]:

$$d'_{1j} = d_{1j} \qquad (1)$$

$$d'_{ij} = d_{ij} - \sum_{\ell=1}^{i-1} d'_{\ell j} \left[\frac{\sum_{k=1}^{E} d_{ik} d'_{\ell k}}{\sum_{k=1}^{E} (d'_{\ell k})^2} \right] \qquad (2)$$

Where: $i=2,3,.....m_d$ = row index

$j = 1, 2,... E$ = column index

m_d = current row index in matrix D

E = total # of elements in the system

d'_{ij}, d_{ij} are matrix elements in DPRME and D respectively.

A listing of TESTD is provided in Figure A10.

A.4.6 ADDRMV

During the iterative calculation to determine chemical equilibrium it is possible that pure condensed phases may be entirely consumed. This situation will cause an entire row in matrix ALEQ (subroutine RAND) to fill with zeros and therefore this matrix becomes singular. In order to allow the iterations to continue these zero composition pure condensed phases must be removed from the calculation and the ALEQ matrix is then reconstructed without them. As the calculation proceeds it is necessary to test the zero composition pure condensed phases at each iteration to see if they should be reinstated since the disappearance of a phase may be only a temporary occurance as a result of the path taken to reach equilibrium. Phases with negative incremental values of Gibbs Free Energy are reinserted into the calculation since their presence lowers the Gibbs Free Energy of the entire system.

A listing of subroutine ADDRMV is shown in Figure A11. Lines 14 through 27 set to zero the composition of any pure condensed phase which has less than one molecule present. An incremental Gibbs Free Energy is calculated for each of the zero composition pure condensed phases at lines 28 through 32. The incremental Gibbs Free Energy, DGTST(I), is given by [8].

$$DGTST_i = \mu_i^\circ - \sum_{j=1}^{E} a_{ij}\,\pi_j \qquad (1)$$

Where π_j is a Lagrange multiplier determined from the solution of the matrix problem in subroutine RAND, a_{ij} is defined in section A.5 and E is the number of elements in the system.

Figure A10. Subroutine TESTD

```
      SUBROUTINE TESTD(D,DPRME,MD,E,IDIM2,ITST)
C
C  THIS SUBROUTINE TESTS THE D MATRIX FOR LINEAR DEPENDENCE
C  USING A GRAM-SCHMIDT ORTHOGONALIZATION ALGORITHUM
C
      DOUBLE PRECISION D,DPRME,ANUM,DENOM
      DIMENSION D(IDIM2,IDIM2),DPRME(IDIM2,IDIM2)
      INTEGER E
      ITST=0
      DO 100 J=1,E
      DPRME(MD,J)=D(MD,J)
  100 CONTINUE
      MDM1=MD-1
      DO 400 L=1,MDM1
      DENOM=0.0
      ANUM=0.0
      DO 200 K=1,E
      ANUM=ANUM+D(MD,K)*DPRME(L,K)
      DENOM=DENOM+DPRME(L,K)**2
  200 CONTINUE
      DO 300 J=1,E
      DPRME(MD,J)=DPRME(MD,J)-DPRME(L,J)*ANUM/DENOM
  300 CONTINUE
  400 CONTINUE
      DO 500 J=1,E
      IF(DABS(DPRME(MD,J)).GT.1.0E-5) ITST=ITST+1
  500 CONTINUE
      RETURN
      END
```

Figure A11. Subroutine ADDRMV

```
      SUBROUTINE ADDRMV(A,N,DGTST,STDCP,BLEQ,SPECIE,DELN,VPSP1,
     &                  VSC,E,C,EPCP2,IOUT,IDIM1,IDIM2,IDIM3)
C
C  SUBROUTINE TO ADD OR REMOVE PURE CONDENSED PHASES
C  IN THE EQUILIBRIUM CALCULATION BASED ON THE INCREMENTAL
C  GIBBS FREE ENERGY OF THESE PHASES
C
      DOUBLE PRECISION BLEQ(IDIM3)
      DIMENSION A(IDIM1,IDIM2),DELN(IDIM1),DGTST(IDIM1),STDCP(IDIM1)
      REAL N(IDIM1)
      INTEGER SPECIE(IDIM1,3),VPSP1,VSC,E,EPCP2,C
      INDEX=0
      IOUT=0
C
C  ZERO THE COMPOSITION OF ANY PURE CONDENSED PHASE WHICH CURRENTLY
C  HAS LESS THAN ONE MOLECULE (1.65E-24 G-MOLES) PRESENT.
C  DETERMINE THE INCREMENTAL CHANGE IN GIBBS FREE ENERGY
C  FOR EACH OF THESE ZERO COMPOSITION PURE CONDENSED PHASES
C
      DO 50 I=1,VSC
      DGTST(I)=0.
   50 CONTINUE
      IF(C.EQ.0) GO TO 500
      DO 200 I=VPSP1,VSC
      IF(N(I).GT.1.65E-24) GO TO 200
      IOUT=IOUT+1
      N(I)=0.0
      DELN(I)=0.0
      DGTST(I)=STDCP(I)
      DO 100 J=1,E
      DGTST(I)=DGTST(I)-A(I,J)*BLEQ(J)
  100 CONTINUE
      IF(DGTST(I).LT.0.0) INDEX=I
  200 CONTINUE
      IF(INDEX.EQ.0) GO TO 400
C
C  FIND THE ZERO COMPOSITION PURE CONDENSED PHASE WITH THE SMALLEST NEGA
C  INCREMENTAL GIBBS FREE ENERGY AND ADD ONE MOLECULE OF IT
C  INTO THE EQUILIBRIUM CALCULATION
C
      DGMIN=DGTST(INDEX)
      DO 300 I=VPSP1,VSC
      IF(N(I).GT.1.65E-24) GO TO 300
      IF(DGTST(I).GT.0.0.OR.DGTST(I).LT.DGMIN) GO TO 300
      INDEX=I
      DGMIN=DGTST(I)
  300 CONTINUE
      N(INDEX)=1.66E-24
      IOUT=IOUT-1
  400 CONTINUE
C
C  REMOVE PURE CONDENSED PHASES WITH ZERO COMPOSITION
C  AND SHIFT NONZERO PURE CONDENSED PHASES UP IN THE ARRAYS
C
```

```
      DO 500 I=VPSP1,VSC
      IF(N(I).GT.1.65E-24) GO TO 500
      IP1=I+1
      IF(IP1.GT.VSC) IP1=VSC
      DO 450 IJ=IP1,VSC
      IF(N(IJ).LT.1.65E-24) GO TO 450
      TMPVAR=N(I)
      N(I)=N(IJ)
      N(IJ)=TMPVAR
      TMPVAR=STDCP(I)
      STDCP(I)=STDCP(IJ)
      STDCP(IJ)=TMPVAR
      TMPVAR=DELN(I)
      DELN(I)=DELN(IJ)
      DELN(IJ)=TMPVAR
      DO 420 J=1,E
      TMPVAR=A(I,J)
      A(I,J)=A(IJ,J)
      A(IJ,J)=TMPVAR
  420 CONTINUE
      DO 430 K=1,3
      ITMPV=SPECIE(I,K)
      SPECIE(I,K)=SPECIE(IJ,K)
      SPECIE(IJ,K)=ITMPV
  430 CONTINUE
      GO TO 500
  450 CONTINUE
  500 CONTINUE
      C=C-IOUT
      VSC=VSC-IOUT
      EPCP2=EPCP2-IOUT
      RETURN
      END
```

The zero composition pure condensed phase which has the smallest negative incremental Gibbs Free Energy is determined in lines 36 through 50 and one molecule of it is inserted into the calculation. This treatment allows pure condensed phases to be reinserted in the calculation while minimizing any perturbation between iterations.

Lines 51 through 85 reformulate the equilibrium problem without the zero composition pure condensed phases by eliminating these phases from matrix ALEQ. The elimination is achieved by shifting the data in these phases to the last positions in arrays A and SPECIE, and in vectors N, DELN, and STDCP. The value of C, VSC and EPCP2 are then reduced to reflect the number of phases which were removed.

A.4.7 ACTCOF

A listing of subroutine ACTCOF, which calculates the activity coefficients for each specie, is shown in Figure A12. Initially all of the activity coefficients are set to unity. The iteration process for the equilibrium composition proceeds under this assumption of an ideal system until RELMAX, the convergence test parameter, becomes less than 0.1. At this point three options become available for the solution phase. The first option (IXSCOR = 0) simply assumes an ideal solution phase. The second option (IXSCOR = 1) treats the solution phase using simple solution theory and is applicable to binary solutions only. The activity coefficient for specie i is given by:

$$\gamma_i = \exp\left[(A_{xs} + B_{xs}) \ (1-X_i)^2 \ / \ RT \right] \qquad (1)$$

The third option (IXSCOR = 2) allows the first specie in the solution phase to have an activity coefficient described by Henry's constant, H.

Figure A12. Subroutine ACTCOF

```
      SUBROUTINE ACTCOF(N,ACOEF,ZACT,IDIM1,IXSCOR,AXS,BXS,T,V,S,C,
     &                  IACFF,RELMAX)
C
C  SUBROUTINE TO CALCULATE ACTIVITY COEFFICIENTS FOR EACH COMPONENT
C
C  IXSCOR  ALGORITHUM
C       1  BINARY SIMPLE SOLUTION THEORY  GE=(AXS+BXS*T)*X1*X2
C       2  HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE  H=AXS*EXP(BXS
C
      DIMENSION ACOEF(IDIM1)
      REAL N(IDIM1),NS
      INTEGER V,S,C,VP1,VPS,VSC
      VP1=V+1
      VPS=V+S
      VSC=V+S+C
      ZACT=1.0
      DO 100 I=1,VSC
      ACOEF(I)=1.0
  100 CONTINUE
      IF(RELMAX.LT.0.1) IACFF=1
      IF(IXSCOR.EQ.2) IACFF=1
      IF(IXSCOR.LT.1.OR.IXSCOR.GT.2.OR.S.LE.1) IACFF=0
      IF(IACFF.EQ.0) GO TO 900
      RT=0.0019872*T
      NS=0.0
      DO 150 I=VP1,VPS
      NS=NS+N(I)
  150 CONTINUE
      IF(IXSCOR.EQ.2) GO TO 200
C
C  BINARY SIMPLE SOLUTION THEORY
C
      X1=N(VP1)/NS
      X2=1.0-X1
      ARG1=(AXS+BXS*T)*X2**2/RT
      ARG2=(AXS+BXS*T)*X1**2/RT
      ACOEF(VP1)=EXP(ARG1)
      ACOEF(VPS)=EXP(ARG2)
      GO TO 900
C
C  HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE
C
  200 ACOEF(VP1)=AXS*EXP(BXS/T)
  900 RETURN
      END
```

$$\gamma_{v+1} = H = A_{xs} \exp [B_{xs}/T] \quad (2)$$

The vapor phase is always assumed to be ideal.

A.4.8 RAND

Subroutine RAND, shown in Figure A13, calculates a step change in each specie composition using the Rand algorithm developed in section A.5. This subroutine is used to solve the set of linear equations described by equations 17, 21, 22 and 23 in section A.5. Details of the matrix formulation are shown in Figures A14 and A15.

Matrix ALEQ is filled in accordance with Figures A14 and A15 in lines 26 through 105. Lines 106 through 175 fill vector BLEQ. The matrix problem

$$ALEQ \cdot X = BLEQ \quad (1)$$

is then solved in line 182 using the double precision version of IMSL routine LEQT1F. Warning messages are written out from lines 183 to 193 if matrix ALEQ is algorithmically singular or if less than three significant figures are present in the solution vector. Parameter ISTOP is set to unity if matrix ALEQ is found to be algorithmically singular (IER = 129). The value of ISTOP is tested in the main program at line 369 and execution is halted if ISTOP = 1.

In order to save on storage space the solution vector X is actually returned in BLEQ. Lines 201 through 238 determine the δn_i values from the solution vector and assign them to their appropriate position in the DELN vector.

Figure A13. Subroutine RAND

```
      SUBROUTINE RAND(A,B,BK,N,DELN,STDCP,ALEQ,BLEQ,WKA,ACOEF,
     &                ZACT,V,S,C,E,VSC,EPCP2,IDIM1,IDIM2,IDIM3,ITER,PO,
     &                P,ZV,ISTOP,IWRT,IDEBUG,IWRAP)
C
C  RAND ALGORITHUM TO MINIMIZE THE GIBBS ENERGY OF A
C  MULTIPHASE, MULTICOMPONENT SYSTEM CONTAINING A VAPOR PHASE INERT
C
C  ****************************************************************
C  *  DOUBLE PRECISION IS USED TO EVALUATE THE MATRIX PROBLEM  *
C  ****************************************************************
C
      DOUBLE PRECISION ALEQ(IDIM3,IDIM3),BLEQ(IDIM3),WKA(IDIM3),
     &                 US,UV,TMPVAR
      DIMENSION A(IDIM1,IDIM2),B(IDIM2),BK(IDIM2),DELN(IDIM1),
     &          STDCP(IDIM1),ACOEF(IDIM1)
      INTEGER V,S,C,E,VSC,EPCP2,VPS,VP1,EP3,EP3PC,
     &        VPSP1
      REAL N(IDIM1),NV,NS
      ISTOP=0
      VPS=V+S
      VPSP1=V+S+1
      VP1=V+1
      EP3=E+3
      EP3PC=E+3+C
   50 CONTINUE
C
C  ZERO MATRIX ALEQ BEFORE ASSIGNING VALUES
C
      DO 100 I=1,EPCP2
      DO 100 J=1,EPCP2
      ALEQ(I,J)=0.
  100 CONTINUE
C
C  FILL THE UPPER E ROWS OF MATRIX ALEQ FROM EQUATION 21
C  THE FIRST E COLUMNS ARE THE LAGRANGE MULTIPLIER COEFFICIENTS
C
      DO 180 I=1,E
      DO 140 J=1,E
      TMPVAR=0.
      DO 130 K=1,VPS
      TMPVAR=TMPVAR+A(K,I)*A(K,J)*N(K)
  130 CONTINUE
      ALEQ(I,J)=TMPVAR
  140 CONTINUE
C
C  COLUMNS E+1 AND E+2 IN MATRIX ALEQ ARE THE
C  COEFFICIENTS FOR VARIABLES UV AND US RESPECTIVELY
C
      IEP1=E+1
      IEP2=E+2
      TMPVAR=0.
      DO 150 K=1,V
      TMPVAR=TMPVAR+A(K,I)*N(K)
  150 CONTINUE
```

```
      ALEQ(I,IEP1)=TMPVAR
      IF(S.EQ.0) GO TO 165
      TMPVAR=0.
      DO 160 K=VP1,VPS
      TMPVAR=TMPVAR+A(K,I)*N(K)
  160 CONTINUE
      ALEQ(I,IEP2)=TMPVAR
  165 CONTINUE
C
C  THE FINAL C COLUMNS OF ALEQ ARE FOR THE DELTA-N
C  COEFFICIENTS RELATING TO THE PURE CONDENSED PHASES
C
      IADD=2
      IF(S.EQ.0) IADD=1
      IF(C.EQ.0) GO TO 180
      DO 170 K=VPSP1,VSC
      INDEX=K-VPS+E+IADD
      ALEQ(I,INDEX)=A(K,I)
  170 CONTINUE
  180 CONTINUE
C
C  FILL THE NEXT TWO ROWS (ROWS E+1 AND E+2) OF MATRIX ALEQ
C  BASED ON EQUATIONS 22 AND 23
C
      DO 250 J=1,E
      TMPVAR=0.
      DO 230 K=1,V
      TMPVAR=TMPVAR+A(K,J)*N(K)
  230 CONTINUE
      ALEQ(IEP1,J)=TMPVAR
      IF(S.EQ.0) GO TO 250
      TMPVAR=0.
      DO 240 K=VP1,VPS
      TMPVAR=TMPVAR+A(K,J)*N(K)
  240 CONTINUE
      ALEQ(IEP2,J)=TMPVAR
  250 CONTINUE
      ALEQ(IEP1,IEP1)=(-1.0)*ZV
C
C  THESE FINAL C ROWS IN MATRIX ALEQ ARE FILLED BY EQUATION 17
C
      EP3=E+1+IADD
      EP3PC=EP3+C
      IF(C.EQ.0) GO TO 300
      INDEX=VPS
      DO 290 I=EP3,EP3PC
      INDEX=INDEX+1
      DO 290 J=1,E
      ALEQ(I,J)=A(INDEX,J)
  290 CONTINUE
  300 CONTINUE
C
C  CALCULATE BK, NV AND NS VALUES FROM THE PREVIOUS ESTIMATE OF N
C
```

```
      DO 360 J=1,E
      TMPVAR=0.
      DO 350 I=1,VSC
      TMPVAR=A(I,J)*N(I)+TMPVAR
  350 CONTINUE
      BK(J)=TMPVAR
  360 CONTINUE
      NV=ZV
      DO 365 I=1,V
      NV=NV+N(I)
  365 CONTINUE
      NS=0.
      IF(S.EQ.0) GO TO 375
      DO 370 I=VP1,VPS
      NS=NS+N(I)
  370 CONTINUE
  375 CONTINUE
C
C  NOW ASSIGN VALUES TO VECTOR BLEQ
C  THE FIRST E VALUES ARE FROM EQUATION 21
C
      DO 400 J=1,E
      TMPVAR=B(J)-BK(J)
      DO 380 I=1,V
      ARG=ACOEF(I)*N(I)*P/P0/NV
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      TMPVAR=TMPVAR+A(I,J)*N(I)*(STDCP(I)+ALOG(ARG))
  380 CONTINUE
      IF(S.EQ.0) GO TO 395
      DO 390 I=VP1,VPS
      ARG=ACOEF(I)*N(I)/NS
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      TMPVAR=TMPVAR+A(I,J)*N(I)*(STDCP(I)+ALOG(ARG))
  390 CONTINUE
  395 CONTINUE
      BLEQ(J)=TMPVAR
  400 CONTINUE
C
C  THE NEXT 2 POSITIONS IN VECTOR BLEQ (POSITIONS E+1 AND E+2)
C  ARE FROM EQUATIONS 22 AND 23
C
      TMPVAR=0.
      DO 410 I=1,V
      ARG=ACOEF(I)*N(I)*P/P0/NV
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      TMPVAR=TMPVAR+N(I)*(STDCP(I)+ALOG(ARG))
  410 CONTINUE
      BLEQ(IF1)=TMPVAR
      TMPVAR=0.
      IF(S.EQ.0) GO TO 425
      DO 420 I=VP1,VPS
      ARG=ACOEF(I)*N(I)/NS
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      TMPVAR=TMPVAR+N(I)*(STDCP(I)+ALOG(ARG))
```

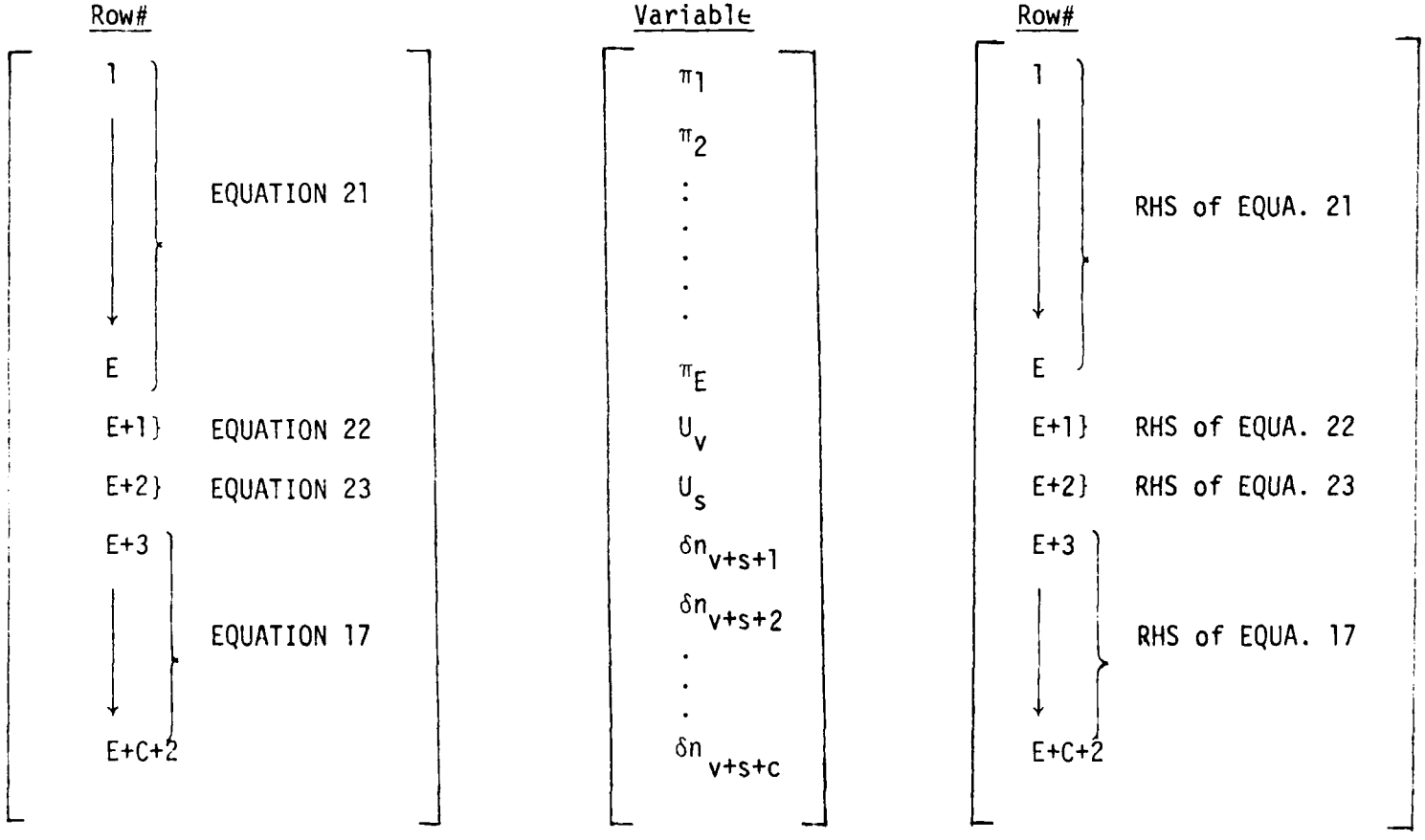
```
  420 CONTINUE
      BLEQ(IEP2)=TMPVAR
  425 CONTINUE
C
C  THE FINAL C POSITIONS OF VECTOR BLEQ ARE FROM EQUATION 17
C
      IF(C.EQ.0) GO TO 435
      INDEX=VPS
      DO 430 I=EP3,EP3PC
      INDEX=INDEX+1
      BLEQ(I)=STDCP(INDEX)
  430 CONTINUE
  435 CONTINUE
      IF(IDEBUG.EQ.2) CALL PRNTAB(ALEQ,BLEQ,EPCP2,IDIM3,IWRT)
C
C  SOLVE THE MATRIX PROBLEM USING SUBROUTINE LEQT1F
C
      M=1
      IDGT=3
      CALL LEQT1F(ALEQ,M,EPCP2,IDIM3,BLEQ,IDGT,WKA,IER)
      IF(IER.NE.34.AND.IER.NE.129) GO TO 490
      IF(ISTOP.EQ.1) GO TO 490
      WRITE(IWRT,438) ITER
  438 FORMAT('0','***** ITERATION ',I5,'  *****')
      IF(IER.EQ.34.AND.IWRAP.LT.2) WRITE(IWRT,440) IER,IDGT
  440 FORMAT(1X,'***** ACCURACY TEST IN SUBROUTINE LEQT1F',
     &       ' FAILED..... IER=',I3,'  IDGT=',I2,' *****',
     &       /,1X,' ')
      IF(IER.EQ.129) WRITE(IWRT,450) IER
  450 FORMAT(1X,'***** MATRIX ALEQ IN SUBROUTINE RAND IS SINGULAR',
     &       ' IER = ',I3,'   ****')
      IF(IER.EQ.129) ISTOP=1
      IDBG=IDEBUG
      IF(IER.EQ.129) IDEBUG=2
      IF(IDBG.LT.2.AND.IER.EQ.129) GO TO 50
  490 CONTINUE
      IF(IDEBUG.EQ.2) WRITE(IWRT,495) (BLEQ(K),K=1,EPCP2)
  495 FORMAT('0','THE TRANSPOSED X VECTOR IS:',/,1X,10(D11.4,2X))
C
C  FILL THE DELN VECTOR FROM BLEQ USING EQUATIONS 19 AND 20
C  THE FIRST E VALUES IN BLEQ ARE NOW THE LAGRANGE MULTIPLIERS;
C  THE NEXT 2 VALUES ARE UV AND US RESPECTIVELY;
C  THE LAST C VALUES ARE THE DELN VALUES FOR THE PURE CONDENSED PHASES
C
      UV=BLEQ(IEP1)
      DO 510 I=1,V
      ARG=ACOEF(I)*N(I)*P/P0/NV
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      TMPVAR=UV-STDCP(I)-ALOG(ARG)
      DO 500 J=1,E
      TMPVAR=TMPVAR+BLEQ(J)*A(I,J)
  500 CONTINUE
      DELN(I)=TMPVAR*N(I)
  510 CONTINUE
```

```
      IF(S.EQ.0) GO TO 535
      US=BLEQ(IEP2)
      DO 530 I=VP1,VPS
      ARG=ACOEF(I)*N(I)/NS
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      TMPVAR=US-STDCP(I)-ALOG(ARG)
      DO 520 J=1,E
      TMPVAR=TMPVAR+BLEQ(J)*A(I,J)
  520 CONTINUE
      DELN(I)=TMPVAR*N(I)
  530 CONTINUE
  535 CONTINUE
C
C  THE FINAL C DELN VALUES ARE THE LAST C VALUES OF BLEQ
C
      IF(C.EQ.0) GO TO 550
      INDEX=E+IADD
      DO 540 I=VPSP1,VSC
      INDEX=INDEX+1
      DELN(I)=BLEQ(INDEX)
  540 CONTINUE
  550 CONTINUE
      RETURN
      END
```

Figure A14

OVERVIEW OF MATRIX FORMULATION

(Equation numbers refer to section A.5)



(Note: RHS = Right Hand Side)

Figure A15

Detailed MATRIX FORMULATION of Linear Equations

SOLVE: $\underline{ALEQ}.\underline{X} = \underline{BLEQ}$ for $\underline{X}$

$$X = \begin{bmatrix} \pi_1 \\ \pi_2 \\ \vdots \\ \pi_E \\ U_v \\ U_s \\ \delta n_{v+s+1} \\ \delta n_{v+s+2} \\ \vdots \\ \delta n_{v+s+c} \end{bmatrix}$$

$$BLEQ = \begin{bmatrix} b_1 - b_1^k + \sum_{i=1}^{v} a_{ii}\, n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i P}{n_v P_o} \right) \right] + \sum_{i=v+1}^{v+s} a_{ii}\, n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i}{n_s} \right) \right] \\ \vdots \\ b_E - b_E^k + \sum_{i=1}^{v} a_{iE} n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i P}{n_v P_o} \right) \right] + \sum_{i=v+1}^{v+s} a_{iE}\, n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i}{n_s} \right) \right] \\ \sum_{i=1}^{v} n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i P}{n_v P_o} \right) \right] \\ \sum_{i=v+1}^{v+s} n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i}{n_s} \right) \right] \\ \mu_{v+s+1}^\circ \\ \mu_{v+s+2}^\circ \\ \vdots \\ \mu_{v+s+c}^\circ \end{bmatrix}$$

$$
\begin{bmatrix}
\sum_{i=1}^{v+s} a_{i1}a_{i1}n_i & \sum_{i=1}^{v+s} a_{i1}a_{i2}n_i & \cdots & \sum_{i=1}^{v+s} a_{i1}a_{iE}n_i & \sum_{i=1}^{v} a_{i1}n_i & \sum_{i=v+1}^{v+s} a_{i1}n_i & a_{v+s+1,1} & \cdots & a_{v+s+c,1} \\
\vdots & & & & & & & & \\
\sum_{i=1}^{v+s} a_{iE}a_{i1}n_i & \sum_{i=1}^{v+s} a_{iE}a_{i2}n_i & \cdots & \sum_{i=1}^{v+1} a_{iE}a_{iE}n_i & \sum_{i=1}^{v} a_{iE}n_i & \sum_{i=v+1}^{v+s} a_{iE}n_i & a_{v+s+1,E} & \cdots & a_{v+s+c,E} \\
\sum_{i=1}^{v} a_{i1}n_i & \sum_{i=1}^{v} a_{i2}n_i & \cdots & \sum_{i=1}^{v} a_{iE}n_i & -Z_v & 0 & 0 & \cdots & 0 \\
\sum_{i=v+1}^{v+s} a_{i1}n_i & \sum_{i=v+1}^{v+s} a_{i2}n_i & \cdots & \sum_{i=v+1}^{v+s} a_{iE}n_i & 0 & 0 & 0 & \cdots & 0 \\
a_{v+s+1,1} & a_{v+s+1,2} & \cdots & a_{v+s+1,E} & 0 & 0 & 0 & \cdots & 0 \\
\vdots & & & & & & & & \\
a_{v+s+c,1} & a_{v+s+c,2} & \cdots & a_{v+s+c,E} & 0 & 0 & 0 & \cdots & 0
\end{bmatrix}
$$

MATRIX ALEQ

A.4.9 CNVFRC and DGDLAM

Subroutine CNVFRC calculates the convergence forcer for the iterative solution and is shown in Figure A16. The convergence forcer is used when the composition estimate is updated during each iteration according to the formula:

$$n_i' = n_i + \lambda\, \delta n_i \qquad (1)$$

Where: n_i' = updated estimate to the equlibrium, composition

n_i = previous estimate of equilibrium, composition

δn_i = step change in composition as calculated in subroutine RAND

λ = convergence forcer

The convergence forcer is also used to prevent negative compositions from appearing. Lines 13 through 22 determine the maximum value of the convergence forcer which will yield positive values for all of the specie molar amounts with the constraint that the convergence forcer must be between zero and one. If parameter IALG is zero this maximum value yielding positive compositions is used for the convergence forcer. If IALG is unity, an optimum value is calculated in lines 29 through 39 using the method of Smith and Missen [9]. This method entails the evaluation of $dG/d\lambda$ at the maximum and minimum allowable values of λ where G is the system Gibbs Free Energy. An estimate to the optimum value of the convergence forcer is then obtained by

$$\lambda \approx \frac{\left(\frac{dG}{d\lambda}\right)_{\lambda=0}}{\left(\frac{dG}{d\lambda}\right)_{\lambda=0} - \left(\frac{dG}{d\lambda}\right)_{\lambda=MAX}} \qquad (2)$$

Figure A16. Subroutine CNVFRC and Function DGDLAM

```
      SUBROUTINE CNVFRC(STDCP,N,DELN,ACOEF,V,S,C,IDIM1,IALG,ZV,
     &                  P,P0,RT,LAMBDA,ITER,IWRT)
C
C  THIS SUBROUTINE CALCULATES THE CONVERGENCE FORCER
C  FOR THE CURRENT ITERATION
C
      DIMENSION STDCP(IDIM1),ACOEF(IDIM1),DELN(IDIM1)
      REAL N(IDIM1),LAMBDA
      INTEGER V,S,C,VSC
      VSC=V+S+C
      AMIN=0.
      AMAX=1.
C
C  LIMIT THE MAXIMUM VALUE OF THE CONVERGENCE FORCER
C  BY APPLYING THE CONSTRAINT OF NON-NEGATIVE COMPOSITION
C
      DO 50 I=1,VSC
      IF(ABS(DELN(I)).LT.1.0E-50) GO TO 50
      LAMBDA=(-1.0)*N(I)/DELN(I)
      IF(LAMBDA.GT.0.0.AND.LAMBDA.LT.AMAX) AMAX=LAMBDA
   50 CONTINUE
      LAMBDA=AMAX
C
C  IF IALG=0 OR ATEST IS SMALL THE MAXIMUM RELAXATION PARAMETER IS USED
C
      IF(IALG.EQ.0) RETURN
      ATEST=AMAX-AMIN
      IF(ATEST.LT.0.01) RETURN
C
C  ESTIMATE THE OPTIMUM VALUE OF THE CONVERGENCE FORCER
C
      DGDMAX=DGDLAM(N,DELN,STDCP,ACOEF,ZV,P,P0,RT,AMAX,
     &              IDIM1,V,S,C)
      DGDMIN=DGDLAM(N,DELN,STDCP,ACOEF,ZV,P,P0,RT,AMIN,
     &              IDIM1,V,S,C)
      IF(DGDMIN.EQ.DGDMAX) DGDMAX=0.0
      LAMBDA=DGDMIN/(DGDMIN-DGDMAX)
      IF(LAMBDA.GT.AMAX) LAMBDA=AMAX
      IF(LAMBDA.LT.AMIN) LAMBDA=0.05
      RETURN
      END
      FUNCTION DGDLAM(N,DELN,STDCP,ACOEF,ZV,P,P0,RT,ALAM,
     &                IDIM1,V,S,C)
C
C  EVALUATION OF DG/DLAMBDA FOR DETERMINING THE CONVERGENCE FORCER
C
      DIMENSION ACOEF(IDIM1),DELN(IDIM1),STDCP(IDIM1)
      REAL N(IDIM1),NV,NS
      INTEGER V,S,C,VP1,VPS,VSC,VS1
      VP1=V+1
      VPS=V+S
      VS1=VPS+1
      VSC=VPS+C
      NV=ZV
```

```
      DO 100 I=1,V
      NV=NV+N(I)
  100 CONTINUE
      IF(S.EQ.0) GO TO 210
      NS=0.0
      DO 200 I=VP1,VPS
      NS=NS+N(I)
  200 CONTINUE
  210 CONTINUE
C
C  CALCULATE DG/DLAMBDA
C
      DGDL=0.0
      DO 300 I=1,VPS
      ARG=ACOEF(I)*(N(I)+ALAM*DELN(I))*P/P0/NV
      IF(I.GT.V) ARG=ACOEF(I)*(N(I)+ALAM*DELN(I))/NS
      DGDL=DGDL+DELN(I)*(STDCP(I)+ALOG(ARG))
  300 CONTINUE
      IF(C.EQ.0) GO TO 410
      DO 400 I=VS1,VSC
      DGDL=DGDL+DELN(I)*STDCP(I)
  400 CONTINUE
  410 DGDLAM=DGDL*RT
      RETURN
      END
```

This equation is essentially a single iteration of a Regula-Falsi root finding algorithm and yields a sufficiently close approximation to the optimum value of λ. The value of λ chosen is further constrained to be between 0.05 and the maximum value which yields positive molar amounts. The lower limit of 0.05 allows the iterative process to continue when zero or negative values for the convergence forcer are predicted.

The derivatives are calculated in function subroutine DGDLAM shown in lines 42 through 79 and are given by

$$\frac{dG}{d\lambda} = RT \left\{ \sum_{i=1}^{v} \delta n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i' P}{P_o n_v} \right) \right] + \sum_{i=v+1}^{v+s} \delta n_i \left[\mu_i^\circ + \ell n \left(\frac{n_i'}{n_s} \right) \right] + \sum_{i=v+s+1}^{v+s+c} \delta n_i \mu_i^\circ \right\} \qquad (3)$$

A.4.10 RESTOR

Subroutine RESTOR, shown in Figure A17, restores the arrays and vectors which were shifted in subroutine ADDRMV to the original order in the problem formulation. This is accomplished by comparing array SPECIE, which has the shifted order of the species, to array ISPCE, which contains the original specie order. The data in the arrays and vectors are then shifted to reflect the original specie order. The constants C, VSC and EPCP2 are also restored to their original values.

A.4.11 GIBBS

Subroutine GIBBS, shown in Figure A13, calculates the system Gibbs Free Energy using equation 1 in section A.5. This subroutine is called after the iteration for equilibrium has terminated and also during debugging (IDEBUG > 1).

Figure A17. Subroutine RESTOR

```
      SUBROUTINE RESTOR(A,SPECIE,ISPCE,STDCP,N,DELN,IDIM1,IDIM2,
     &                  VSC,EPCP2,C,VPSP1,E,IOUT)
C
C  THIS SUBROUTINE RESTORES MATRICIES AND VECTORS A, SPECIE, STDCP,
C  N AND DELN ALONG WITH CONSTANTS VSC, C AND EPCP2 TO THEIR ORIGINAL
C  ORDER AND VALUES IN THE INITIAL PROBLEM FORMULATION
C
      DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1),DELN(IDIM1),ISPCE(IDIM1,3)
      INTEGER SPECIE(IDIM1,3),VSC,E,EPCP2,C,VPSP1,VSCM1
      REAL N(IDIM1)
      IF(IOUT.EQ.0) GO TO 400
      EPCP2=EPCP2+IOUT
      C=C+IOUT
      VSC=VSC+IOUT
      VSCM1=VSC-1
C
C  DO A CHARACTER STRING COMPARISON OF SPECIE WITH ISPCE AND PUT
C  THE ARRAYS AND VECTORS INTO THEIR ORIGINAL ORDERS
C
      DO 300 I=VPSP1,VSCM1
      IP1=I+1
      IF(IP1.GT.VSC) IP1=VSC
      DO 200 II=IP1,VSC
      IF(ISPCE(I,1).EQ.SPECIE(II,1).AND.
     &   ISPCE(I,2).EQ.SPECIE(II,2).AND.
     &   ISPCE(I,3).EQ.SPECIE(II,3)) GO TO 50
      GO TO 200
   50 TEMP=N(I)
      N(I)=N(II)
      N(II)=TEMP
      TEMP=STDCP(I)
      STDCP(I)=STDCP(II)
      STDCP(II)=TEMP
      TEMP=DELN(I)
      DELN(I)=DELN(II)
      DELN(II)=TEMP
      DO 100 J=1,E
      TEMP=A(I,J)
      A(I,J)=A(II,J)
      A(II,J)=TEMP
  100 CONTINUE
      DO 120 K=1,3
      ITEMP=SPECIE(I,K)
      SPECIE(I,K)=SPECIE(II,K)
      SPECIE(II,K)=ITEMP
  120 CONTINUE
      GO TO 300
  200 CONTINUE
  300 CONTINUE
  400 RETURN
      END
```

Figure A18. Subroutine GIBBS

```
      SUBROUTINE GIBBS(N,STDCP,STDCPZ,ACOEF,ZACT,ZV,T,P,P0,IDIM1,
     &                 V,S,C,GFE)
C
C  SUBROUTINE TO CALCULATE THE GIBBS FREE ENERGY OF THE SYSTEM
C  USING EQUATION 1 IN THE PROPOSAL
C
      DIMENSION STDCP(IDIM1),ACOEF(IDIM1)
      REAL N(IDIM1),NV,NS
      INTEGER V,S,C,VP1,VPS,VS1,VSC
      VP1=V+1
      VPS=V+S
      VS1=VPS+1
      VSC=VPS+C
C
C  GAS CONSTANT IS IN UNITS OF: KCAL/G-MOLE-K
C
      R=0.0019872
      NV=ZV
      DO 100 I=1,V
      NV=NV+N(I)
  100 CONTINUE
      NS=0.
      IF(S.EQ.0) GO TO 120
      DO 110 I=VP1,VPS
      NS=NS+N(I)
  110 CONTINUE
  120 CONTINUE
      ARG=ZACT*ZV*P/P0/NV
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      GSTAR=ZV*(STDCPZ+ALOG(ARG))
      DO 150 I=1,V
      ARG=ACOEF(I)*N(I)*P/P0/NV
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      GSTAR=GSTAR+N(I)*(STDCP(I)+ALOG(ARG))
  150 CONTINUE
      IF(S.EQ.0) GO TO 170
      DO 160 I=VP1,VPS
      ARG=ACOEF(I)*N(I)*P/P0/NS
      IF(ARG.LE.1.0E-50) ARG=1.0E-50
      GSTAR=GSTAR+N(I)*(STDCP(I)+ALOG(ARG))
  160 CONTINUE
  170 CONTINUE
      IF(C.EQ.0) GO TO 190
      DO 180 I=VS1,VSC
      GSTAR=GSTAR+N(I)*STDCP(I)
  180 CONTINUE
  190 CONTINUE
      GFE=GSTAR*R*T
      RETURN
      END
```

A.4.12 CALCQ

A listing of CALCQ is shown in Figure A19. This subroutine calculates the equilibrium constants for each of the independent formation reactions based on the composition of the system. These equilibrium constants are given by:

$$Q_i = \gamma_i X_i P_{poi} \Big/ \prod_{k=1}^{E} (\gamma_k X_k P_{po_k})^{\nu_{ik}} \qquad (1)$$

Where:

γ_i = activity coefficient of specie i

X_i = mole fraction of specie i in its phase

ν_j = stoichiometric reaction coefficient

$$P_{poi} = \begin{cases} 1 \text{ for solution or pure condensed phase} \\ P/P_o \text{ for vapor phase} \end{cases}$$

The product in the denominator is taken over the basis species used in the formation reaction equations.

A.4.13 TOTSI

Subroutine TOTSI, shown in Figure A20 calculates the total moles and mole fraction of silicon species in the vapor phase. A character string comparison is made to determine which member of vector ELMNT is assigned the string 'SI'. Then the moles of all vapor species with a nonzero value in their elemental abundance vector corresponding to this position are summed.

A.4.14 RATIO

Subroutine RATIO, shown in Figure A21 calculates the group III/V atom ratio in the vapor phase. All of the elements in columns III and V

Figure A19. Subroutine CALCQ

```
      SUBROUTINE CALCQ(GNU,N,ACOEF,FRAC,IDXBAS,Q,
     &                 P,P0,V,S,C,E,IDIM1,IDIM2)
C
C  SUBROUTINE TO CALCULATE EQUILIBRIUM CONSTANTS FROM COMPOSITION
C
      DIMENSION GNU(IDIM1,IDIM2),ACOEF(IDIM1),FRAC(IDIM1),
     &          IDXBAS(IDIM2),Q(IDIM1)
      INTEGER V,S,C,E,VSC
      REAL N(IDIM1)
      VSC=V+S+C
C
C  CALCULATE THE EQUILIBRIUM CONSTANTS
C
      DO 400 I=1,VSC
      PP0=1.0
      IF(I.LE.V) PP0=P/P0
      Q(I)=ACOEF(I)*FRAC(I)*PP0
      DO 300 J=1,E
      K=IDXBAS(J)
      PP0=1.0
      IF(K.LE.V) PP0=P/P0
      Q(I)=Q(I)/(ACOEF(K)*FRAC(K)*PP0)**GNU(I,J)
  300 CONTINUE
  400 CONTINUE
      RETURN
      END
```

Figure A20. Subroutine TOTSI

```
      SUBROUTINE TOTSI(A,ELMNT,FRAC,N,SITOT,SIMF,IDIM1,IDIM2,V,E)
C
C  SUBROUTINE TO CALCULATE THE TOTAL SI IN THE VAPOR PHASE
C
      DIMENSION A(IDIM1,IDIM2),FRAC(IDIM1)
      INTEGER ELMNT(IDIM2),V,E,SIVPR/'SI'/
      REAL N(IDIM1)
      SITOT=0.0
      SIMF=0.0
      DO 100 J=1,E
      KSI=J
      IF(ELMNT(J).EQ.SIVPR) GO TO 130
  100 CONTINUE
      GO TO 150
  130 CONTINUE
      DO 140 I=1,V
      IF(A(I,KSI).LT.0.001) GO TO 140
      SITOT=SITOT+N(I)
      SIMF=SIMF+FRAC(I)
  140 CONTINUE
  150 CONTINUE
      RETURN
      END
```

Figure A21. Subroutine RATIO

```
      SUBROUTINE RATIO(A,ELMNT,FRAC,RIIIV,IDIM1,IDIM2,V,E)
C
C  THIS SUBROUTINE CALCULATES THE VAPOR III/V RATIO
C
      DIMENSION A(IDIM1,IDIM2),FRAC(IDIM1),KIII(5),KV(5)
      INTEGER ELMNT(IDIM2),ELIII(5),ELV(5),V,E
      DATA ELIII(1)/' B'/,ELIII(2)/'AL'/,ELIII(3)/'GA'/,ELIII(4)/'IN'/,
     &     ELIII(5)/'TL'/,ELV(1)/' N'/,ELV(2)/' P'/,ELV(3)/'AS'/,
     &     ELV(4)/'SB'/,ELV(5)/'BI'/
C
C  DETERMINE WHICH INDECIES CORRESPOND TO COLUMN III AND V ELEMENTS
C
      DO 100 K=1,5
      KIII(K)=0
      KV(K)=0
      DO 100 J=1,E
      IF(ELMNT(J).EQ.ELIII(K)) KIII(K)=J
      IF(ELMNT(J).EQ.ELV(K)) KV(K)=J
  100 CONTINUE
C
C  SUM-UP THE GROUP III AND V SPECIES AND CALCULATE THE RATIO
C
      SUMIII=0.0
      SUMV=0.0
      DO 200 I=1,V
      DO 200 K=1,5
      IDXIII=KIII(K)
      IDXV=KV(K)
      IF(IDXIII.EQ.0) GO TO 120
      SUMIII=SUMIII+A(I,IDXIII)*FRAC(I)
  120 CONTINUE
      IF(IDXV.EQ.0) GO TO 200
      SUMV=SUMV+A(I,IDXV)*FRAC(I)
  200 CONTINUE
      RIIIV=1.0E10
      IF(SUMV.GT.0.0) RIIIV=SUMIII/SUMV
      RETURN
      END
```

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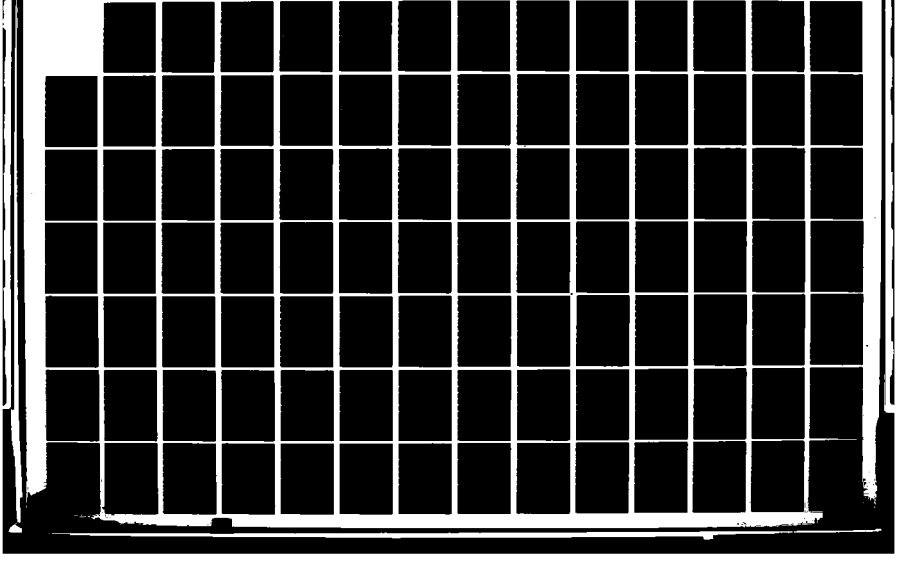

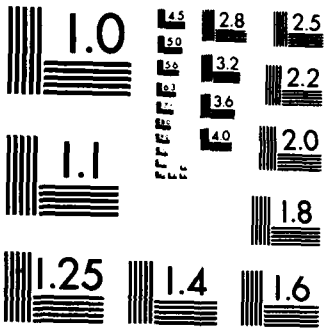

of the periodic table are included. This results in a total III/V ratio which does not distinguish between the various elements in each group. Since character string comparisons are made in order to locate the positions of the appropriate elements in vector ELMNT it is essential that all group III and V elements which have single letter representations (B, N, P) be entered right justified in the input data set.

A.4.15 WRAPUP

Subroutine WRAPUP, shown in Figure A22, writes a wrap-up file to logical unit designator IFILE. This subroutine is accessed when parameter IWRAP > 0. For IWRAP = 1 or 2 the value of IFILE is set to 2. For IWRAP = 3 IFILE is set equal to IWRT which is the line printer logical unit designator. This subroutine provides concise data output and is quite useful when the input data set has been verified to be correct and parametric studies are desired.

A.4.16 DEBUG

Subroutine DEBUG is accessed when parameter IDEBUG > 1. This subroutine provides an output of the convergence forcer, system Gibbs Free Energy, the relative state of convergence, specie molar amounts, changes in specie molar amounts and the incremental Gibbs Free Energy of each specie at each iteration. A listing of DEBUG is shown in Figure A 23.

A.4.17 PRNTAB

Subroutine PRNTAB, shown in Figure A24 writes out matrix ALEQ and vector BLEQ for diagnostic purposes when parameter IDEBUG = 2. This subroutine is accessed from line 176 of subroutine RAND.

Figure A22. Subroutine WRAPUP

```
      SUBROUTINE WRAPUP(TITLE,SPECIE,INERT,N,FRAC,ZV,FRACZ,SITOT,SIMF
     &                  RIIIV,RELMAX,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE
     &                  V,VSC)
C
C  SUBROUTINE TO WRITE-OUT A SUMMARY OF THE RESULTS TO A FILE
C
      DIMENSION INERT(3),FRAC(IDIM1)
      INTEGER TITLE(20),SPECIE(IDIM1,3),V,VSC
      REAL N(IDIM1)
      IF(IDATA.EQ.0) WRITE(IFILE,50) (TITLE(K),K=1,20)
   50 FORMAT(20A4)
      WRITE(IFILE,55) T,P
   55 FORMAT('TEMPERATURE = ',F7.1,' K',/,'PRESSURE = ',E12.5,' PA')
      IF(ABS(RELMAX).GT.CNVG.AND.IDATA.NE.0)WRITE(IFILE,58) RELMAX,CNV
   58 FORMAT(66('*'),/,'*',5X,'ITERATION FOR EQUILIBRIUM COMPOSITION '
     &       'DID NOT CONVERGE',5X,'*',/,'*',1X,'MAXIMUM ERROR = ',
     &       E12.5,2X,'CONVERGENCE CRITERION = ',E12.5,1X,'*',
     &       /,66('*'))
      IF(IDATA.EQ.0) WRITE(IFILE,60)
   60 FORMAT(13X,'INITIAL COMPOSITIONS')
      IF(IDATA.EQ.1) WRITE(IFILE,70)
   70 FORMAT(13X,'EQUILIBRIUM COMPOSITIONS')
      IF(IDATA.EQ.0) WRITE(IFILE,80)
   80 FORMAT('SPECIE',7X,'MOLE FRACTION',4X,'GRAM MOLES')
      DO 200 I=1,VSC
      WRITE(IFILE,100) (SPECIE(I,K),K=1,3),FRAC(I),N(I)
      IF(I.EQ.V) WRITE(IFILE,100) (INERT(K),K=1,3),FRACZ,ZV
  100 FORMAT(3A4,2X,E12.5,2X,E12.5)
      IF(I.EQ.V) WRITE(IFILE,105) RIIIV
  105 FORMAT('VAPOR III/V ',10X,F9.4)
      IF(I.EQ.V) WRITE(IFILE,110) SIMF,SITOT
  110 FORMAT('SI IN VAPOR ',2X,E12.5,2X,E12.5)
  200 CONTINUE
      IF(ISS.GT.0) WRITE(IFILE,205) XIII
  205 FORMAT(3X,'X=',F6.4)
      WRITE(IFILE,210)
  210 FORMAT('      ')
      IDATA=1
      RETURN
      END
```

Figure A23. Subroutine DEBUG

```
      SUBROUTINE DEBUG(N,DELN,DGTST,VSC,IDIM1,ITER,LAMBDA,GFE,
     &                 RMX,IWRT)
C
C  ROUTINE TO WRITE-OUT N, DELN, ALMBDA DURING THE ITERATON PROCESS
C
      REAL LAMBDA,N(IDIM1),DGTST(IDIM1),DELN(IDIM1)
      INTEGER VSC
      WRITE(IWRT,10) ITER,LAMBDA,GFE,RMX
   10 FORMAT('0','ITERATION = ',I5,5X,'LAMBDA = ',E14.7,
     &       5X,'GIBBS FREE ENERGY = ',E14.7,' KCAL',
     &       5X,'RELATIVE ERROR = ',E12.5,/,1X,
     &       'N-VALUES',T20,'DELTA-N VALUES',
     &       T40,'DGTST VALUES')
      DO 50 I=1,VSC
      WRITE(IWRT,20) N(I),DELN(I),DGTST(I)
   20 FORMAT(1X,E14.7,T20,E14.7,T40,E14.7)
   50 CONTINUE
      RETURN
      END
```

Figure A24. Subroutine PRNTAB

```
      SUBROUTINE PRNTAB(A,B,N,IDIM3,IWRT)
C
C  MATRIX OUTPUT ROUTINE FOR DIAGNOSTIC USE
C
      DOUBLE PRECISION A(IDIM3,IDIM3),B(IDIM3)
      MAX=N/10+1
      LINE=0
      IST=1
      DO 50 I=1,MAX
      LINE=LINE+N+2
      IEND=IST+9
      IF(IEND.GT.N) IEND=N
      IF(LINE.GT.80) WRITE(IWRT,10) IST,IEND
      IF(I.EQ.1) WRITE(IWRT,10) IST,IEND
      IF(LINE.LE.80.AND.I.GT.1) WRITE(IWRT,20) IST,IEND
   10 FORMAT('1','COLUMNS ',I2,' THROUGH ',I2,' OF MATRIX ALEQ:')
   20 FORMAT('0','COLUMNS ',I2,' THROUGH ',I2,' OF MATRIX ALEQ:')
      IF(LINE.GT.80) LINE=0
      DO 40 ILIN=1,N
      WRITE(IWRT,30) (A(ILIN,J),J=IST,IEND)
   30 FORMAT(1X,10(D11.4,2X))
   40 CONTINUE
      IST=IEND+1
      IF(IST.GT.N) GO TO 60
   50 CONTINUE
   60 CONTINUE
      WRITE(IWRT,70)
   70 FORMAT('0','THE TRANSPOSED BLEQ VECTOR IS:')
      IST=1
      DO 90 I=1,MAX
      IEND=IST+9
      IF(IEND.GT.N) IEND=N
      WRITE(IWRT,80) (B(J),J=IST,IEND)
   80 FORMAT(1X,10(D11.4,2X))
      IST=IEND+1
      IF(IST.GT.N) RETURN
   90 CONTINUE
      RETURN
      END
```

A.4.18 IMSL Subroutines LINV1F, LEQT1F, LUDATF, LUELMF

The calling sequence of the IMSL subroutines is shown in Figure A25 and a listing of these subroutines is provided in Figure A26. These IMSL subroutines are used to perform matrix inversions and solve the matrix problem

$$A\ X = B \tag{1}$$

for vector X. The matrix inversion subroutine, LINV1F, is called from line 43 of subroutine IDPTEQ. LINV1F defines B to be a matrix instead of a vector and simply puts ones on the diagonal of this matrix and zeros elsewhere. Subroutine LEQT1F is then called upon to solve the matrix problem

$$A\ AINV = B \tag{2}$$

to yield the inverted A matrix AINV.

Subroutine LEQT1F is called from line 182 of subroutine RAND to solve the linear algebra problem in equation 1 for the vector X. The X vector solution is then returned as vector B in order to save on storage requirements. Double precision arithmetic is used in the calculations and the routines check for IDGT significant figures in the answers. If less than IDGT significant figures are found parameter IER is returned as 34. If matrix A is singular IER is returned as 129.

Figure A25

IMSL Subroutine Calling Sequence

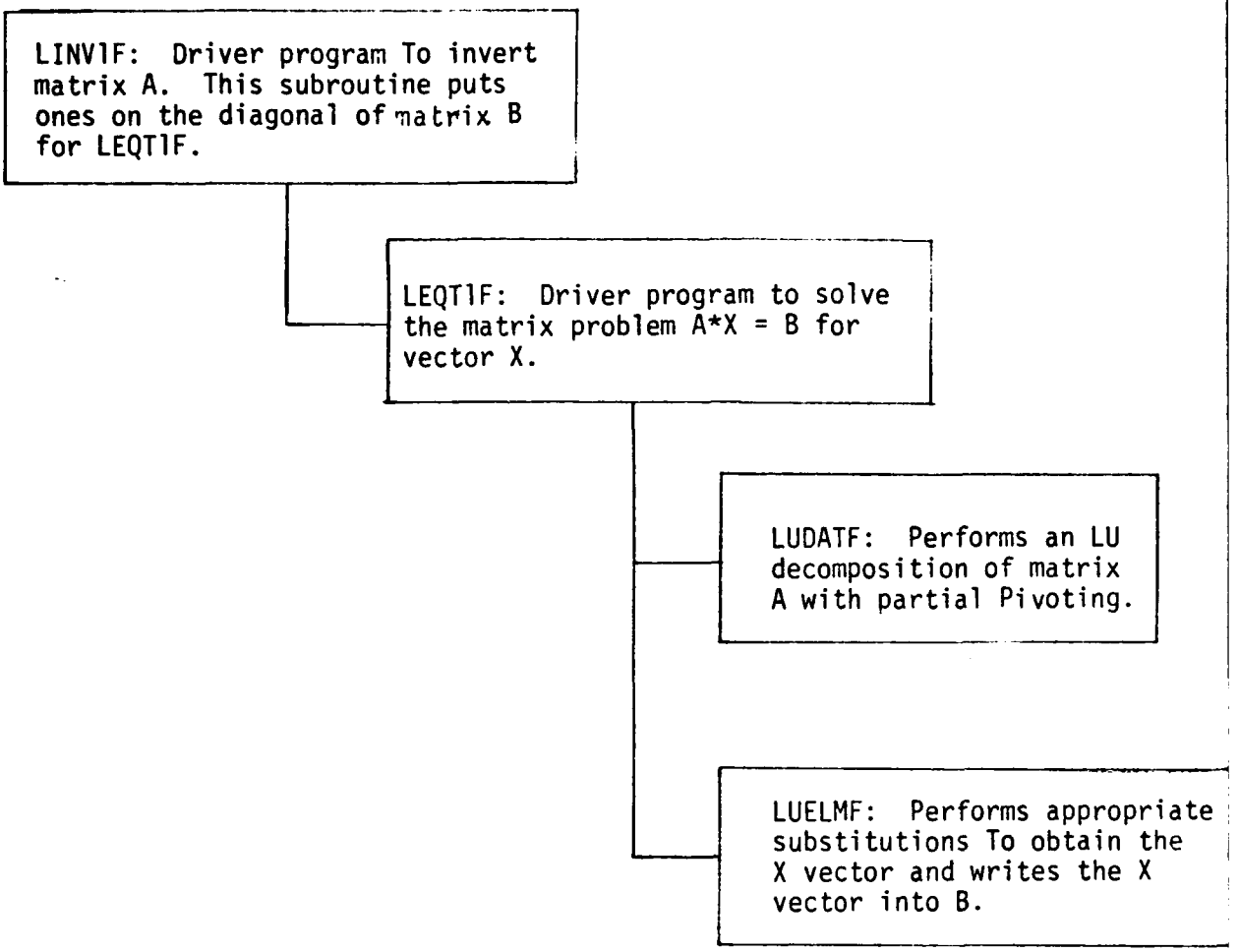

Figure A26. IMSL Subroutines LINV1F, LEQT1F, LUDATF and LUELMF.

```
      SUBROUTINE LINV1F (A,N,IA,AINV,IDGT,WKAREA,IER)
C
C  IMSL SUBROUTINE FOR INVERTING REAL MATRICIES
C
      DOUBLE PRECISION A(IA,N),AINV(IA,N),WKAREA(1),ZERO,ONE
      DATA                 ZERO/0.0D0/,ONE/1.0D0/
      IER=0
      DO 10 I=1,N
         DO 5 J=1,N
            AINV(I,J) = ZERO
    5    CONTINUE
         AINV(I,I) = ONE
   10 CONTINUE
      CALL LEQT1F (A,N,N,IA,AINV,IDGT,WKAREA,IER)
      IF (IER .EQ. 0) GO TO 9005
 9000 CONTINUE
 9005 RETURN
      END
```

```
      SUBROUTINE LEQT1F (A,M,N,IA,B,IDGT,WKAREA,IER)
C
C  IMSL SUBROUTINE LEQT1F FOR SOLVING THE MATRIX PROBLEM A*X=B
C
      DIMENSION          A(IA,1),B(IA,1),WKAREA(1)
      DOUBLE PRECISION   A,B,WKAREA,D1,D2,WA
C                                     INITIALIZE IER
C                                     FIRST EXECUTABLE STATEMENT
      IER=0
C                                     DECOMPOSE A
      CALL LUDATF (A,A,N,IA,IDGT,D1,D2,WKAREA,WKAREA,WA,IER)
      IF (IER .GT. 128) GO TO 9005
C                                     CALL ROUTINE LUELMF (FORWARD AND
C                                     BACKWARD SUBSTITUTIONS)
      DO 10 J=1,M
         CALL LUELMF (A,B(1,J),WKAREA,N,IA,B(1,J))
   10 CONTINUE
 9005 RETURN
      END
```

```
      SUBROUTINE LUDATF (A,LU,N,IA,IDGT,D1,D2,IPVT,EQUIL,WA,IER)
C
C  THIS SUBROUTINE IS USED WITH SUBROUTINE LEQTIF
C
      DIMENSION          A(IA,1),LU(IA,1),IPVT(1),EQUIL(1)
      DOUBLE PRECISION   A,LU,D1,D2,EQUIL,WA,ZERO,ONE,FOUR,SIXTN,SIXTH
     *                   RN,WREL,BIGA,BIG,P,SUM,AI,WI,T,TEST,Q
      DATA               ZERO,ONE,FOUR,SIXTN,SIXTH/0.D0,1.D0,4.D0,
     *                   16.D0,.0625D0/
C                                        FIRST EXECUTABLE STATEMENT
C                                        INITIALIZATION
      IER = 0
      RN = N
      WREL = ZERO
      D1 = ONE
      D2 = ZERO
      BIGA = ZERO
      DO 10 I=1,N
         BIG = ZERO
         DO 5 J=1,N
            P = A(I,J)
            LU(I,J) = P
            P = DABS(P)
            IF (P .GT. BIG) BIG = P
    5    CONTINUE
         IF (BIG .GT. BIGA) BIGA = BIG
         IF (BIG .EQ. ZERO) GO TO 110
         EQUIL(I) = ONE/BIG
   10 CONTINUE
      DO 105 J=1,N
         JM1 = J-1
         IF (JM1 .LT. 1) GO TO 40
C                                        COMPUTE U(I,J), I=1,...,J-1
         DO 35 I=1,JM1
            SUM = LU(I,J)
            IM1 = I-1
            IF (IDGT .EQ. 0) GO TO 25
C                                        WITH ACCURACY TEST
            AI = DABS(SUM)
            WI = ZERO
            IF (IM1 .LT. 1) GO TO 20
            DO 15 K=1,IM1
               T = LU(I,K)*LU(K,J)
               SUM = SUM-T
               WI = WI+DABS(T)
   15       CONTINUE
            LU(I,J) = SUM
   20       WI = WI+DABS(SUM)
            IF (AI .EQ. ZERO) AI = BIGA
            TEST = WI/AI
            IF (TEST .GT. WREL) WREL = TEST
            GO TO 35
C                                        WITHOUT ACCURACY
   25       IF (IM1 .LT. 1) GO TO 35
```

```
      DO 30 K=1,IM1
         SUM = SUM-LU(I,K)*LU(K,J)
30    CONTINUE
      LU(I,J) = SUM
35  CONTINUE
40  P = ZERO
C                                     COMPUTE U(J,J) AND L(I,J), I=J+1,...,
    DO 70 I=J,N
      SUM = LU(I,J)
      IF (IDGT .EQ. 0) GO TO 55
C                                     WITH ACCURACY TEST
      AI = DABS(SUM)
      WI = ZERO
      IF (JM1 .LT. 1) GO TO 50
      DO 45 K=1,JM1
         T = LU(I,K)*LU(K,J)
         SUM = SUM-T
         WI = WI+DABS(T)
45    CONTINUE
      LU(I,J) = SUM
50    WI = WI+DABS(SUM)
      IF (AI .EQ. ZERO) AI = BIGA
      TEST = WI/AI
      IF (TEST .GT. WREL) WREL = TEST
      GO TO 65
C                                     WITHOUT ACCURACY TEST
55    IF (JM1 .LT. 1) GO TO 65
      DO 60 K=1,JM1
         SUM = SUM-LU(I,K)*LU(K,J)
60    CONTINUE
      LU(I,J) = SUM
65    Q = EQUIL(I)*DABS(SUM)
      IF (P .GE. Q) GO TO 70
      P = Q
      IMAX = I
70  CONTINUE
C                                     TEST FOR ALGORITHMIC SINGULARITY
    IF (RN+P .EQ. RN) GO TO 110
    IF (J .EQ. IMAX) GO TO 80
C                                     INTERCHANGE ROWS J AND IMAX
    D1 = -D1
    DO 75 K=1,N
      P = LU(IMAX,K)
      LU(IMAX,K) = LU(J,K)
      LU(J,K) = P
75  CONTINUE
    EQUIL(IMAX) = EQUIL(J)
80  IPVT(J) = IMAX
    D1 = D1*LU(J,J)
85  IF (DABS(D1) .LE. ONE) GO TO 90
    D1 = D1*SIXTH
    D2 = D2+FOUR
    GO TO 85
90  IF (DABS(D1) .GE. SIXTH) GO TO 95
```

```
109           D1 = D1*SIXTN
110           D2 = D2-FOUR
111           GO TO 90
112     95    CONTINUE
113           JP1 = J+1
114           IF (JP1 .GT. N) GO TO 105
115 C                                       DIVIDE BY PIVOT ELEMENT U(J,J)
116           P = LU(J,J)
117           DO 100 I=JP1,N
118              LU(I,J) = LU(I,J)/P
119    100    CONTINUE
120    105 CONTINUE
121 C                                       PERFORM ACCURACY TEST
122        IF (IDGT .EQ. 0) GO TO 9005
123        P = 3*N+3
124        WA = P*WREL
125        IF (WA+10.D0**(-IDGT) .NE. WA) GO    9005
126        IER = 34
127        GO TO 9005
128 C                                       ALGOR   IC SINGULARITY
129    110 IER = 129
130        D1 = ZERO
131        D2 = ZERO
132   9005 RETURN
133        END
```

```
      SUBROUTINE LUELMF (A,B,IPVT,N,IA,X)
C
C  THIS SUBROUTINE IS USED WITH SUBROUTINE LEQTIF
C
      DIMENSION          A(IA,1),B(1),IPVT(1),X(1)
      DOUBLE PRECISION   A,B,X,SUM
C                                        FIRST EXECUTABLE STATEMENT
C                                        SOLVE LY = B FOR Y
      DO 5 I=1,N
    5 X(I) = B(I)
      IW = 0
      DO 20 I=1,N
         IP = IPVT(I)
         SUM = X(IP)
         X(IP) = X(I)
         IF (IW .EQ. 0) GO TO 15
         IM1 = I-1
         DO 10 J=IW,IM1
            SUM = SUM-A(I,J)*X(J)
   10    CONTINUE
         GO TO 20
   15    IF (SUM .NE. 0.D0) IW = I
   20 X(I) = SUM
C                                        SOLVE UX = Y FOR X
      DO 30 IB=1,N
         I = N+1-IB
         IP1 = I+1
         SUM = X(I)
         IF (IP1 .GT. N) GO TO 30
         DO 25 J=IP1,N
            SUM = SUM-A(I,J)*X(J)
   25    CONTINUE
   30 X(I) = SUM/A(I,I)
      RETURN
      END
```

A.5 Theoretical Development of the Rand algorithm

A variety of methods have been proposed for calculating compositions in multiphase, reacting systems at equilibrium. The technique derived here employs the Newton-Raphson method to minimize the Gibbs Energy of an ideal system. The problem may be formulated as follows: Given the initial mole numbers of all species, the temperature, and the pressure, determine the composition which minimizes the Gibbs Energy of an ideal mixture subject to atom balance constraints. The system considered here allows for the presence of a gas phase (with an inert species permitted), multiple pure condensed phases, and a condensed solution phase all existing in equilibrium. If we assume all mixtures behave in an ideal manner, the total Gibbs energy of the system, $G^*(T, P, n_i)$, can be expressed in terms of the temperature (T), pressure (P) and chemical species mole numbers (n_i) as

$$G^*(T,P,n_i)/RT = G = \sum_{i=1}^{v} n_i \left(\mu_i^\circ + \ell n \frac{n_i P}{n_v} \right) + Z_v \left(\mu_z^\circ + \ell n \frac{Z_v P}{n_v} \right) + \sum_{i=v+1}^{v+s} n_i \left(\mu_i^\circ + \ell n \frac{n_i}{n_s} \right) + \sum_{i=v+s+1}^{v+s+c} n_i \mu_i^\circ \qquad (1)$$

In this expression the following notation is used:

n_i = moles of species i

z_v = moles of inert specie in the vapor phase

$n_v = \sum_{i=1}^{v} n_i + Z_v$ = total moles of vapor

$n_s = \sum_{i=v+1}^{v+s} n_i$ = total moles of condensed solution

μ_i° = standard state chemical potential divided by RT

v = number of vapor specie

s = number of solution specie

c = number of pure condensed phases present

The minimization problem is constrained by the conservation of atomic elements such that

$$\sum_{i=1}^{v+s+c} a_{ji} n_i - b_j = 0, \qquad (2)$$

where a_{ji} is the number of atoms of element j per molecule of species i and b_j is the total number of gram-atoms of each of the E elements present in the system.

The first step involves an expansion of G in a quadratic Taylor series about a solution estimate $\underline{n}^k$ as

$$G^{k+1} \simeq G^k + \sum_{i=1}^{v+s+c} \delta n_i \frac{\partial G^k}{\partial n_i} + \frac{1}{2} \sum_{i=1}^{v+s+c} \sum_{\ell=1}^{v+s+c} \delta n_i \delta n_\ell \frac{\partial^2 G^k}{\partial n_i \partial n_\ell} \qquad (3)$$

where $\delta n_i = n_i^{k+1} - n_i^k$. The partial derivatives required in Equation (3) are found by analytical differentiation of Equation 1 . After differentiation and simplification the results are:

For i = 1,....,v

$$\partial G^k / \partial n_i = \mu_i^\circ + \ell n \frac{n_i P}{n_v} \qquad (4)$$

$$\frac{\partial^2 G^k}{\partial n_i^2} = \frac{1}{n_i} - \frac{1}{n_v} \qquad (5)$$

and

$$\frac{\partial^2 G^K}{\partial n_i \partial n_{\ell \neq i}} = - 1/n_v \qquad (6)$$

For i = v+1,.....,V+s

$$\partial G^K / \partial n_i = \mu_i^\circ + \ell n \frac{n_i}{n_s} \qquad (7)$$

$$\partial^2 G^k / \partial n_i^2 = 1/n_i - 1/n_s \qquad (8)$$

$$\partial^2 G^k / \partial n_i \partial n_{\ell \neq i} = - 1/n_s \qquad (9)$$

and

For i = v+s+1,...,v+s+c

$$\partial G^k/\partial n_i = \mu_i^\circ \tag{10}$$

$$\partial^2 G^k/\partial n_i^2 = \frac{\partial^2 G^k}{\partial n_i \partial n_{\ell \neq i}} = 0 \tag{11}$$

Upon substituting Equations 4 - 11 into 3 and simplifying the following result is found

$$G^{k+1} = G^k + \sum_{i=1}^{v} \delta n_i \left(\mu_i^\circ + \ell n \frac{n_i P}{n_v} \right) + \frac{1}{2} \sum_{i=1}^{v} \left[\frac{\delta n_i^2}{n_i} - \frac{\delta n_i \delta n_v}{n_v} \right]$$
$$+ \frac{1}{2} \sum_{i=v+1}^{v+s} \left[\frac{\delta n_i^2}{n_i} - \frac{\delta n_i \delta n_s}{n_s} \right] + \sum_{i=v+s+1}^{v+s+c} \delta n_i \mu_i^\circ \tag{12}$$

Since the atom balance must also be satisfied for the new solution estimate, $\underline{n}^{k+1}$, the subtraction of $\sum_{i=1}^{v+s+c} a_{ji} n_i^{K+1} - b_j$ for all elements E from G^{k+1} will not change its value as is easily ascertained from Equation 2 . An unconstrained objective function, ϕ^{k+1} , results when using Lagrange multipliers for each atom balance, π_j (j=1,2,.....E).

$$\phi^{k+1} = G^{k+1} + \sum_{j=1}^{E} \pi_j \left(- \sum_{i=1}^{v+s+c} a_{ji} n_i^{k+1} + b_j \right) \tag{13}$$

The problem has now been reduced to minimizing ϕ^{k+1} as:

$$\frac{\partial \phi^{k+1}}{\partial n_i^{k+1}} = 0 \tag{14}$$

$$= \mu_i^\circ + \ell n \frac{n_i P}{n_v} + \frac{\delta n_i}{n_i} - \sum_{j=1}^{v} \frac{\delta n_j}{n_v} - \sum_{j=1}^{E} \pi_j a_{ji} \quad \text{for } 1 \leq i \leq v \tag{15}$$

$$= \mu_i^\circ + \ell n \frac{n_i}{n_s} + \frac{\delta n_i}{n_i} - \sum_{j=v+1}^{v+s} \frac{\delta n_j}{n_s} - \sum_{j=1}^{E} \pi_j a_{ji} \quad \text{for } v+1 < i < v+s \tag{16}$$

$$= \mu_i^\circ - \sum_{j=1}^{E} \pi_j a_{ji} \quad \text{for } v+s+1 < i < v+s+c \tag{17}$$

with the addition of Equation 2 rewritten as

$$\sum_{i=1}^{v+s+c} a_{ji}(\delta n_i + n_i) = b_j \qquad \text{for } 1< j< E \qquad (18)$$

we now have v+s+c+E linear equations (Equations 15 - 18) in the same number of unknowns (v+s+c δn_i's and E π_j's). The number of independent linear equations that must be solved simultaneously can be reduced by hand elimination of v+s-2 equations as follows: Solving Equations 15 and 16 for δn_i yields

$$\delta n_i = n_i \left[\sum_{j=1}^{v} \frac{\delta n_j}{n_v} + \sum_{j=1}^{E} \pi_j a_{ji} - \mu_i^\circ - \ell n \frac{n_i p}{n_v} \right] \qquad \text{for } 1 < i < v \qquad (19)$$

and

$$\delta n_i = n_i \left[\sum_{j=v+1}^{v+s} \frac{\delta n_j}{n_s} + \sum_{j=1}^{E} \pi_j a_{ji} - \mu_i^\circ - \ell n \frac{n_i}{n_s} \right] \qquad \text{for } v+1< i < v+s \qquad (20)$$

Equations 19 and 20 contain only δn_i on the right hand side in terms of $\sum_{j=1}^{v} \frac{n_j}{n_v}$ and $\sum_{j=v+1}^{v+s} \frac{\delta n_j}{n_s}$ and we shall designate these two summations as the new variables u_v and u_s, respectively. With Equations 19 and 20 δn_i for $1 < i < v+s$ can be eliminated in Equation 18 with the result

$$\sum_{\ell=1}^{E} \pi_\ell \sum_{i=1}^{v+s} a_{ji} a_{\ell i} n_i + u_v \sum_{i=1}^{v} a_{ji} n_i + u_s \sum_{i=v+1}^{v+s} a_{ji} n_i + \sum_{i=v+s+1}^{v+s+c} a_{ji} \delta n_i =$$

$$b_j - b_j^k + \sum_{i=1}^{v} a_{ji} n_i \left(\mu_i^\circ + \ell n \frac{n_i p}{n_v} \right) + \sum_{i=v+1}^{v+s} \left(\mu_i^\circ + \ell n \frac{n_i}{n_s} \right) a_{ji} n_i \quad \text{for } 1< j< E \qquad \ldots.(21)$$

where b_j^k is the gram-atoms of element j in system as determined by the mole numbers n_i^k and b_j is provided by the initial condition.

Besides Equations 17 and 21 , two additional equations are required. As only v+s-2 δn_i variables were hand eliminated, the remaining two equations must be a linear combination of this set, for example $\sum_{i=1}^{v} \delta n_i$ and $\sum_{i=v+1}^{v+s} \delta n_i$ results in

$$\sum_{\ell=1}^{E} \pi_\ell \sum_{i=1}^{v} a_{\ell i} n_i - z_v u_v = \sum_{i=1}^{v} n_i \left(\mu_i^\circ + \ln \frac{n_i P}{n_v} \right) \qquad (22)$$

and

$$\sum_{\ell=1}^{E} \pi_\ell \sum_{i=v+1}^{v+s} a_{\ell i} n_i = \sum_{i=v+1}^{v+s} n_i \left(\mu_i^o + \ln \frac{n_i}{n_s} \right) \qquad (23)$$

Thus the final set of linear equations to be solved includes Equations 17 , 21 - 23 (E + c + 2 equations) for unknowns π_ℓ ($1 < \ell < E$), δn_i ($v+s+1 < i < v+s+c$), U_v and u_s.

The procedure is thus to input the temperature, pressure, all species possibly present along with their standard state chemical potential and formula vector (a_{ji}), total gram-atoms of each element present (b_j), and an initial guess of the equilibrium composition. The solution of Equations 17 and 21 - 23 for π_ℓ, u_v, u_s and the C δn_i's allows the computation of the remaining v+s δn_i's with Equations 19 and 20 . A new solution estimate can now be obtained as

$$n_i^{k+1} = n_i^k + \delta n_i \qquad (24)$$

This procedure is repeated with the new solution estimate until the composition converges to within a specified increment of the last two solutions estimates.

A.6 Example Calculation: The Ga, As, H System.

Figure A27 shows the results of an equilibrium calculation for the Ga, As and H system. The wrap-up file output is shown in Figure A28 and the data file which yielded these results is shown in Figure A29. This calculation determines the equilibrium composition of a system which initially consisted of 10% As, 10% Ga, 10% H_2 and 70% inert in the vapor phase. The calculation was performed for a temperature of 1000 C at one atmosphere pressure.

This example is provided as a demonstration of the data file required and type of output received. It is not intended to represent a CVD process.

Figure A27
Results for the Ga, As, H System

RAND ALGORITHUM FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS/H SYSTEM WITH AN INERT PRESENT A TEST OF MCMPEC.RAND. PAGE 1

TEMPERATURE = 1273.2 K PRESSURE = 0.10133E 06 PA

SPECIE SYMBOL	ENTHALPY OF FORMATION DHO (KCAL/G-MOLE)	ENTROPY OF FORMATION DSO (KCAL/G-MOLE-K)	HEAT CAPACITY CORRELATION COEFFICIENTS ICP=0: CP = A0 + A1*T + A2/T**2 + A3*LN(T) ICP=1: CP = A0 + A1*T + A2*T**2 + A3*T**3 A0 (KCAL/G-MOLE-K)	A1 (KCAL/G-MOLE-K**2)	A2 (.....)	A3 (.....)	ICP (-)
AS (V)	58.700	0.031081	0.004968	0.0	0.0	0.0	0
AS2 (V)	45.950	0.040496	0.007630	-0.16900E-06	-0.37080E 02	0.21120E-03	0
AS3 (V)	52.200	0.048531	0.013836	-0.13650E-06	-0.58890E 02	0.17200E-03	0
AS4 (V)	37.500	0.044112	0.018516	-0.17560E-06	-0.11120E 03	0.21800E-03	0
AS-H (V)	58.000	0.026867	0.006400	0.14320E-05	0.10800E 02	0.0	0
AS-H3 (V)	16.000	-0.002120	0.010070	0.54200E-05	-0.22000E 03	0.0	0
GA (V)	65.000	0.030617	0.020138	0.20900E-05	-0.26620E 03	-0.38120E-02	0
H (V)	52.103	0.011788	0.004968	0.0	0.0	0.0	0
H2 (V)	0.0	0.0	0.015256	0.21200E-05	-0.59060E 02	-0.14620E-02	0
INERT (V)	0.0	0.0	0.0	0.0	0.0	0.0	0
GA-AS (S)	-19.520	-0.002948	0.010460	0.28000E-05	0.0	0.0	0

THE ENTHALPY AND ENTROPY OF FORMATION REFERENCE TEMPERATURE AND PRESSURE ARE: TO = 298.2 K PO = 101325.0 PA

MAXIMUM NUMBER OF ITERATIONS ALLOWED = 1000

CONVERGENCE CRITERION = 0.1000E-03

OUTPUT PARAMETER IDEBUG = 0

RAND ALGORITHUM FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS/H SYSTEM WITH AN INERT PRESENT A TEST OF MCMPEC RAND

TEMPERATURE = 1273.2 K PRESSURE = 0.10133E 06 PA

INPUT DATA AND INITIAL COMPOSITION ESTIMATES

SPECIE SYMBOL	PHASE	INITIAL COMPOSITION ESTIMATE (G-MOLES)	STANDARD CHEMICAL POTENTIAL (KCAL/G-MOLE)	ELEMENTAL ABUNDANCE MATRIX H	GA	AS
AS (V)	VAPOR	0.9999992E-01	22.244	0.0	0.0	1.000
AS2 (V)	VAPOR	0.1000000E-19	-13.172	0.0	0.0	2.000
AS3 (V)	VAPOR	0.1000000E-19	-22.294	0.0	0.0	3.000
AS4 (V)	VAPOR	0.1000000E-19	-35.465	0.0	0.0	4.000
AS-H (V)	VAPOR	0.1000000E-19	17.479	1.000	0.0	1.000
AS-H3 (V)	VAPOR	0.1000000E-19	8.255	3.000	0.0	1.000
GA (V)	VAPOR	0.9999996E-01	20.578	0.0	1.000	0.0
H (V)	VAPOR	0.1000000E-19	38.757	1.000	0.0	0.0
H2 (V)	VAPOR	0.9999998E-01	-6.122	2.000	0.0	0.0
INERT (V)	VAPOR	0.7000000E 00	0.0			
GA-AS (S)	CONDENSED	0.1000000E-19	-26.230	0.0	1.000	1.000

TOTAL GRAM-MOLES OF EACH ELEMENT FROM INPUT DATA AND AS CALCULATED FROM THE INITIAL COMPOSITION ESTIMATES

	INPUT DATA	CALCULATED		INPUT DATA	CALCULATED		INPUT DATA	CALCULATED		INPUT DATA	CALCULATED
H	0.20000E 00	0.20000E 00	GA	0.10000E 00	0.10000E 00	AS	0.10000E 00	0.10000E 00			

RAND ALGORITHUM FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS/H SYSTEM WITH AN INERT PRESENT. A TEST OF MCMPEC.RAND

TEMPERATURE = 1273.2 K PRESSURE = 0.10133E 06 PA

EQUILIBRIUM COMPOSITIONS AFTER 22 ITERATIONS

SYSTEM GIBBS FREE ENERGY = -0.3997902E 01 (KCAL)

RELATIVE ERROR = 0.82001E-04 CONVERGENCE CRITERION = 0.10000E-03 RELAXATION PARAMETER AT LAST ITERATION = 0.10000E 01

SPECIE SYMBOL	PHASE	EQUILIBRIUM MOLE FRACTION	EQUILIBRIUM COMPOSITION (G MOLES)	ESTIMATED COMPOSITION UNCERTAINTY (G MOLES)	CHEMICAL POTENTIAL (KCAL/G-MOLE)	ACTIVITY COEFFICIENT
AS (V)	VAPOR	0.44039E-07	0.3547271E-07	0.1098651E-12	-48.594	0.10000E 01
AS2 (V)	VAPOR	0.15520E-04	0.1241640E-04	0.1005951E-09	-41.189	0.10000E 01
AS3 (V)	VAPOR	0.16657E-06	0.1332643E-06	0.1746611E-11	-61.793	0.10000E 01
AS4 (V)	VAPOR	0.88608E-08	0.7089000E-08	0.5813029E-12	-82.377	0.10000E 01
ASH (V)	VAPOR	0.30736E-07	0.2458966E-07	0.1003569E-10	-26.286	0.10000E 01
ASH3 (V)	VAPOR	0.13091E-07	0.1047311E-07	-0.6556140E-14	-37.669	0.10000E 01
GA (V)	VAPOR	0.31692E-04	0.2532825E-04	-0.1026088E-09	-5.636	0.10000E 01
H (V)	VAPOR	0.25132E-06	0.2010690E-06	0.6104726E-14	-5.692	0.10000E 01
H2 (V)	VAPOR	0.12499E 00	0.9999985E-01	0.6086701E-08	-11.383	0.10000E 01
INERT (V)	VAPOR	0.87496E 00	0.7000000E 00	0.0	-0.338	0.10000E 01
GA-AS (S)	CONDENSED	0.10000E 01	0.9997469E-01	0.1141959E-09	-26.230	0.10000E 01

MOLE FRACTION OF SILICON SPECIES IN VAPOR PHASE = 0.0

III/V RATIO IN THE VAPOR PHASE = 0.9999

TOTAL GRAM MOLES OF EACH ELEMENT FROM INPUT DATA AND AS CALCULATED FROM THE EQUILIBRIUM COMPOSITIONS

	INPUT DATA	CALCULATED		INPUT DATA	CALCULATED		INPUT DATA	CALCULATED		INPUT DATA	CALCULATED
H	0.20000E 01	0.20000E 00	GA	0.10000E 00	0.10000E 00	AS	0.10000E 00	0.10000E 00			

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RAND ALGORITHUM FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS/H SYSTEM WITH AN INERT PRESENT A TEST OF MCMPEC RAND

TEMPERATURE = 1273.2 K PRESSURE = 0.10133E 06 PA

A SET OF INDEPENDENT REACTION EQUATIONS FOR THIS SYSTEM IS AS FOLLOWS

(1.00 AS2 (V)) = (0.200E 01 AS (V))

(1.00 AS3 (V)) = (0.300E 01 AS (V))

(1.00 AS4 (V)) = (0.400E 01 AS (V))

(1.00 AS-H3 (V)) = (0.200E 01 AS (V)) + (0.300E 01 AS-H (V))

(1.00 H (V)) = (0.100E 01 AS (V)) + (0.100E 01 AS-H (V))

(1.00 H2 (V)) = (0.200E 01 AS (V)) + (0.200E 01 AS-H (V))

(1.00 GA-AS (S)) = (0.100E 01 AS (V)) + (0.100E 01 GA (V))

TEMPERATURE = 1273.2 K PRESSURE = 0.10133E 06 PA

EQUILIBRIUM CONSTANTS FOR THE INDEPENDENT REACTIONS

REACTION PRODUCT	GIBBS FREE ENERGY CHANGE (KCAL/G MOLE)	EQUILIBRIUM CONSTANT FROM GIBBS FREE ENERGY	EQUILIBRIUM CONSTANT FROM PREDICTED COMPOSITION
AS (V)	0.0	0.10000E 01	0.99999E 00
AS2 (V)	-97.660	0.78941E 10	0.78942E 10
AS3 (V)	-149.025	0.17109E 16	0.17109E 16
AS4 (V)	-194.440	0.22925E 22	0.22926E 22
AS H (V)	0.0	0.10000E 01	0.99999E 00
AS H3 (V)	3.305	0.88635E 00	0.88635E 00
GA (V)	0.0	0.10000E 01	0.10000E 01
H (V)	52.522	0.36256E-06	0.36256E-06
H2 (V)	-3.407	0.75012E 00	0.75012E 00
GA-AS (S)	69.051	0.71209E 12	0.71209E 12

Figure A28. Wrap-Up File Results

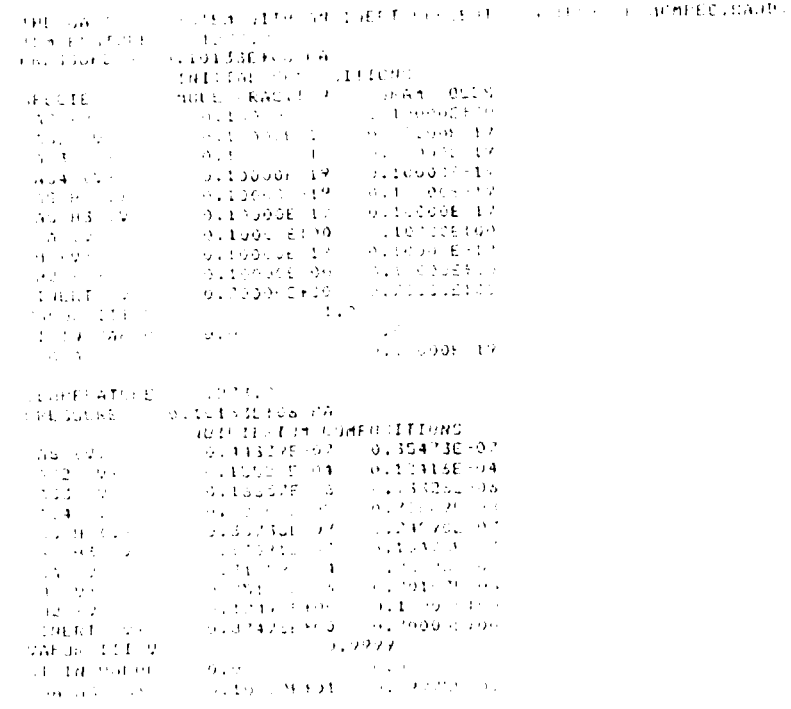
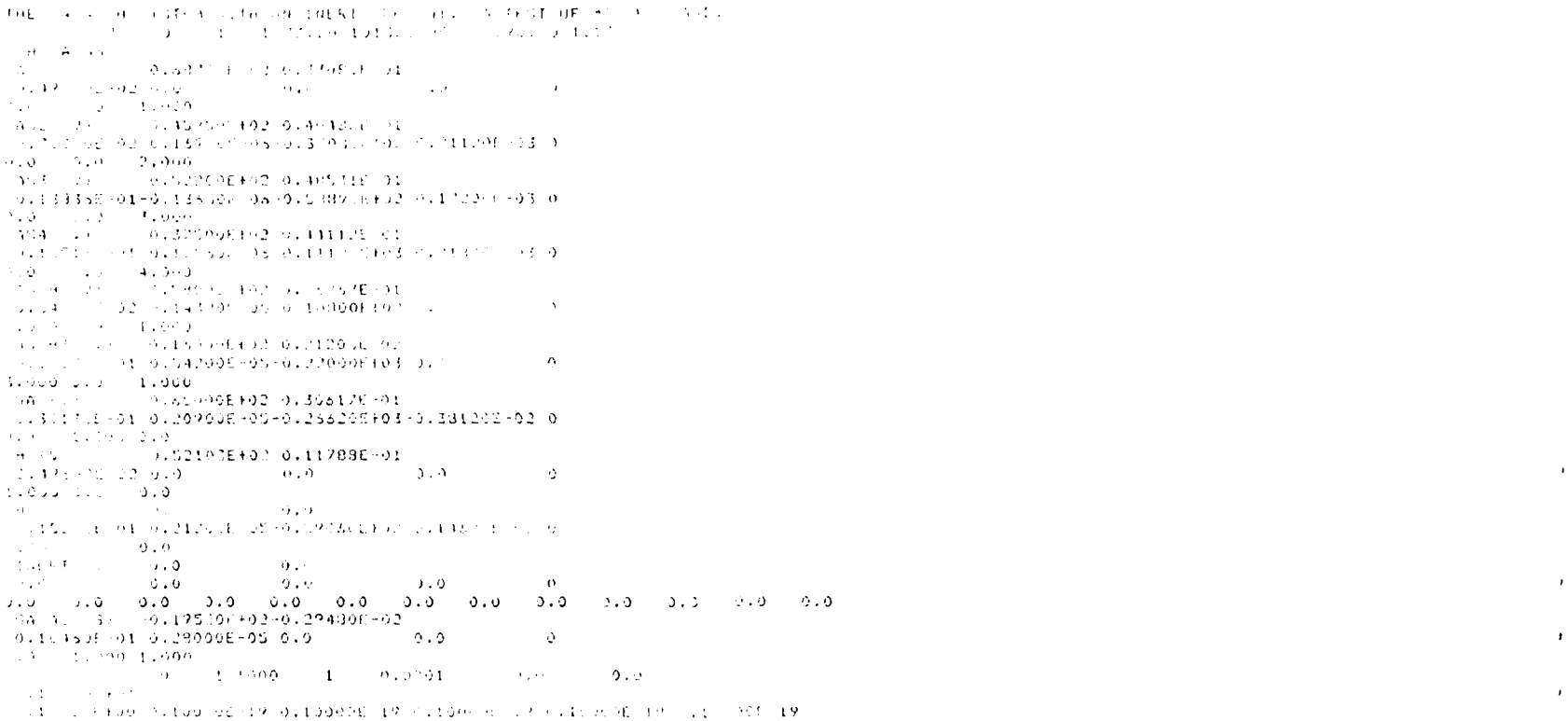


Figure A29. The Input Data File



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10. Appendix B. MCMPEC.STOIC: A Computer Code for Calculating Chemical Equilibria Using a Stoichiometric Algorithm

Appendix B

MCMPEC.STOIC: A Computer Code for Calculating Chemical Equilibria Using a Stoichiometric Algorithm.

B.1 Introduction

The calculation of chemical equilibirum using a stoichiometric algorithm is based on the work of Cruise [1] and Smith and Missen [2]. The stoichiometric algorithm requires a set of formation reaction equations for each specie of the form

$$S_i = \sum_{j=1}^{E} \nu_{ij} \, S_i^b \qquad (1)$$

where: S_i = specie being formed

S_i^b = basis specie in the system

ν_{ij} = reaction coefficient

E = number of elements in the system

An optimum set of basis species is chosen by selecting those species which represent all of the elements present in the system, are linearly independent from each other and are present in the greatest molar amounts. Employing this set of optimum basis species minimizes the number of iterations required in the numerical solution.

The iterative solution for equilibrium composition proceeds by calculating equilibrium constants for each formation reaction using the Gibbs Free Energy change of the reaction and the current estimate to the equilibrium composition. These two values are compared and the extents of each formation reaction are then adjusted to yield a better approximation to the system equilibrium composition. Since the formation reactions are initially balanced the conservation of mass constraint is implicitly included.

The application of an explicit set of formation reaction equations results in a greater flexibility for stoichiometric algorithms as compared to nonstoichiometric algorithms. There are no restrictions upon the types of phases which must be present, i.e. systems which do not include a vapor phase are solvable. Also, it is not necessary to remove pure condensed phases as their compositions vanish since the reaction extents simply vanish. The storage requirements for this stoichiometric algorithm are much less than those of the Rand algorithm in Appendix A. Only 87 k-bytes are required for a system consisting of 50 species composed of up to 13 elements.

MCMPEC.STOIC assumes the vapor phase to be ideal and includes an inert specie. The solution phase may have nonidealities described by Henry's Law, simple solution theory or may be modelled as ideal. The code includes options to allow temperature, pressure and inlet composition loops in order to generate data for parametric analyses.

Currently there is evidence which suggests that the liquid solution in the source zone of the CVD halide system is at steady state [3]. An option has therefore been included to model this situation in the Ga/As and In/P systems. Several data output and debugging options have also been included and are discussed in subsection B.2.2.

The structure of the main program along with data input and output are discussed in section B.2. A description of the major varaibles in the code is located in section B.3 and discussions of each subroutine are presented in section B.4. The theoretical development of the stoichiometric algorithm is presented in section B.5 and an example calculation is located in section B.6.

B.2 The Main Program

A flowsheet for MCMPEC.STOIC is shown in Figure B1. The main program sets array dimensions, provides a framework for calling the subroutines and performs data input and output. The temperature, pressure and composition loops, for generating parametric data, and the iteration loop for determining the equilibrium composition are also located in the main program. Data output which does not take place in the main program occurs in subroutines DEBUG, PMAT, DPMAT, PVEC, IPVEC and WRAPUP. Output which is useful for debugging purposes is written by DEBUG, PMAT, DPMAT, PVEC and IPVEC while WRAPUP writes out a concise file which summarizes the results. Also, execution diagnostics which pertain to the various subroutines are written out by the appropriate subroutine.

A listing of the main program is located in section B.2.6.

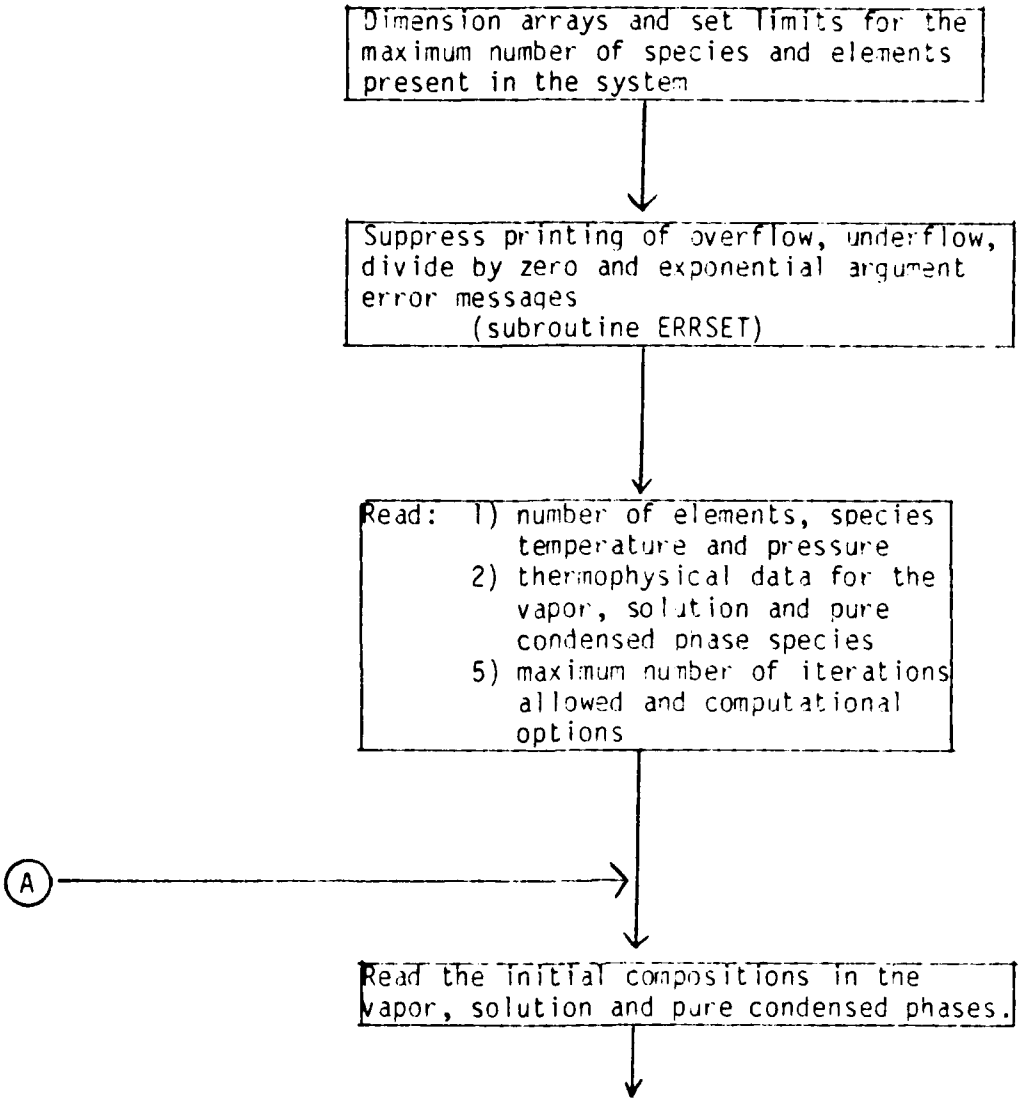
B.2.1. Array Dimensions, Expandability and Initialization.

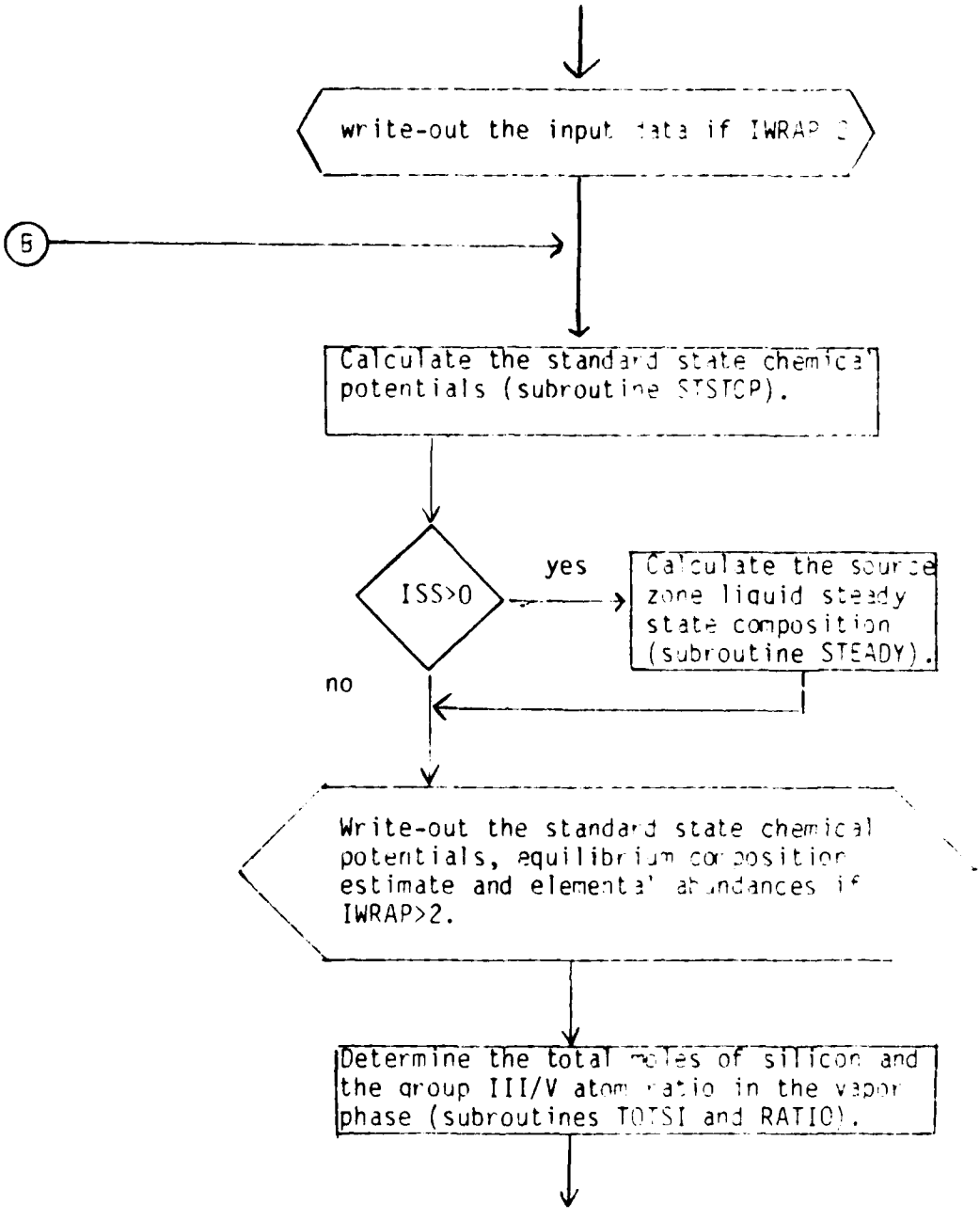
The arrays used in MCMPEC.STOIC are dimesioned in lines 5 through 19. Currently, systems containing up to 50 different species comprised of up to 13 different elements may be modelled. The variables IDIM1 and IDIM2, which are initialized in lines 35 and 36, are used to set the array dimensions in the subroutines. Therefore, the code may be expanded to accomodate larger systems simply by modifying the array dimensions in the main program and the values of IDIM1 and IDIM2. It is suggested that the element dimension IDIM2 not be increased beyond 13 as this will result in output line lengths greater than 132 characters which will be difficult to read as a result of printer "wrap-around". There are no restrictions (other than available computer memory) to the number of species which the code may be expanded to accomodate.

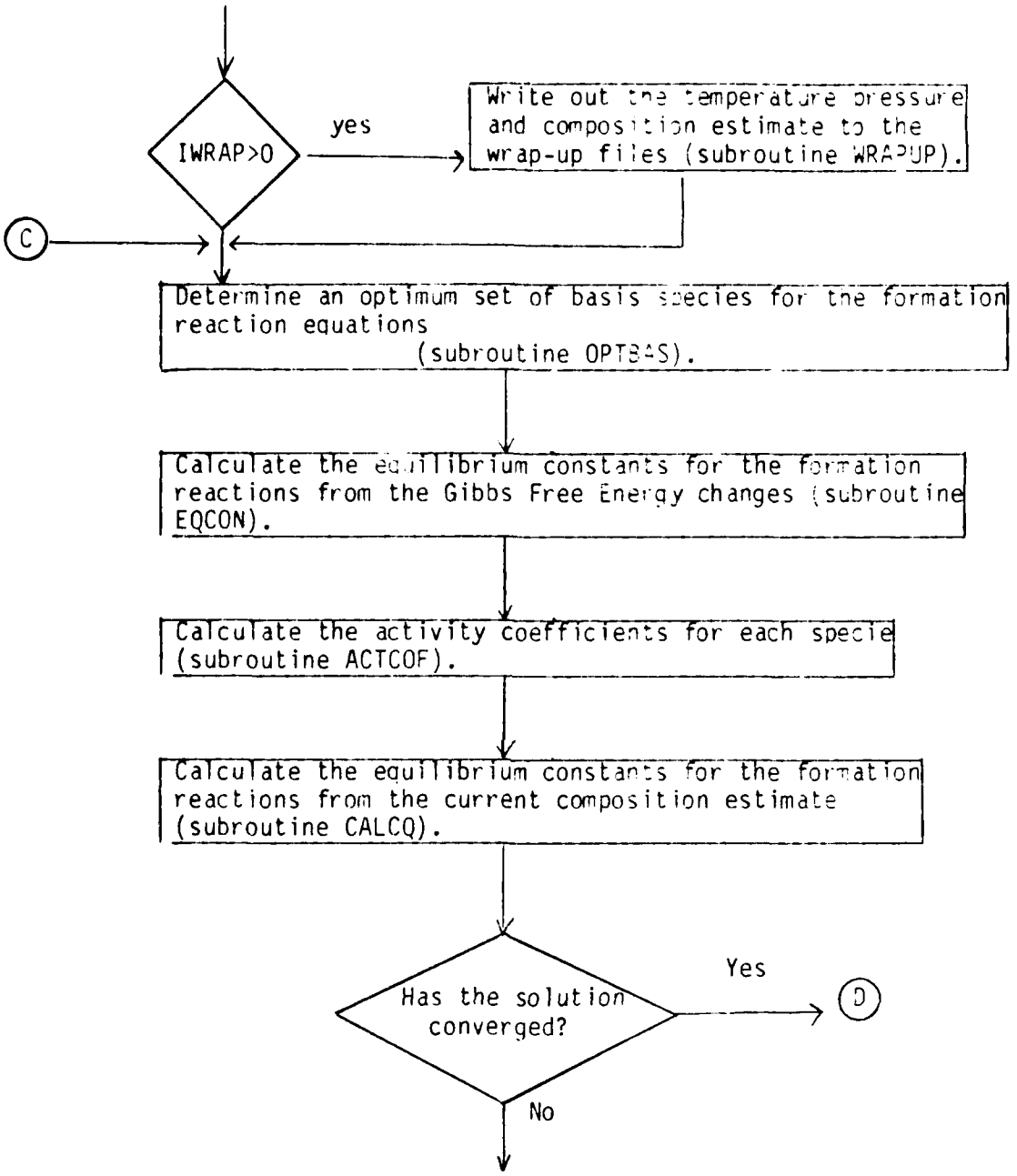
The logical unit designators for the input file, printed output and the wrap-up file are initialized at lines 32, 33 and 34.

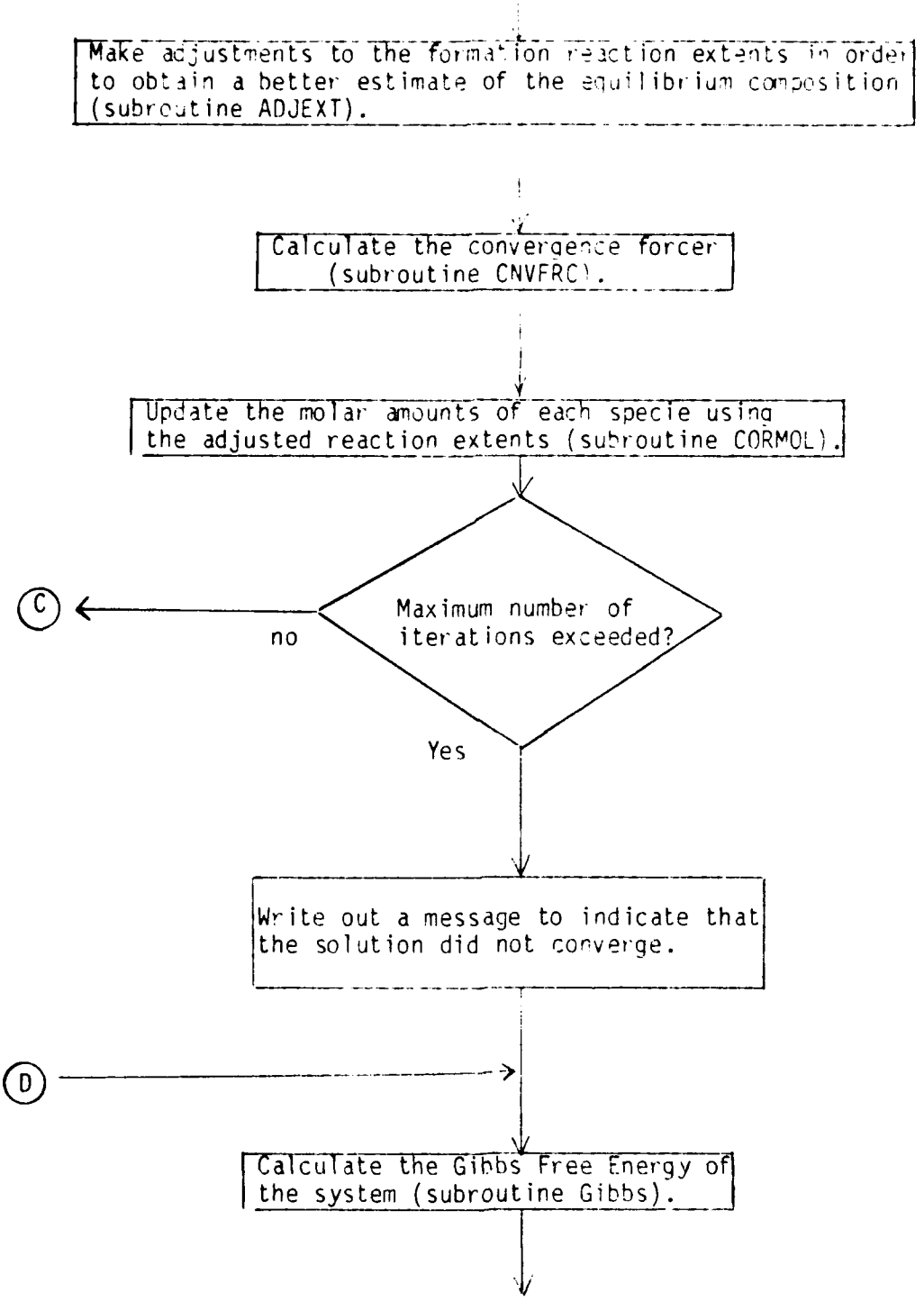
Figure 31

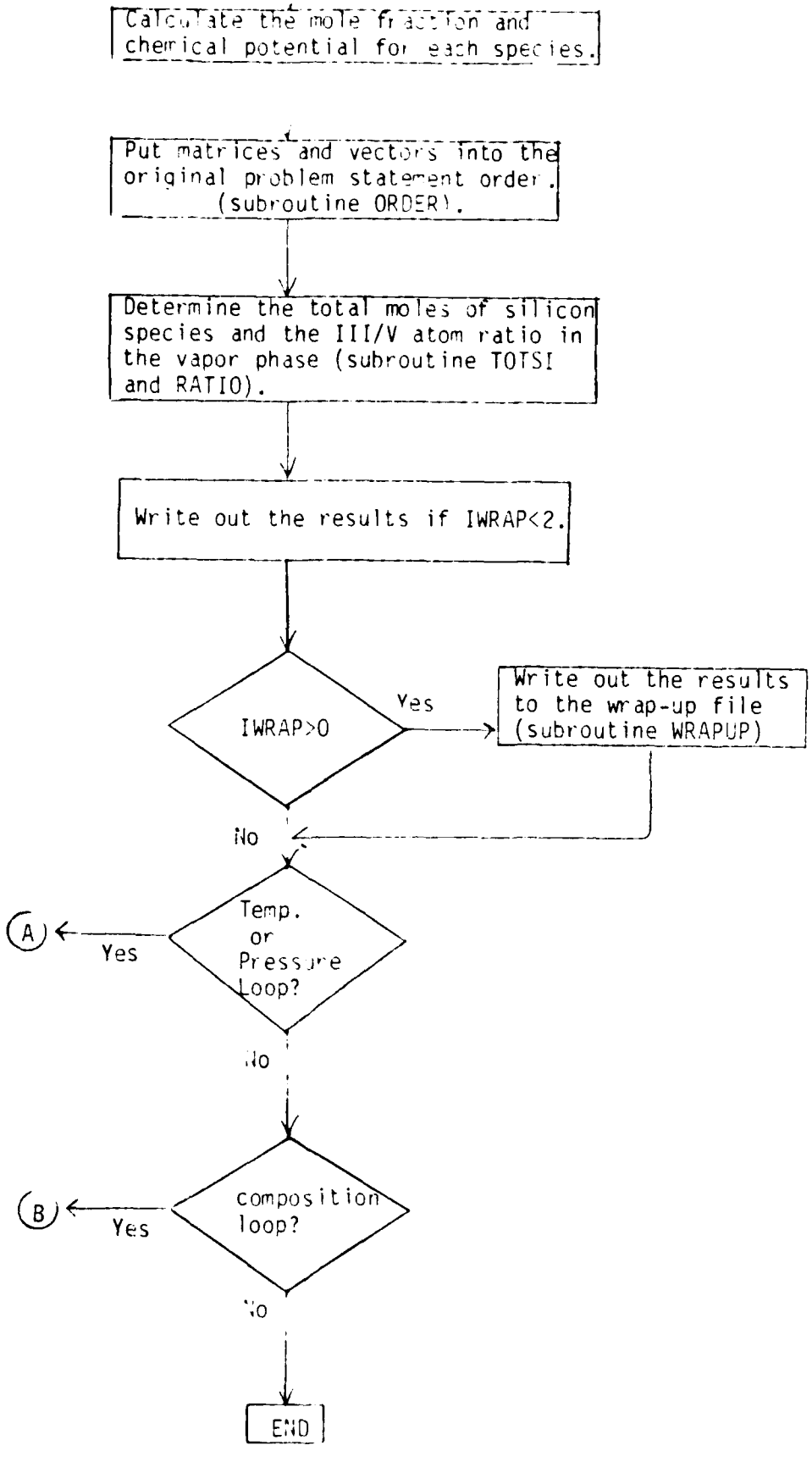
Main Program Flowsheet for MCMPEC.STOIC




write-out the input data if IWRAP 2
5
Calculate the standard state chemical potentials (subroutine STSTCP).
ISS>0
yes
Calculate the source zone liquid steady state composition (subroutine STEADY).
no
Write-out the standard state chemical potentials, equilibrium composition estimate and elemental abundances if IWRAP>2.
Determine the total moles of silicon and the group III/V atom ratio in the vapor phase (subroutines TOTSI and RATIO).


IWRAP>0
yes
Write out the temperature pressure and composition estimate to the wrap-up files (subroutine WRAPUP).
C
Determine an optimum set of basis species for the formation reaction equations (subroutine OPTBAS).
Calculate the equilibrium constants for the formation reactions from the Gibbs Free Energy changes (subroutine EQCON).
Calculate the activity coefficients for each specie (subroutine ACTCOF).
Calculate the equilibrium constants for the formation reactions from the current composition estimate (subroutine CALCQ).
Has the solution converged?
Yes
D
No


Make adjustments to the formation reaction extents in order to obtain a better estimate of the equilibrium composition (subroutine ADJEXT).
Calculate the convergence forcer (subroutine CNVFRC).
Update the molar amounts of each specie using the adjusted reaction extents (subroutine CORMOL).
Maximum number of iterations exceeded?
no
C
Yes
Write out a message to indicate that the solution did not converge.
D
Calculate the Gibbs Free Energy of the system (subroutine Gibbs).


Calculate the mole fraction and chemical potential for each species.
Put matrices and vectors into the original problem statement order. (subroutine ORDER).
Determine the total moles of silicon species and the III/V atom ratio in the vapor phase (subroutine TOTSI and RATIO).
Write out the results if IWRAP<2.
IWRAP>0
Yes
Write out the results to the wrap-up file (subroutine WRAPUP)
No
Temp. or Pressure Loop?
A
Yes
No
composition loop?
B
Yes
No
END

Lines 49 and 50 call the system subroutine ERRSET to suppress printing of overflow, underflow, divide by zero and exponential argument error messages. These errors occur quite frequently in subroutine CALCQ during the first few iterations as a result of the small initial concentrations of some of the species.

B.2.2 Data Input

Data input is accomplished in lines 51 through 159. A summary of the input data set is shown in Table B.1 and a description of each input variable is located in Table B.2.

The first input record consists of a data set title which may be up to 80 characters in length. The second record consists of the number of elements in the system, the number of species in the vapor, solution and pure condensed phases, followed by the system temperature and pressure. The last two pieces of information on this record are the reference temperature and pressure for the enthalpies and entropies of formation. The symbols for each element are on the third record. Two characters are allowed for each element symbol.

The next 3V records contain information regarding the species present in the vapor phase. The first record contains a 12 character specie name and the enthalpy and entropy of formation at temperature T_0 and pressure P_0 for this specie. Heat capacity correlation information is contained on the second record and the number of atoms of each element which are present in a single molecule of the specie are on the third record. Records 3V+1 to 3V+3 contain this same information for an inert specie in the vapor phase. The inert specie information must always be present in the data set. When it is desired to perform a calculation without the inert, its initial concentration is simply set to zero. This same information must also be provided for each specie in the solution phase and each pure condensed phase.

Table B.1
Input Data Set for MCMPEC.STOIC

Record	Comments	Format
Title (1),.... TITLE (20)	80 Character Title	20A4
E, V, S, C, T, P, T_o, P_o		4I5, 4F10.0
ELMNT (1), ELMNT (2) .... ELMNT (E)	Element Symbols	13 (1X, A2)
SPECIE (I,K), DMO(I), DSO(I)		3A4, 2E12.5
AO(I), AI(I), A2(I), A3(I), ICP(I)	Each vapor phase specie	4E12.5, I2
A(I,1), A(I,2).... A(I,E)		13(F5.0, 1X)
Inert(K), DHOZ, DSOZ		3A4, 12E12.5
AOZ, AIZ, A2Z, A3Z, ICPZ	Inert vapor phase specie	4E12.5, I2
IDUMMY		13(F5.0, 1X)
SPECIE(I, K), DHO(I), DSO(I)		3A4, 12E12.5
AO(I), AI(I), A2(I), A3(I), ICP(I)	Each solution phase specie	4E12.5, I2
A(I,1), A(I,2),...A(I,E)		13(F5.0,1X)
SPECIE(I,K), A2(I), A3(I), ICP(I)		3A4, 12E12.5
AO(I), AI(I), A2(I), A3(I), ICP(I)	Each pure condensed phase	4E12.5, I2
A(I,1), A(I,2)...A(I,E)		13(F5.0,1X)
IDEBUG, IOPT, ISS, IWRAP, MAXIT, NMAX CNVG, TINC, PINC, RLXMIN		6I5, 4F10.0
TOTMV		E12.5
FRAC(1), FRAC(2).... FRAC(V), FRACZ		6E12.5
TOTMS		E12.5
FRAC(V+1), FRAC(V+2)... FRAC(V+S)		6E12.5
IXSCOR, AXS, BXS		I5, 2E12.5
TOTMC(V+S+1)...TOTMC(V+S+C)		6E12.5

Table B.2

Description of Input Variables

Variable	Description
TITLE (20)	80 Character data set title
E	Number of elements (E ≤13)
V	Number of vapor species excluding the inert
S	Number of solution species
C	Number of pure condensed phases
T	System Temperature (K)
P	System Pressure (Pa)
TO	Reference Temperature for ΔH and ΔS formation
PO	Reference Pressure for ΔH and ΔS formation
ELMNT (13)	2 character symbol for each element (right justified)
SPECIE (50, 3)	12 character symbol for each specie
A (50, 13)	Elemental abundance matrix
DHO (50)	Enthalpy of formation (kcal/g-mole) for each specie at Temperature TO and Pressure PO.
DSO (50)	Entropy of formation (kcal/g-mole-K) for each specie at Temperature TO and Pressure PO.
AO (50)	Heat capacity correlation parameter (kcal/g-mole-K)
A1 (50)	Heat capacity correlation parameter (kcal/g-mole-K^2)
A2 (50)	Heat capacity correlation parameter (see Table)
A3 (50)	Heat capacity correlation parameter (see Table)
ICP (50)	Heat capacity correlation parameter (see Table)

Heat Capacity Correlations

ICP (I)	A2 (I)	A3 (I)	Correlation
0	kcal-K/g-mole	kcal/g-mole-K-ℓn(k)	$AO+A1*T+A2/T^2+A3*\ell n(T)$
1	kcal/g-mole-K^3	kcal/g-mole-K^4	$AO+A1*T+A2*T^2+A3*T^3$

INERT(3) — 12 Character name for inert vapor specie

DHOZ — Inert Specie enthalpy of formation

DSOZ — Inert Specie entropy of formation

AOZ, A1Z, A2Z, A3Z, ICPZ — Inert specie heat capacity correlation parameter

IDEBUG — Debugging Outout parameter

IDEBUG	Function
0	Warning messages are printed when problems are encountered in the IMSL subroutines
1	Prints IDEBUG=0 option plus composition changes and Gibbs energy for each iteration.
2	Prints IDEBUG=1 option plus matricies and vectors D, DPRME, KEQ and Q for each iteration

IOPT — Looping Option Parameter

IOPT	Function
0	One pass through routine
1	Temperature loop
2	Pressure loop
3	Composition loop

ISS — Source Zone Steady State Option Parameter

ISS	Function
0	Steady state option is inactive
1	Ga/As liquid composition is at steady state with GaAs solid.
2	In/P liquid composition is at steady state with InP solid.

IWRAP — Data output option parameter

IWRAP	Function
0	Write-out input data, execution diagnostics and results to printer
1	IWRAP=0 function plus writes-out a concise wrap-up file.
2	No printer output, just a wrap-up file
3	Write wrap-up to the printer

MAXIT — Maximum number of iterations allowed for the equilibrium composition to converge

NMAX — maximum number of loops allowed for the IOPT parameter

CNVG — convergence criterion

TINC — temperature increment for each loop if IOPT=1

PINC — pressure increment for each loop if IOPT=2

TOTMV — total moles in the vapor phase

TOTMS — total moles in the solution phase

TOTMC(I) — total moles in each pure condensed phase

FRAC(I) — mole fraction of specie I in vapor ($1 \leq I \leq V$)

mole fraction of specie I in solution ($V+1 \leq I \leq V$)

FRACZ — mole fraction of inert in vapor

IXSCOR — activity coefficient correlation parameter for the solution phase

IXSCOR	Correlation
0	ideal solution
1	binary single solution
2	Henry's law

AXS, BXS — activity coefficient correlation coefficient for the solution phase

IXSCOR	Correlation
0	ideal solution
1	$G^E = (AXS + BXS * T) * X1 * X2$
2	$H = AXS * EXP (BXS/T)$

RLXMIN — minimum value of the convergence factor

Following the data for each individual specie is a record describing the various options available and numerical methods information. Parameter IDEBUG should be set to zero for production jobs but may be set to 1 or 2 to provide information which allows the code to be examined in a step by step fashion.

Parameter IOPT allows the code to be looped in order to generate temperature, pressure or composition parametric curves. NMAX sets the number of loops to be executed while TINC and PINC are the temperature and pressure increments per loop. If a composition loop is desired a new initial composition data set must be provided for each loop.

Parameter ISS is used to activate the steady state liquid source option. If ISS is set to 1 the composition of a liquid containing Ga and As in equilibrium with GaAs solid is calculated. This liquid is inserted as the last pure condensed phase in the system. Thus when the value of C (number of pure condensed phases) is specified it must include a steady state phase if ISS>0 otherwise the last pure condensed phase in the system will be replaced with the steady state liquid. Setting ISS=2 will model a liquid of In and P in equilibrium with InP solid.

The parameter IWRAP is used to choose the amount of data output desired. When IWRAP=0 the input data is written out in tabulated form along with a description of the options chosen, execution diagnostics, equilibrium compositions, reaction formation equations and a comparison between the equilibrium constants for these equations as calculated from the free energy changes and the compositions. With IWRAP=1 a concise wrap-up file is written to logical unit designator IFILE (IFILE=2) in addition to the IWRAP=0 option. These two output options are quite useful when one is becoming acquainted with the code as they provide an echo of the input data set and a verification of the results. Options IWRAP=2 and IWRAP=3 provide only wrap-up file output to IFILE and IWRT respectively.

MAXIT sets the maximum number of interations to be performed for calculating the equilibrium compositions. Typically MAXIT is set to 1000. The equilibrium compositions are considered converged when the relative difference between the equilibrium constants, as calculated from the Gibbs Free Energy change of the formation reactions and from the estimate to the equilibrium composition, is less than CNVG. A typical value for CNVG is 10^{-4}.

The inlet compositions for the vapor, solution and pure condensed phases are next in the input data set. The total moles in the vapor are on one record and the following records contain the mole fractions of each component in the vapor, the last value being the mole fraction of the inert. The solution phase inlet compositions are done the same way except that there is no inert. Following the solution phase mole fractions is a record which determines the activity coefficient model to be used in the solution phase. For IXSCOR=0 the solution is considered to be ideal. Setting IXSCOR=1 yields a binary simple solution model for the excess Gibbs Free Energy. A Henry's Law constant for the first component in the solution phase is activated by setting IXSCOR=2. The parameters AXS and BXS are used in the activity coefficient models as shown in Table B.2.

The final records of the input data set contain the number of moles in each pure condensed phase.

B.2.3. Preparation for the Iterative Solution

The limits for the temperature, pressure and composition loops are set at lines 126 through 133. The composition loop (IOPT=3) starts at line 134.

The input specie order is saved so that the results may be output in this order. This step is necessary since the specie order is shifted during the iterative procedure in order to obtain an optimum set of basis species and it is convenient to compare the equilibrium results to the input concentrations in the same sequence.

The specie names along with their associated enthapy of formation, entropy of formation and heat capacity correlation data are then written to IWRT if IWRAP<2. Also, the temperature and pressure of the reference state, maximum number of iterations, convergence criterion and the debugging, steady-state and solution phase excess free energy correlation options are identified.

The temperature and pressure loops (IOPT=1 or IOPT=2) start at line 209. Subroutine STSTCP is called to calculate the standard state chemical potential of each specie. Subroutine ESTMTE is then called to provide an estimate to the equilibrium composition during the first pass through the temperature/pressure loop. Succeeding passes through this loop utilize the equilibrium composition of the preceding pass as an estimate of the current equilibrium composition when ISS=0.

If the steady state option is activated (ISS>0) subroutine STEADY inserts, as the last pure condensed phase, a liquid phase composed of group III and V elements which has a composition determined by the liquidus line of the III-V system at the specified temperature. The total moles of each element present is then calculated based on the estimate of the equilibrium compositions. This result is later written out along with the previous determination of each element to provide a means of verifying that mass has been conserved in the calculations.

The initial composition estimate, standard chemical potential and elemental abundance vector for each specie along with the amount of each element present in the system are written out if IWRAP<2. This occurs in lines 245 through 286. Headings for a page containing execution diagnostics are set up in lines 289 through 294 and the standard state chemical potentials are divided by R and T in accord with the derivation in section B.5.

During the first pass through the temperature or pressure loop the total moles of silicon compounds and the group III to group V atom ratio in the vapor phase are calculated in subroutines TOTSI and RATIO. The specie initial concentrations along with the total silicon and III-V atom ratio in the vapor are then written to a wrap-up file if IWRAP>0.

B.2.4 Iterative Solution for the Equilibrium Composition.

The iterative scheme for determining the equilibrium compositions is located at lines 319 through 421. Before entering the loop RELMAX, the relative maximum error between the actual and approximated equilibrium constants, is set to a large number and IACFF is set to zero to prevent the inclusion of nonidealities in the solution phase until a close approximation to the equilibrium composition is attained.

Subroutine OPTBAS is called to determine the optimum set of basis species for the current iteration. If a complete set of basis species cannot be found parameter ISTOP is set to unity and program execution is halted. If parameter ICHNG is returned as zero the optimum set of basis species for the current iteration is the same as the previous iteration and an unnecessary recalculation of the equilibrium constants for the formation reactions is omitted. If IC-NG is not zero subroutine EQCON is called to calculate the equilibrium constants for each formation reaction from the Gibbs Free Energy change of the reaction. Parameter ISTOP is set to unity in subroutine EQCON and execution is halted if the matrix containing the basis species appears to be algorithmically singular to subroutine LINVIF.

Subroutine ACTCOF calculates the equilibrium constants for each of the species and subroutine CALCQ calculates the equilibrium constants for each of the formation reactions from the current estimate to the equilibrium composition.

The test for convergence of the iteration scheme is performed in lines 360 through 393. The solution is considered to have converged when the maximum fractional disagreement between the equilibrium constants calculated from the free energy change and the composition estimate is less than CNVG.

If the convergence test fails subroutine ADJEXT is called to adjust the extents of the formation reactions in order to obtain a better estimate to the equilibrium composition. The convergence forcer is calculated in subroutine CNVFRC and the molar amounts of each specie are updated in subroutine CORMOL. Subroutine CALCQ is then called again so that the mole fractions sent to ACTCOF during the next iteration correctly reflect the composition. A message is written out at lines 423 through 428 if the iterative procedure terminates without converging.

Throughout the iterative procedure subroutines GIBBS, DEBUG, PMAT, DPMAT, PVEC and IPVEC are called, depending upon the value of IDEBUG, to provide intermediate information concerning the basis species and convergence of the numerical scheme.

B.2.5 Output of Results

Following the loop for determining the equilibrium compositions subroutine GIBBS is called to calculate the final system Gibbs Free Energy. Lines 439 through 454 then determine chemical potentials for each of the species. Subroutine ORDER is called to return the species to the original order of the problem statement. Subroutines TOTSI and RATIO then determine the total silicon concentration, the group III-V atom ratio in the vapor phase, the activities of Si, Ga, As, In and P in a solid phase and the III/V saturation ratio.

The results of the equilibrium calculation are written out at lines 468 through 520 if IWRAP<2. A wrap-up file is written at line 521 if IWRAP>0. If a temperature, pressure or composition loop option has been chosen (IOPT>0) the program jumps to the bottom of this loop at line 606. Otherwise the set of independent formation reaction equations are written out followed by a comparison of the equilibrium constants for these reactions as calculated by the free energy change and the equilibrium compositions.

The phrase "NOT BINDING" frequently appears to the right of the equilibrium constant comparisons and indicates that these particular reactions were not included in the convergence test due to the small concentration ($N_i < 10^{-21}$ g-moles) of the reaction products. Thus the two calculated equilibrium constants for these species may not be in agreement.

The punctuation ? and ?? sometimes accompany specie mole numbers in the wrap-up file. A single question mark indicates that the equilibrium constant for this formation reaction did not converge but is within 10% of the desired value. Double question marks indicate that the discrepancy between the equilibrium constants as calculated from the free energy change and the final composition is greater than 10%. Occasionally, values which are accompanied by a single question mark may be useful.

If the iteration for equilibrium does not converge there are several options which may be used. First, the results reported are always the best results which were obtained during the iterative procedure. This is true even if the solution diverges because the set of mole numbers which most closely approximate equilibrium is stored in vector BESTN. Therefore, if the solution fails to converge but the BESTN values are found to have sufficient accuracy, simply use the result.

In other situations the value of RLXMIN may be adjusted. Typically RLXMIN is set to 0.05 to allow the interative procedure to continue over unusually intricate contours on the Gibbs Free Energy surface. If the solution has not diverged, i.e. the last interation is the best estimate to the equilibrium solution, then increasing the value of RLXMIN will usually allow the solution to converge. If the solution has diverged the value of RLXMIN should be decreased to allow smaller steps to be taken.

Finally, if all else fails, the temperature and pressure looping options may be used to approach the desired equilibrium conditions from above or below the parameters of interest.

Table B.2.6 Listing of the Main Program

```
C  MCMPEC.STOIC .... MULTICOMPONENT MULTIPHASE EQUILIBRIUM CODE
C                   STOICIOMETRIC FORMULATION
C
C
      DIMENSION A(50,13),ACOEF(50),A0(50),A1(50),A2(50),A3(50),
     &          B(13),BCALC(13),CHMPT(50),COEFF(6),
     &          D(13,13),DINV(13,13),DD(13,13),DG(50),DH0(50),DS0(50),
     &          DZETA(50),FRAC(50),FRACIN(50),GNU(50,13),
     &          ICP(50),IDXBAS(13),INDEX(50),INERT(3),G(50),STDCP(50),
     &          TOTMC(50),WKA(50)
      INTEGER BSPCE(50,3),ISPCE(50,3),PHASE(50,3),SPECIE(50,3),
     &        STRING(6,4),TITLE(20),V,S,C,E,VP1,VPS,VPSP1,VSC,VSCF,
     &        BQUES(50),QUES(50),QUEST1/'?   '/,QUEST2/'??  '/,
     &        ELMNT(13)/13*'  '/,VAPOR(3)/'  V','APO','R  '/,
     &        SOLN(3)/'SOL','UTI','ON '/,COND(3)/'CON','DEN','SED'/,
     &        RPSPS/'=> + '/,RPAS/')<= '/,RPBL/')   '/,SSPS/'  + '/,
     &        BLNKS/'    '/,LP/'('/
      REAL KEQ(50),NV,NS,LAMBDA
      REAL*8 DD,DINV,WKA,N(50),BESTN(50),NTEMP(50),DPRME(13,13),DZETA
C
C  A(I,J)    : ELEMENTAL ABUNDANCE MATRIX
C  B(J)      : TOTAL NUMBER OF GRAM-MOLES OF ELEMENT J
C  DH0(I)    : ENTHALPY OF FORMATION OF SPECIES I
C  DS0(I)    : ENTROPY OF FORMATION OF SPECIES I
C  STDCP(I)  : STANDARD CHEMICAL POTENTIAL OF SPECIES I
C
C  **********  HEAT CAPACITY CORRELATIONS  **********
C  ICP(I)=0 : CP(I) = A0(I) + A1(I)*T + A2(I)/T**2 + A3(I)*ALOG(T)
C  ICP(I)=1 : CP(I) = A0(I) + A1(I)*T + A2(I)*T**2 + A3(I)*T**3
C
C
      IRD=5
      IWRT=6
      IFILE=2
      IDIM1=50
      IDIM2=13
      FRCZIN=0.0
      DH0Z=0.0
      DS0Z=0.0
      A0Z=0.0
      A1Z=0.0
      A2Z=0.0
      A3Z=0.0
      TOTMV=0.0
C
C  SUPPRESS PRINTING OF OVERFLOW, UNDERFLOW, DIVIDE BY ZERO
C  AND EXPONENTIAL ARGUMENT ERROR MESSAGES
C
      CALL ERRSET(207,0,-1,0,0,209)
      CALL ERRSET(252,),-1,0,0,253)
C
C  READ TITLE
C
      READ(IRD,5) (TITLE(K),K=1,20)
```

```
      5 FORMAT(20A4)
C
C  NUMBER OF ELEMENTS, VAPOR SPECIES, SOLUTION SPECIES,
C  CONDENSED PURE PHASES, SYSTEM TEMPERATURE (K) AND PRESSURE (PA)
C
      READ(IRD,10) E,V,S,C,T,P,TD,PD
   10 FORMAT(4I3,4F10.0)
      VP1=V+1
      VPS=V+S
      VPSP1=V+S+1
      VSC=V+S+C
      VSCE=V+S+C+E
C
C  READ ELEMENTS
C
      READ(IRD,15) (ELMNT(J),J=1,E)
   15 FORMAT(13(1X,A2))
C
C  VAPOR SPECIES INFORMATION
C
      IF(V.EQ.0) GO TO 118
      DO 110 I=1,V
      READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
      READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
      READ(IRD,22) (A(I,J),J=1,13)
   20 FORMAT(3A4,2E12.5)
   21 FORMAT(4E12.5,I2)
   22 FORMAT(13(F5.0,1X))
      DO 110 J=1,3
      PHASE(I,J)=VAPOR(J)
  110 CONTINUE
C
C  INERT SPECIE
C
      READ(IRD,20) (INERT(K),K=1,3),DH0Z,DS0Z
      READ(IRD,21) A0Z,A1Z,A2Z,A3Z,ICPZ
      READ(IRD,22) DUMMY
  118 CONTINUE
C
C  SOLUTION SPECIES INFORMATION
C
      IF(S.EQ.0) GO TO 125
      DO 120 I=VP1,VPS
      READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
      READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
      READ(IRD,22) (A(I,J),J=1,13)
      DO 120 J=1,3
      PHASE(I,J)=SOLN(J)
  120 CONTINUE
  125 CONTINUE
C
C  CONDENSED PHASE DATA
C
      IF(C.EQ.0) GO TO 135
```

```
      DO 130 I=VPSP1,VSC
      READ(IRD,20) (SPECIE(I,K),K=1,3),DHJ(I),DSJ(I)
      READ(IRD,21) AJ(I),A1(I),A2(I),A3(I),ICP(I)
      READ(IRD,22) (A(I,J),J=1,13)
      FRAC(I)=1.0
      FRACIN(I)=1.0
      DO 130 J=1,3
      PHASE(I,J)=COND(J)
  130 CONTINUE
  135 CONTINUE
C
C  MAXIMUM NUMBER OF ITERATIONS, CONVERGENCE CRITERION AND OPTIONS
C
      READ(IRD,136) IDEBUG,IOPT,ISS,IWRAP,MAXIT,NMAX,CNVG,TINC,PINC,
     &              RLXMIN
  136 FORMAT(6I5,4F10.0)
      IF(IWRAP.EQ.3) IFILE=IART
C
C  SET THE LOOP LIMITS FOR THE TEMPERATURE, PRESSURE AND COMPOSITION
C  LOOPS.  THE COMPOSITION LOOP STARTS HERE
C
      NCMP=1
      NTP=1
      IF(ICPT.EQ.1.OR.IOPT.EQ.2) NTP=NMAX
      IF(ICPT.EQ.3) NCMP=NMAX
      DO 2000 ICMP=1,NCMP
      IDATA=0
C
C  TOTAL NUMBER OF MOLES OF VAPOR AND MOLE FRACTIONS
C
      IF(V.EQ.0) GO TO 138
      READ(IRD,137) TOTMV
      READ(IRD,137) (FRACIN(I),I=1,V),FRCZIN
  137 FORMAT(6E12.5)
C
C  TOTAL NUMBER OF MOLES OF SOLUTION SPECIES, MOLE FRACTIONS
C  AND EXCESS FREE ENERGY CORRELATION PARAMETERS
C
  138 CONTINUE
      IF(S.EQ.0) GO TO 140
      READ(IRD,137) TOTMS
      READ(IRD,137) (FRACIN(I),I=VP1,VPS)
      READ(IRD,139) IXSCOR,AXS,BXS
  139 FORMAT(I5,2E12.5)
  140 CONTINUE
C
C  TOTAL NUMBER OF MOLES IN PURE CONDENSED PHASES
C
      IF(C.EQ.0) GO TO 142
      READ(IRD,137) (TOTMC(I),I=VPSP1,VSC)
  142 CONTINUE
C
C  SAVE THE ORIGINAL SPECIE ORDER SO THE PROBLEM
C  CAN BE PLACED IN THIS ORDER AFTER THE ITERATIVE PROCEDURE
```

```
C
      DO 165 I=1,VSC
      DO 165 K=1,3
      ISPCE(I,K)=SPECIE(I,K)
  165 CONTINUE
      IF(ICMP.GT.1.OR.IWRAP.EQ.3) GO TO 187
C
C  WRITE-OUT SOME OF THE INPUT DATA
C
      IPAGE=1
      WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
      WRITE(IWRT,410) T,P
      IF(IWRAP.GT.1) GO TO 187
      WRITE(IWRT,170)
  170 FORMAT('0',/,1X,T55,'HEAT CAPACITY CORRELATION COEFFICIENTS',
     &/,1X,T16,'ENTHALPY OF',T33,'ENTROPY OF',T58,'ICP=0:  CP = A0',
     &' + A1*T + A2/T**2 + A3*LN(T)',/,1X,T17,'FORMATION',T33,'FORMAT',
     &'ION',T58,'ICP=1:  CP = A0 + A1*T + A2*T**2 + A3*T**3',/,1X,T4,
     &'SPECIES',T20,'DH0',T37,'DS0',T54,'A0',T73,'A1',T93,'A2',T113,
     &'A3',T122,'ICP',/,1X,T4,'SYMBOL',T15,'(KCAL/G-MOLE)',T30,
     &'(KCAL/G-MOLE-K)',T47,'(KCAL/G-MOLE-K)',T65,'(KCAL/G-MOLE-K**2)',
     &T86,'(.............)',T106,'(.............)',T122,'(-)',
     &/,'+',12('_'),T15,13('_'),T30,15('_'),T47,15('_'),
     &T65,18('_'),T86,15('_'),T106,15('_'),T122,3('_'))
      DO 180 I=1,VSC
      WRITE(IWRT,175) (SPECIE(I,K),K=1,3),DH0(I),DS0(I),A0(I),A1(I),
     &                A2(I),A3(I),ICP(I)
      IF(I.EQ.V) WRITE(IWRT,175) (INERT(K),K=1,3),DH0Z,DS0Z,A0Z,A1Z,
     &                           A2Z,A3Z,ICPZ
  175 FORMAT(1X,3A4,T17,F9.3,T33,F9.6,T50,F9.6,T68,E12.5,T88,E12.5,
     &T108,E12.5,T123,I1)
  180 CONTINUE
      WRITE(IWRT,184) T0,P0,MAXIT,CNVG,IDEBUG
  184 FORMAT('0',/,'0',T10,'THE ENTHALPY AND ENTROPY OF FORMATION ',
     &'REFERENCE TEMPERATURE AND PRESSURE ARE:',5X,'T0 = ',F6.1,' K',
     &5X,'P0 = ',F9.1,' PA',/,'0',T35,'MAXIMUM NUMBER OF ITERATIONS ',
     &'ALLOWED = ',I5,/,'0',T50,'CONVERGENCE CRITERION = ',E12.4,
     &/,'0',T48,'OUTPUT PARAMETER IDEBUG = ',I2)
      IF(S.GT.1) WRITE(IWRT,185) IXSCOR,AXS,BXS
  185 FORMAT('0','EXCESS FREE ENERGY CORRELATION DATA :',
     &       2X,'IXSCOR = ',I5,5X,'AXS = ',E12.5,5X,'BXS = ',E12.5)
      IF(ISS.GT.0) WRITE(IWRT,186) ISS
  186 FORMAT('0',T24,'ISS= ',I2,'  THE III-V LIQUID SOLUTION IS ',
     &       'AT EQUILIBRIUM WITH THE III-V STOICHIOMETRIC SOLID')
  187 CONTINUE
C
C  THE TEMPERATURE AND PRESSURE LOOPS BEGIN HERE
C
      DO 2000 ITP=1,NTP
      IF(ICPT.EQ.1.AND.ITP.GT.1) T=T+TINC
      IF(ICPT.EQ.2.AND.ITP.GT.1) P=P+PINC
C
C  CALCULATE THE STANDARD STATE CHEMICAL POTENTIALS
C  AND AN INITIAL ESTIMATE OF THE EQUILIBRIUM COMPOSITIONS
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217 C
218       CALL STSTCP(A0,A1,A2,A3,A0Z,A1Z,A2Z,A3Z,DH0,DS0,DH0Z,DS0Z,STDCP,
219      &            STDCPZ,ICP,ICPZ,T0,T,IDIM1,V,S,C)
220       IF(ITP.GT.1.AND.ISS.EQ.0) GO TO 195
221       DO 190 I=1,VPS
222       FRAC(I)=FRACIN(I)
223   190 CONTINUE
224       FRACZ=FRCZIN
225       CALL ESTMTE(TOTMV,TOTMS,TOTMC,FRAC,N,FRACZ,ZV,
226      &                              IDIM1,V,S,C)
227   195 CONTINUE
228 C
229 C  SOURCE ZONE STEADY-STATE LIQUID COMPOSITION MODEL
230 C
231       IF(ISS.GT.0) CALL STEADY(SPECIE,A,STDCP,ELMNT,XIII,T,T0,V,S,C,
232      &                              IDIM1,IDIM2,ISS,IWRT)
233 C
234 C  CALCULATE THE TOTAL GRAM-MOLES OF EACH ELEMENT
235 C  BASED ON THE INITIAL COMPOSITION ESTIMATES IN THE PHASES
236 C
237       DO 200 J=1,E
238       BCALC(J)=0.
239       DO 200 I=1,VSC
240       BCALC(J)=A(I,J)*N(I)+BCALC(J)
241       B(J)=BCALC(J)
242   200 CONTINUE
243       IF(IWRAP.GT.1) GO TO 476
244       IF(ITP.GT.1) GO TO 472
245 C
246 C  WRITE-OUT THE INITIAL COMPOSITION ESTIMATES, STANDARD STATE
247 C  CHEMICAL POTENTIALS AND THE ELEMENTAL ABUNDANCE MATRIX
248 C
249       IPAGE=IPAGE+1
250       WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
251   400 FORMAT('1',/,'0',T34,'STOICHIOMETRIC FORMULATION FOR DETERMINING',
252      &       ' EQUILIBRIUM COMPOSITIONS',/,'0',T30,20A4,T120,
253      &       'PAGE ',I2)
254       WRITE(IWRT,410) T,P
255   410 FORMAT('0',T43,'TEMPERATURE = ',F6.1,' K',5X,'PRESSURE = ',E12.5,
256      &       ' PA')
257       WRITE(IWRT,420) (ELMNT(K),K=1,13)
258   420 FORMAT('0',/,T48,'INPUT DATA AND INITIAL COMPOSITION ESTIMATES',
259      &/,'0',T29,'INITIAL',T43,'STANDARD',/,1X,T27,'COMPOSITION',
260      &T43,'CHEMICAL',/,1X,T4,'SPECIES',T29,'ESTIMATE',T42,'POTENTIAL',
261      &T72,'ELEMENTAL ABUNDANCE MATRIX',/,1X,T4,'SYMBOL',T17,'PHASE',
262      &T28,'(G-MOLES)',T40,'(KCAL/G-MOLE)',T55,13(A2,4X),/,'+',
263      &12('_'),T15,9('_'),T25,14('_'),T40,13('_'),T55,78('_'))
264       DO 440 I=1,VSC
265       WRITE(IWRT,430) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),N(I),
266      &                    STDCP(I),(A(I,J),J=1,E)
267         IF(I.EQ.V) WRITE(IWRT,430) (INERT(K),K=1,3),(PHASE(I,K),K=1,3),
268      &                              ZV,STDCPZ
269   430 FORMAT(1X,3A4,T15,3A3,T25,G14.7,T42,F6.3,T55,13(F5.3,1X))
270   440 CONTINUE
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      IF(ISS.GT.0) WRITE(IWRT,445) XIII
  445 FORMAT(4X,'X=',F6.4)
      WRITE(IWRT,450)
  450 FORMAT('0',/,'0',T44,'TOTAL GRAM-MOLES OF EACH ELEMENT FROM IN',
     &       'PUT DATA',/,1X,T40,'AND AS CALCULATED FROM THE INITIAL',
     &       ' COMPOSITION ESTIMATES',/,'0',4(4X,'INPUT DAT-',3X,
     &       'CALCULATED',5X))
      NPRT=E/4
      NCHK=NPRT*4
      IF(NCHK.NE.E) NPRT=NPRT+1
      ISTRT=1
      DO 470 K=1,NPRT
      NEND=ISTRT+3
      IF(NEND.GT.E) NEND=E
      WRITE(IWRT,460) (ELMNT(J),B(J),BCALC(J),J=ISTRT,NEND)
  460 FORMAT(1X,4(A2,1X,E12.5,1X,E12.5,4X))
      ISTRT=NEND+1
  470 CONTINUE
  472 CONTINUE
      IPAGE=IPAGE+1
      WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
      WRITE(IWRT,410) T,P
      WRITE(IWRT,475)
  475 FORMAT('0',T58,'EXECUTION DIAGNOSTICS',/,'+',T58,9('_'),1X,
     &       11('_'),/,'0')
  476 CONTINUE
C
C  DIVIDE THE STANDARD STATE CHEMICAL POTENTIALS BY RT
C
      RT=0.0019872*T
      DO 480 I=1,VSC
      STDCP(I)=STDCP(I)/RT
  480 CONTINUE
      STDCPZ=STDCPZ/RT
C
C  CALCULATE THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR PHASE
C  AND WRITE-OUT THE INITIAL RESULTS TO THE WRAPUP FILE
C
      IF(ITP.GT.1.OR.IWRAP.EQ.0) GO TO 485
      CALL TOTSI(A,ELMNT,FRAC,N,SITOT,SIMF,ACTSIS,T,P,IDIM1,IDIM2,V,E)
      CALL RATIO(A,ELMNT,FRAC,N,STDCP,ACTGAS,ACTINS,ACTASS,ACTPS,
     &           RIIIV,RGAAS,RINP,T,P,T0,P0,IDIM1,IDIM2,V,E)
      ITBST=1
      BSTCVG=0
      CALL WRAPUP(TITLE,SPECIE,INERT,N,FRAC,QUES,ZV,FRACZ,SITOT,SIMF,
     &          ACTSIS,ACTGAS,ACTINS,ACTPS,ACTASS,RIIIV,RGAAS,RINP,
     &    BSTCVG,ITBST,CNVG0,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE,V,VSC)
  485 CONTINUE
C
C  ITERATIVE SOLUTION FOR THE EQUILIBRIUM COMPOSITIONS
C
      RELMAX=1.0E10
      IACPP=0
      DO 600 ITER=1,MAXIT
```

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C
C  DETERMINE THE OPTIMUM SET OF BASIS SPECIES
C
      CALL CPTBAS(N,NESTN,A,D,DPRIME,STOCP,SPECIE,PHASE,AC,A1,A2,A3,
     &BGUESS,IHD,IBD,ICP,IDXBAS,ITER,IDIM1,IDIM2,V,S,C,E,ISTOP,ICHNG,
     &IWRT)
      IF(ISTOP.EQ.1) GO TO 604
      IF(ITER.GT.1.AND.ICHNG.EQ.0) GO TO 500
      IF(IDEBUG.LT.2) GO TO 490
      CALL IPVEC(IDXBAS,IDIM2,E,6HIDXBAS,IWRT)
      CALL PMAT(A,IDIM1,IDIM2,VSC,E,6HA     ,IWRT)
      CALL PMAT(D,IDIM2,IDIM2,E,E,6HD     ,IWRT)
      CALL DPMAT(DPRIME,IDIM2,IDIM2,E,E,6HDPRIME ,IWRT)
  490 CONTINUE
C
C CALCULATE THE STOICHIOMETRIC COEFFICIENTS AND THE EQUILIBRIUM CONSTANTS
C
      CALL EQCON(A,D,DD,DINV,DO,GNU,STOCP,KEQ,IDXBAS,WKA,ET,
     &           ITER,IDIM1,IDIM2,V,S,C,E,ISTOP,IWRT)
      IF(ISTOP.EQ.1) GO TO 604
      IF(IDEBUG.LT.2) GO TO 500
      CALL DPMAT(DINV,IDIM2,IDIM2,E,E,6HDINV  ,IWRT)
      CALL PMAT(GNU,IDIM1,IDIM2,VSC,E,6HGNU   ,IWRT)
      CALL PVEC(KEQ,IDIM1,VSC,6HKEQ   ,IWRT)
  500 CONTINUE
C
C  CALCULATE THE ACTIVITY COEFFICIENTS
C
      CALL ACTCOF(FRAC,ACOEF,ISPCE,SPECIE,INDEX,IDIM1,RELMAX,IXSOLV,
     &           AXS,BXS,T,IACOF,V,S,C,IWRT)
C
C  CALCULATE THE EQUILIBRIUM CONSTANTS FROM THE CURRENT COMPOSITIONS
C
      CALL CALCQ(GNU,N,ACOEF,FRAC,PHASE,VAPOR,SOLN,IDXBAS,C,
     &           ZV,FRACZ,P,PO,V,S,C,E,IDIM1,IDIM2,IWRT)
C
C  CALCULATE THE ERROR BETWEEN THE EQUILIBRIUM CONSTANTS
C  CALCULATED BY THE COMPOSITIONS AND THE EQUILIBRIUM CONSTANTS
C  CALCULATED FROM THE GIBBS FREE ENERGY CHANGE
C
      RELMAX=0.
      DO 590 I=1,VSC
      QUES(I)=BLNKS
      DO 570 J=1,E
      IF(I.EQ.IDXBAS(J)) GO TO 590
  570 CONTINUE
      RELERR=(KEQ(I)-Q(I))/KEQ(I)
C
C  ASSIGN "?" TO QUES(I) IF THE CONVERGENCE CRITERION IS NOT MET
C  AND "??" TO QUES(I) IF THERE IS LESS THAN ONE SIGNIFICANT FIGURE
C
      IF(ABS(RELERR).GT.CNVG) QUES(I)=QUEST1
      IF(ABS(RELERR).GT.0.1) QUES(I)=QUEST2
      IF(ABS(RELERR).GT.RELMAX.AND.N(I).GT.1.0E-21)
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379       &                    RELMAX=ABS(RELERR)
380    590 CONTINUE
381 C
382 C  KEEP THE BEST ESTIMATE TO THE EQUILIBRIUM SOLUTION
383 C  IN CASE THE NUMERICAL PROCEDURE DIVERGES
384 C
385        IF(ITER.GT.1.AND.RELMAX.GT.BSTCVG) GO TO 594
386        BSTCVG=RELMAX
387        ITBST=ITER
388        DO 593 IBEST=1,VSC
389        BQUES(IBEST)=QUES(IBEST)
390        BESTN(IBEST)=N(IBEST)
391    593 CONTINUE
392    594 CONTINUE
393        IF(RELMAX.LE.CNVG) GO TO 610
394        IF(IDEBUG.EQ.2) CALL PVEC(FRAC,IDIM1,VSC,6HFRAC  ,IWRT)
395        IF(IDEBUG.GE.1) CALL PVEC(Q,IDIM1,VSC,6HQ      ,IWRT)
396        IF(ITER.EQ.MAXIT) GO TO 595
397 C
398 C  MAKE ADJUSTMENTS TO THE EXTENTS OF REACTION
399 C
400        CALL ADJEXT(N,KEQ,Q,GNU,DZETA,IDXBAS,COND,PHASE,IDIM1,IDIM2,
401       &            V,S,C,E,IWRT)
402        CALL CNVFRC(N,NTEMP,STDCP,ACOEF,DZETA,GNU,IDXBAS,VAPOR,COND,
403       &      SOLN,PHASE,ZV,RT,P,P0,RLXMIN,LAMBDA,IDIM1,IDIM2,V,S,C,E)
404        CALL CONVEL(N,DZETA,GNU,IDXBAS,IDIM1,IDIM2,LAMBDA,VSC,E)
405    595 IF(ITER.LT.MAXIT) GO TO 597
406 C
407 C  IF THE SOLUTION DID NOT CONVERGE TRANSFER THE BEST ESTIMATE
408 C  TO THE EQUILIBRIUM SOLUTION FROM VECTOR BESTN INTO N.
409 C
410        DO 596 IBEST=1,VSC
411        QUES(IBEST)=BQUES(IBEST)
412        N(IBEST)=BESTN(IBEST)
413    596 CONTINUE
414    597 CONTINUE
415        CALL CALCQ(GNU,N,ACOEF,FRAC,PHASE,VAPOR,SOLN,IDXBAS,Q,
416       &            ZV,FRACZ,P,P0,V,S,C,E,IDIM1,IDIM2,IWRT)
417        IF(IDEBUG.EQ.0) GO TO 600
418        CALL GIBBS(N,STDCP,STDCPZ,ACOEF,FRAC,ZV,FRACZ,COND,SOLN,PHASE,
419       &            RT,P,P0,IDIM1,V,S,C,GFE)
420        CALL DEBUG(N,DZETA,VSC,IDIM1,ITER,LAMBDA,GFE,RELMAX,IWRT)
421    600 CONTINUE
422    604 CONTINUE
423        IF(IWRAP.LT.3) WRITE(IWRT,605)MAXIT,RELMAX,BSTCVG,ITBST
424    605 FORMAT('0','***** ITERATION FOR EQUILIBRIUM COMPOSITION ',
425       &       'DID NOT CONVERGE *****',
426       &'       (AFTER ',I4,' ITERATIONS RELMAX =',E12.5,' )',
427       &/,'0','  BEST CONVERG. WAS',E12.5,' AT ITERATION ',I4)
428    610 CONTINUE
429        CALL GIBBS(N,STDCP,STDCPZ,ACOEF,FRAC,ZV,FRACZ,COND,SOLN,PHASE,
430       &            RT,P,P0,IDIM1,V,S,C,GFE)
431 C
432 C  CALCULATE THE GRAM-MOLES OF EACH ELEMENT AFTER THE ITERATIONS
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      C
            DO 700 J=1,E
            BCALC(J)=0.0
            DO 700 I=1,VSC
            BCALC(J)=BCALC(J)+A(I,J)*N(I)
        700 CONTINUE
      C
      C  CALCULATE THE CHEMICAL POTENTIAL OF EACH SPECIE
      C
            DO 800 I=1,VSC
            PPO=1.0
            IF(PHASE(I,1).EQ.VAPOR(1)) PPO=P/PO
            ARG=FRAC(I)*ACOEF(I)*PPO
            CHMPT(I)=RT*(STDCP(I)+ALOG(ARG))
        800 CONTINUE
            ARG=1.0
            IF(FRACZ.GT.0.0) ARG=FRACZ*P/PO
            CHMPTZ=RT*(STDCPZ+ALOG(ARG))
            DO 810 I=1,VSC
            DO 810 K=1,3
            BSPCE(I,K)=SPECIE(I,K)
        810 CONTINUE
      C
      C  PUT THE MATRICIES AND VECTORS INTO THE ORIGINAL PROBLEM STATEMENT ORDE
      C
            CALL ORDER(ISPCE,SPECIE,PHASE,N,A,STDCP,BO,A1,A2,A3,DH0,DS0,
           &DZETA,CHMPT,ACOEF,FRAC,GUESS,DG,G,KEQ,ICP,IDIM1,IDIM2,E,VSC,
           &IWRT)
      C
      C  CALCULATE THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR PHASE
      C
            CALL TOTSI(A,ELMNT,FRAC,N,SITOT,SIMP,ACTSIS,T,P,IDIM1,IDIM2,V,E)
            CALL RATIO(A,ELMNT,FRAC,N,STDCP,ACTGAS,ACTINS,ACTAUS,ACTPS,
           &           RIIIV,AGAAS,PINP,T,P,T0,PO,IDIM1,IDIM2,V,E)
            IF(IWRAP.GT.1) GO TO 971
      C
      C  WRITE-OUT THE RESULTS
      C
             IPAGE=IPAGE+1
            WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
            WRITE(IWRT,410) T,P
            WRITE(IWRT,900) ITBST,CFE,BSTCVG,CNVG,LAMBDA
        900 FORMAT('0',/,1X,T45,'EQUILIBRIUM COMPOSITIONS AFTER ',I5,
           &' ITERATIONS',/,'0',T42,'SYSTEM GIBBS FREE ENERGY = ',E14.7,
           &' (KCAL)',
           & /,'0','RELATIVE ERROR = ',E12.5,5X,'CONVERGENCE CRITERION = ',
           & E12.5,5X,'RELAXATION PARAMETER AT LAST ITERATION = ',E12.5,
           & /,'0',T57,'ESTIMATED',/,1X,T25,'EQUILIBRIUM',T39,'EQUILIBRIUM',
           & T56,'COMPOSITION',T92,'CHEMICAL',
           & /,1X,T4,'SPECIE',T29,'MOLE',T39,'COMPOSITION',T56,
           & 'UNCERTAINTY',T91,'POTENTIAL',T109,'ACTIVITY',
           & /,1X,T4,'SYMBOL',T17,'PHASE',T27,'FRACTION',T40,'(G-MOLES)',
           & T57,'(G-MOLES)',T90,'(KCAL/G-MOLE)',T107,'COEFFICIENT',
           & /,'+',12('_'),T15,9('_'),T25,12('_'),T37,14('_'),T54,
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     &  14('_'),T59,14('_'),T106,12('_'))
      ZZETA=0.0
      ZACT=1.0
      DO 920 I=1,VSC
      WRITE(IWRT,910) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),FRAC(I),
     &                 N(I),DZETA(I),CHMPT(I),ACTCF(I)
      IF(I.EQ.V) WRITE(IWRT,910) (INERT(K),K=1,3),(PHASE(I,K),K=1,3),
     &                           FRACZ,ZV,ZZETA,CHMPTZ,ZACT
  910 FORMAT(1X,3A4,T15,3A3,T24,E12.5,T37,E14.7,T54,E14.7,T92,F9.5,
     &T106,E12.5)
  920 CONTINUE
      IF(ISS.GT.0) WRITE(IWRT,945) XIII
      WRITE(IWRT,930) SIMF
  930 FORMAT('0',T35,'MOLE FRACTION OF SILICON SPECIES IN ',
     &       'VAPOR PHASE = ',E12.5)
      WRITE(IWRT,940) RIIIV
  940 FORMAT('0',T50,'III/V RATIO IN THE VAPOR PHASE = ',F9.4)
      WRITE(IWRT,950)
  950 FORMAT('0',/,'0',T44,'TOTAL GRAM-MOLES OF EACH ELEMENT FROM INP',
     &'PUT DATA',/,1X,T42,'AND AS CALCULATED FROM THE EQUILIBRIUM',
     &       ' COMPOSITIONS',/,'0',4(4X,'INPUT DATA',3X,
     &       'CALCULATED',5X))
      NPRT=E/4
      NCHK=NPRT*4
      IF(NCHK.NE.E) NPRT=NPRT+1
      ISTRT=1
      DO 970 K=1,NPRT
      NEND=ISTRT+3
      IF(NEND.GT.E) NEND=E
      WRITE(IWRT,960) (ELMNT(J),E(J),FCALC(J),J=ISTRT,NEND)
  960 FORMAT(1X,4(A2,1X,F12.5,1X,E12.5,4X))
      ISTRT=NEND+1
  970 CONTINUE
  971 CONTINUE
      IF(IWRAP.GT.3) CALL WRAPUP(TITLE,SPECIE,INERT,N,FRAC,QUEST,ZV,FRACZ
     &,SITCT,SIMF,ACTSIS,ACTCAS,ACTINS,ACTRS,ACTASS,RIIIV,AGAMF,SINF,
     &BSTCVG,ITOST,RELMAX,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE,V,VSC)
      IF(ITP.GT.1.OR.ICMP.GT.1.OR.IWRAP.GT.1) GO TO 1000
C
C  WRITE-OUT THE INDEPENDENT REACTION EQUATIONS
C
      IPAGE=IPAGE+1
      WRITE(IWRT,400) (TITLE(K),K=1,20), IPAGE
      WRITE(IWRT,410) T,P
      WRITE(IWRT,980)
  980 FORMAT('0',T34,'A SET OF INDEPENDENT REACTION EQUATIONS FOR ',
     &       'THIS SYSTEM IS AS FOLLOWS:',/,'0')
      DO 1100 I=1,VSC
C
C  DETERMINE THE NUMBER OF BASIS SPECIES IN EACH FORMATION REACTION
C
      NSPEC=0
      DO 990 K=1,E
      IF(I.EQ.IDXBAS(K)) GO TO 1100
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      IF(ABS(GNU(I,K)).LT.1.0E-6) GO TO 990
      NSPEC=NSPEC+1
  990 CONTINUE
C
C  FILL THE CHARACTER ARRAY "STRING" WITH THE FORMULA OF EACH SPECIES
C
      NLOOP=1
      IF(NSPEC.GT.4) NLOOP=FLOAT(NSPEC)/4.0+0.5
      DO 1000 K=1,3
      STRING(1,K)=BSPCE(I,K)
 1000 CONTINUE
      STRING(1,4)=RPAS
      COEFF(1)=1.0
      IST=1
      ICNT=0
      DO 1060 ILOOP=1,NLOOP
      NCNT=NSPEC-ICNT+1
      IF(NCNT.GT.5) NCNT=5
      DO 1020 IDX=2,NCNT
      ICNT=ICNT+1
      DO 1015 IBASE=IST,5
      IF(ABS(GNU(I,IBASE)).LT.1.0E-6) GO TO 1015
      IDXB=IDXBAS(IBASE)
      DO 1010 K=1,3
      STRING(IDX,K)=BSPCE(IDXB,K)
 1010 CONTINUE
      COEFF(IDX)=GNU(I,IBASE)
      STRING(IDX,4)=RPSPS
      GO TO 1018
 1015 CONTINUE
 1018 IST=IBASE+1
 1020 CONTINUE
      STRING(NCNT,4)=RPBL
      IF(ILOOP.EQ.1) WRITE(IWRT,1040)(LP,COEFF(IJK),
     &                                (STRING(IJK,K),K=1,4),IJK=1,NCNT)
 1040 FORMAT('0',A1,F5.2,4A4,4(A1,E10.3,4A4))
      IF(ILOOP.GT.1) WRITE(IWRT,1050) SSPS,(LP,COEFF(IJK),
     &                                (STRING(IJK,K),K=1,4),IJK=2,NCNT)
 1050 FORMAT(1X,T20,A4,4(A1,E10.3,4A4))
 1060 CONTINUE
 1100 CONTINUE
C
C  WRITE-OUT A COMPARISON BETWEEN THE EQUILIBRIUM CONSTANTS
C  AS CALCULATED BY THE GIBBS FREE ENERGY CHANGE AND BY COMPOSITION
C
      IPAGE=IPAGE+1
      WRITE(IWRT,400) (TITLE(K),K=1,20), IPAGE
      WRITE(IWRT,410) T,P
      WRITE(IWRT,1110)
 1110 FORMAT('0',/,1X,T43,'EQUILIBRIUM CONSTANTS FOR THE INDEPENDENT',
     &' REACTIONS',/,'0',T20,'GIBBS FREE ENERGY CHANGE',T47,
     &'EQUILIBRIUM CONSTANT',T73,'EQUILIBRIUM CONSTANT',/,1X,
     &'REACTION PRODUCT',T25,'(KCAL/G-MOLE)',T43,'FROM GIBBS FREE ',
     &'ENERGY',T70,'FROM PREDICTED COMPOSITION',/,'+',132('_'),T20),
```

```
595       &24('_'),T45,22('_'),T70,2e('_'))
596        DO 1200 I=1,NSC
597        IF(N(I).GT.1.0D-21) WRITE(IWRT,1120) (SPECIE(I,K),K=1,3),G(I),
598       &                                                  KEQ(I),Q(I)
599        IF(N(I).LE.1.0D-21) WRITE(IWRT,1121) (SPECIE(I,K),K=1,3),G(I),
600       &                                                  KEQ(I),Q(I)
601   1120 FORMAT(1X,3A4,T28,F8.3,T51,E12.5,T77,E12.5)
602   1121 FORMAT(1X,3A4,T28,F8.3,T51,E12.5,T77,E12.5,2X,'(NOT BINDING)')
603   1200 CONTINUE
604        IF(ISS.GT.0) WRITE(IWRT,445) XIII
605   1900 IF(ISTOP.EQ.1) GO TO 3000
606   2000 CONTINUE
607   3000 WRITE(IWRT,3001)
608   3001 FORMAT('1',' ')
609        STOP
610        END
```

B.3 A Description of the Major Variables in MCMPEQ.STOIC

Variables which are used in the IMSL subroutines LINVIF, LEQTIF, LUDATF and LUELMF are not included in this list. FORTRAN default typing applies unless otherwise specified.

Variable	Description	Units
A (I,J)	elemental abundance matrix	$\frac{\text{atoms of element j}}{\text{molecule of specie i}}$
ACOEF (I)	activity coefficient of specie i	-
AMAX	maximum value the convergence forcer may attain	-
AMIN	minimum value the convergence forcer may attain	-
AXS	activity coefficient correlation parameter	variable
A0 (I)	heat capacity correlation parameter	kcal/g-mole-K
A1 (I)	heat capacity correlation parameter	kcal/g-mole-K^2
A2 (I)	heat capacity correlation parameter	variable
A3 (I)	heat capacity correlation parameter	variable
A0Z	inert specie heat capacity correlation parameter	kcal/g-mole-K
A1Z	inert specie heat capacity correlation parameter	kcal/g-mole-K^2
A2Z	inert specie heat capacity correlation parameter	variable
A3Z	inert specie heat capacity correlation parameter	variable

Variable	Description	Units
B (J)	moles of element J specified in the system	g-moles
BCALC (J)	moles of element J as calculated by algorithm	g-moles
BESTN	The best estimate to the equilibrium mole numbers	g-moles
BXS	activity coefficient correlation parameter	variable
C	number of pure condensed phases (integer)	-
CHMPT (I)	chemical potential of specie i	kcal/g-mole
CHMPTZ	chemical potential of the inert	kcal/g-mole
CNVG	composition convergence criterion	-
COND (3)	vector containing the character string 'CONDENSED'	-
D (I, J)	matrix of basis species	$\frac{\text{atoms of j}}{\text{molecule of i}}$
DELH	total enthalpy change	kcal/g-mole
DELN (I)	change in moles of specie i	g-mole
DELS	total entropy change	kcal/g-mole-K
DG (I)	Gibbs Free Energy change of reaction i	kcal/g-mole
DGDL	change in system Gibbs Free Energy with respect to the convergence forcer	kcal/g-mole

Variable	Description	Units
DHO (I)	enthalpy of formation of specie i	kcal/g-mole
DHOZ	enthalpy of formation of the inert specie	kcal/g-mole
DINV (I, J)	inverse of matrix D	-
DPRME (I, J)	Gram-Schmidt orthogonalization of matrix D	-
DSO (I)	entropy of formation of specie i	kcal/g-mole-K
DSOZ	entropy of formation of the inert specie	kcal/g-mole-K
DZETA(I)	change in reaction extent for specie	-
E	number of elements in the system (integer)	-
ELIII (K)	vector containing character string of group III elements	-
ELMNT (J)	vector containing character strings of the elements present in the system	-
ELV (K)	vector containing character strings of group V element	-
EPCP2	E + C + 2 (integer)	-
EP3	E + 3 (integer)	-
EP3PC	E + 3 + C (integer)	-
FRAC (I)	mole fraction of specie i in its phase	-
FRACZ	mole fraction of inert in the vapor	-

Variable	Description	Units
GNU (I, J)	formation reaction coefficient matrix	g-mole
GFE	Gibbs free energy of the system	kcal/g-mole
GSTAR	GFE divided by RT	-
IACFF	activity coefficient switch	-
IALG	convergence forcer algorithm switch	-
ICHNG	parameter which indicates whether or not the basis species have changed	-
ICMP	index for the composition loop	-
ICP (I)	heat capacity correlation parameter	-
IDATA	switch used with the wrap-up file	-
IDGT	number of significant figures in each matrix element	-
IDIM1	maximum number of species allowed in system	-
IDIM2	maximum number of elements allowed in system	-
IDEBUG	option to aid in trouble-shooting	-
IDXBAS (J)	vector containing the index of each basis specie	-
IFILE	logical unit designator of the wrap-up file	-
INERT (3)	vector containing the inert specie name	-

Variable	Description	Units
IOPT	parameter to allow various computational options	-
IOUT	number of pure condensed phases removed by subroutine ADDRMV	-
IRD	logical unit designator for data input	-
ISPCE (I, J)	array containing the original specie order	-
ISS	steady state option parameter	-
ISTOP	switch which halts the computation if problems develope	-
ITER	current iteration number in the equilibrium calculation	-
ITP	index for the temperature and pressure loop	-
ITST	parameter which indicates linear dependence in the basis specie matrix	-
IWRAP	switch used with the wrap-up file	-
IWRT	logical unit designator for data output	-
IXSCOR	parameter which chooses the solution phase activity coefficient model	-
KEQ (I)	equilibrium constant for formation reaction i as calculated from the Gibbs Free Energy change (real)	-
LAMBDA	convergence forcer (real)	-
MAXIT	maximum number of iterations to be used	-
N (I)	moles of specie i (real)	g-moles
NMAX	total number of loops to be made in the composition or temperature and pressure loops	-

Variable	Description	Units
NS	total moles in solution (real)	g-moles
NSPEC	number of species in the formation reaction	-
NV	total moles in the vapor (real)	g-moles
P	system pressure	Pa
PHASE (I, 3)	matrix containing a character string to denote the phase of each specie	-
PINC	pressure increment for each loop	Pa
PO	formation data reference pressure	Pa
Q (I)	equilibrium constant for formation reaction i as calculated from composition	-
RELERR	fractional change between KEQ(I) and Q(I)	-
RELMAX	maximum value of RELERR during an iteration	-
RLXMIN	The minimum allowable valve of the convergence forcer	-
RIIIV	vapor phase III/V atomic ratio	-
RT	product of the ideal gas constant and the temperature	kcal/g-mole
S	total number of species in the solution phase	-
SIMF	mole fraction of silicon species in the vapor	-
SITOT	moles of silicon species in the vapor	g-moles
SOLN (3)	vector containing the character string 'SOLUTION'	-

Variable	Description	Units
SPECIE (I, 3)	matrix of character strings containing the names of each specie	-
STDCP (I)	standard chemical potential of specie i	kcal/g-mole
STDCPZ	standard chemical potential of the inert	kcal/g-mole
SUMIII	total moles of group III atoms in the vapor	g-mole
SUMV	total moles of group V atoms in the vapor	g-mole
T	system temperature	K
TITLE (K)	vector containing an 80 character title	-
TINC	temperature increment for each loop	K
TOTMC (I)	total moles of pure condensed phase i as input	g-moles
TOTMOL	total moles in a single phase	g-moles
TOTMS	total moles in the solution phase	g-moles
TOTMV	total moles in the vapor phase	g-moles
TO	formation data reference temperature	K
V	total number of species in the vapor (integer)	-
VAPOR (3)	vector containing the character string 'VAPOR'	-

Variable	Description	Units
WKA	work area for LEQT1F	
WKA1	work area for LINV1F	
XIII	group III specie fraction in the steady state liquid "pure" condensed phase	-
ZV	moles of inert in the system	g-moles
ZACT	activity coefficient of the inert	-

B.4 Descriptions of the Subroutines

The subroutine structure of MCMPEC.STOIC is shown in Figure B2. Subroutine ERRSET is a system routine which is used to suppress the printing of various arithmetic error messages. This subroutine may not be available at all installations and therefore the two calls to ERRSET may have to be removed if this code is to be implemented on other systems.

The IMSL subroutine LINVIF is part of a package of routines which include LEQTIF, LUELMF and LUDATF. A brief discussion of this IMSL package is located in section B.4.19. The remaining subroutines are discussed in the following sections.

B.4.1 STSTCP

A listing of subroutine STSTCP is shown in Figure B3. STSTCP calculates the standard state chemical potential for each specie in the system. The reference state is the system temperature T, the formation pressure P_o, and pure component in the phase in which the specie is present.

The pure component Gibbs Free Energy (standard chemical potential) of specie i at temperatue T_o and pressure P_o is:

$$\mu_i^o (To,Po) = \underline{G}_i^o = \Delta\underline{H}_f^o - T_o \Delta\underline{S}_f^o \qquad (1)$$

For a system temperature T the standard chemical potential of specie i is given by:

$$\mu_i^o(T,Po) = \Delta\underline{H}_f\ (T_o) + \int_{T_o}^{T} C_p^i\, dT$$

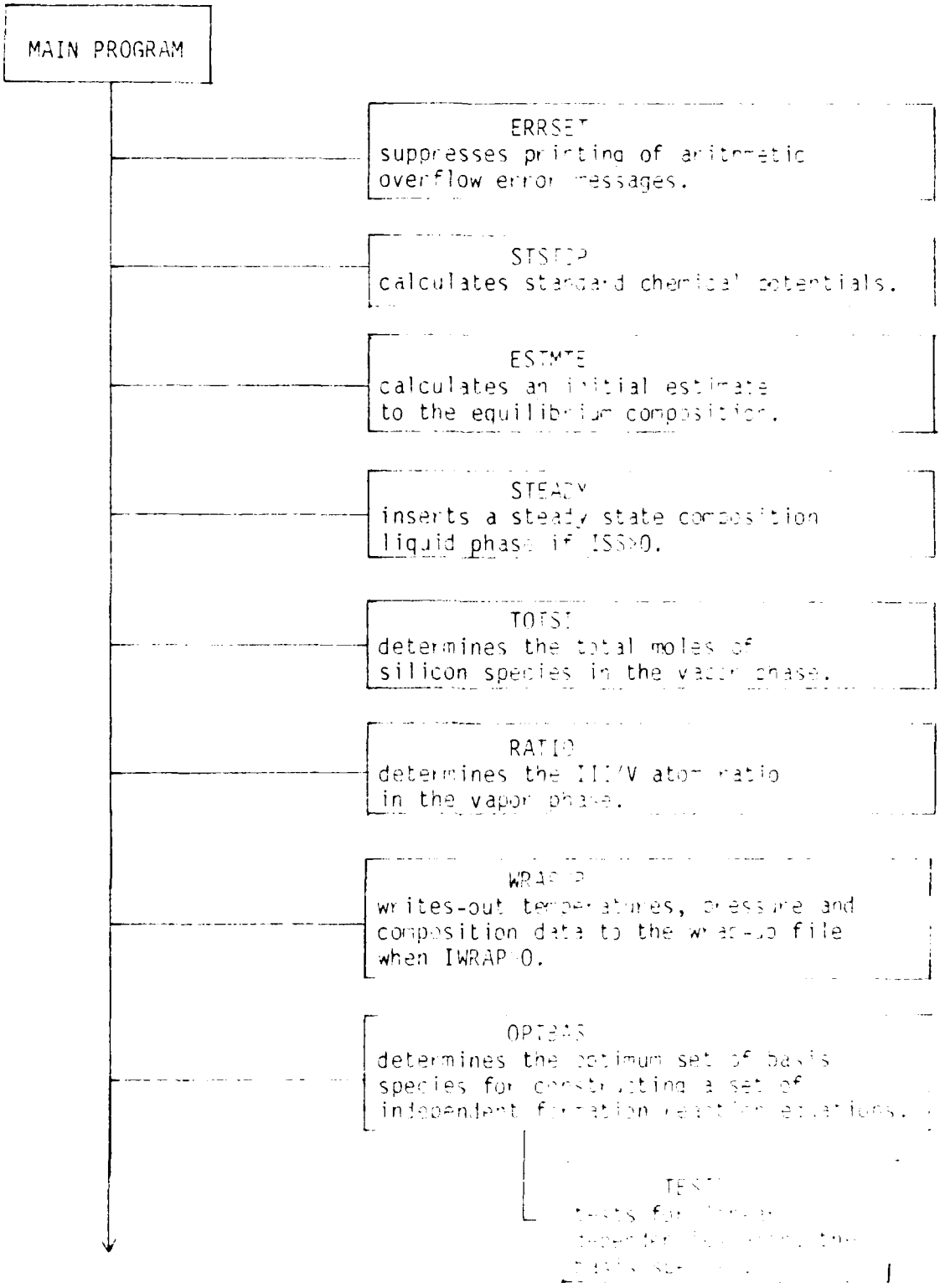
$$- T \left[\Delta\underline{S}_f(To) + \int_{T_o}^{T} \frac{C_p^i}{T}\, dT\right] \qquad (2)$$

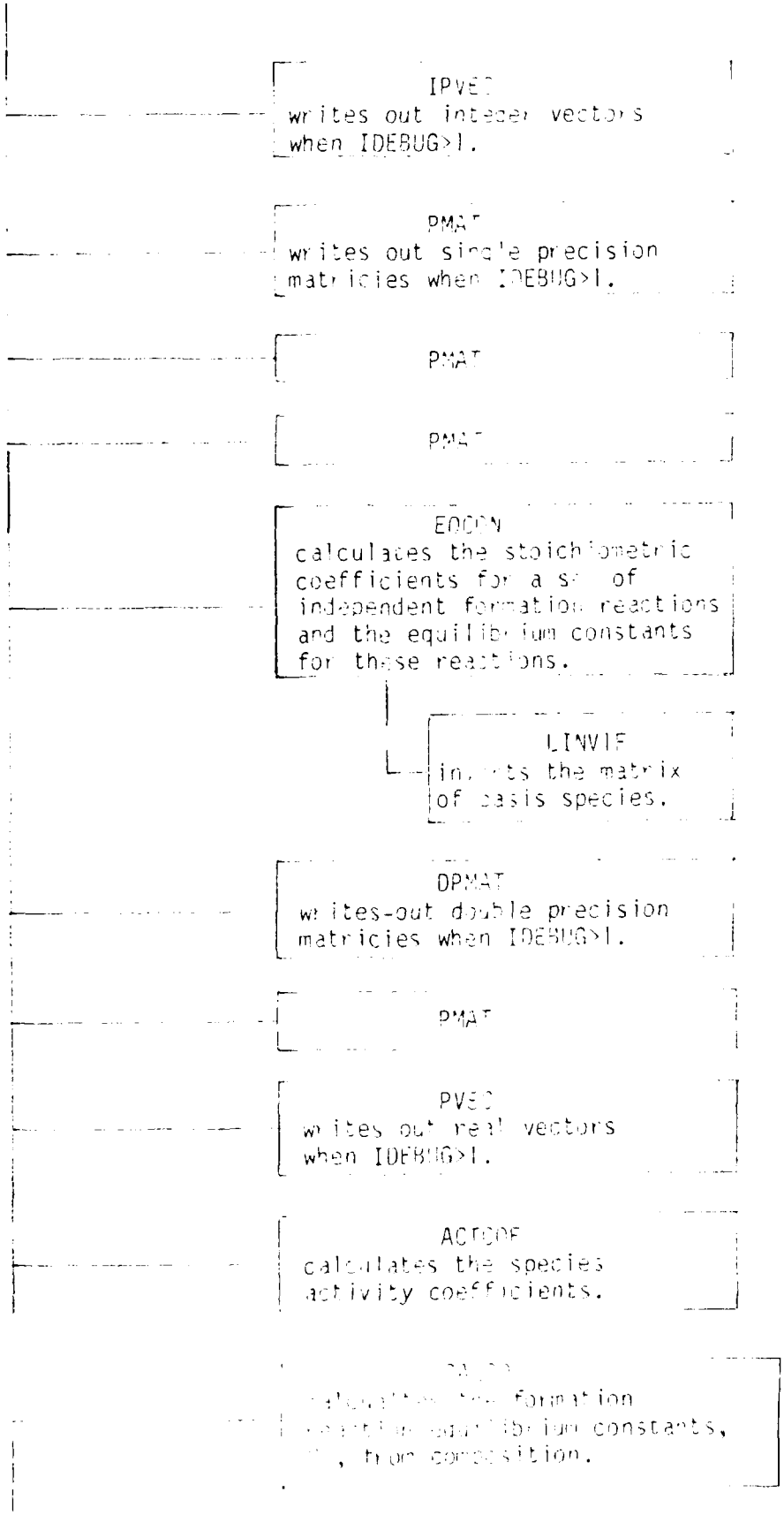
Two heat capacity correlations are available and are chosen by the parameter ICP. These correlations are:

ICP	Heat Capacity Correlation	
0	$Cp(T) = a_0 + a_1T + a_2T^{-2} + a_3\ ln(T)$	(3)
1	$Cp(T) = a_0 + a_1T + a_2T^2 + a_3\ T3$	(4)

Figure 32

Subprogram Structure of MOMPEC.STD11




IPVEC
writes out integer vectors when IDEBUG>1.
PMAT
writes out single precision matricies when IDEBUG>1.
PMAT
PMAT
EQCON
calculates the stoichiometric coefficients for a set of independent formation reactions and the equilibrium constants for these reactions.
LINVIF
inverts the matrix of basis species.
DPMAT
writes-out double precision matricies when IDEBUG>1.
PMAT
PVEC
writes out real vectors when IDEBUG>1.
ACTCOF
calculates the species activity coefficients.

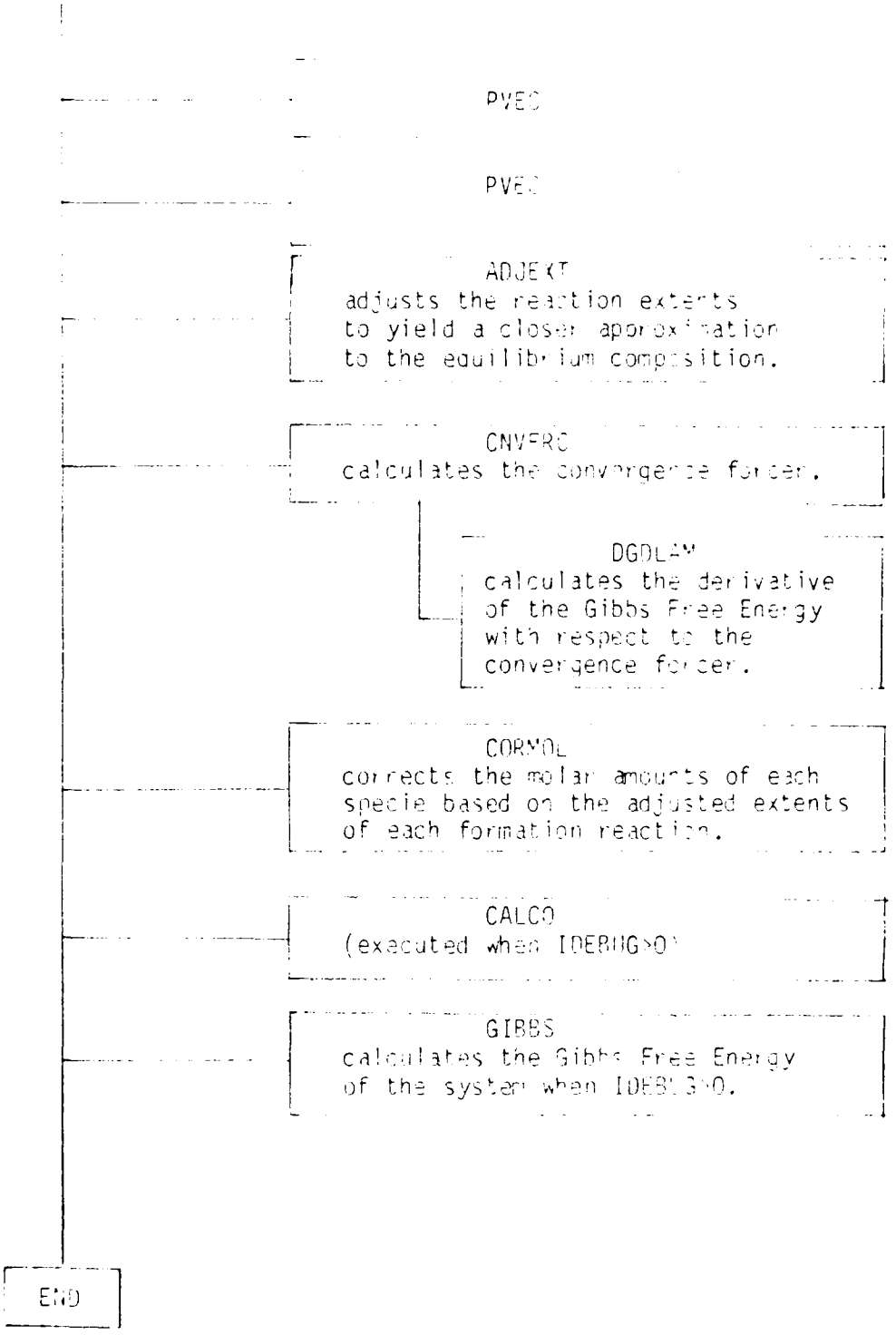

PVEC
PVEC
ADJEKT
adjusts the reaction extents
to yield a closer approximation
to the equilibrium composition.
CNVERG
calculates the convergence forcer.
DGDLAM
calculates the derivative
of the Gibbs Free Energy
with respect to the
convergence forcer.
CORMOL
corrects the molar amounts of each
specie based on the adjusted extents
of each formation reaction.
CALCO
(executed when IDEBUG>0)
GIBBS
calculates the Gibbs Free Energy
of the system when IDEBUG>0.
END

Figure B3. Subroutine STSTCP

```
      SUBROUTINE STSTCP(A0,A1,A2,A3,A0Z,A1Z,A2Z,A3Z,DH0,DS0,DH0Z,
     &                  STDCP,STDCPZ,ICP,ICPZ,T0,T,IDIM1,V,S,C)
C
C  THIS SUBROUTINE CALCULATES THE STANDARD STATE CHEMICAL POTENTIALS
C  REFERENCE STATE: PURE COMPONENT (APPROPRIATE PHASE)
C                   AT TEMPERATURE T.
C
      DIMENSION A0(IDIM1),A1(IDIM1),A2(IDIM1),A3(IDIM1),DH0(IDIM1),
     &          DS0(IDIM1),STDCP(IDIM1),ICP(IDIM1)
      INTEGER V,S,C,VSC
      VSC=V+S+C
      DT=T-T0
      DT2=T**2-T0**2
      DT3=T**3-T0**3
      DT4=T**4-T0**4
      DTM1=1.0/T-1.0/T0
      DTM2=1.0/T/T-1.0/T0/T0
      DLNT=ALOG(T)-ALOG(T0)
      DLNT2=ALOG(T)**2-ALOG(T0)**2
      DTLNT=T*ALOG(T)-T0*ALOG(T0)
C
C CHEMICAL POTENTIALS FOR THE VAPOR, SOLUTION AND CONDENSED PHASES
C
      DO 100 I=1,VSC
      DELH=A0(I)*DT+A1(I)*DT2/2.-A2(I)*DTM1+A3(I)*(DTLNT-DT)
      DELS=A0(I)*DLNT+A1(I)*DT-A2(I)*DTM2/2.+A3(I)*DLNT2/2.
      IF(ICP(I).EQ.1) DELH=A0(I)*DT+A1(I)*DT2/2.+A2(I)*DT3/3.
     &                          +A3(I)*DT4/4.
      IF(ICP(I).EQ.1) DELS=A0(I)*DLNT+A1(I)*DT+A2(I)*DT2/2.
     &                          +A3(I)*DT3/3.
      STDCP(I)=DH0(I)+DELH-T*(DS0(I)+DELS)
  100 CONTINUE
C
C  CHEMICAL POTENTIAL FOR THE INERT COMPONENT IN THE VAPOR PHASE
C
      DELH=A0Z*DT+A1Z*DT2/2.-A2Z*DTM1+A3Z*(DTLNT-DT)
      DELS=A0Z*DLNT+A1Z*DT-A2Z*DTM2/2.+A3Z*DLNT2/2.
      IF(ICPZ.EQ.1) DELH=A0Z*DT+A1Z*DT2/2.+A2Z*DT3/3.
     &                         +A3Z*DT4/4.
      IF(ICPZ.EQ.1) DELS=A0Z*DLNT+A1Z*DT+A2Z*DT2/2.
     &                         +A3Z*DT3/3.
      STDCPZ=DH0Z+DELH-T*(DS0Z+DELS)
      RETURN
      END
```

Obviously various other correlations (constant, linear, quadratic, etc.) may be generated from these two functions by simply setting the appropriate coefficients to zero.

Lines 12 through 20 calculate the necessary limit differentials which result from performing the indicated integrations in equation 2 using the heat capacity correlations in equations 3 and 4. The integrals are evaluated as DELH and DELS and the standard chemical potential for each specie, STDCP(I), is then calculated.

B.4.2 ESTMTE

A listing of subroutine ESTMTE is provided in Figure 34. ESTMTE simply calculates the number of moles of each specie from the specie mole fraction and the total number of moles in the phase. ESTMTE is provided as a subroutine to allow the inclusion of an algorithum which will yield an estimate to the equilibrium composition and therefore reduce the number of iterations required to obtain convergence. Currently the inlet composition is used as this initial estimate.

B.4.3 STEADY

Subroutine STEADY inserts a pure condensed phase into the system in order to model a III-V liquid solution with a steady state composition. The composition of this liquid is that which would exist at equilibrium with the stoichiometric III-V solid at the system temperature. This subroutine is invoked when ISS>0, a Ga/As liquid phase being inserted for ISS=1 and and In/P liquid phase for ISS=2. This phase is inserted as the last pure condensed phase in the system (specie V+S+C).

A solid liquid equilibrium model for a binary liquid with the mole fraction of group V specie designated as x is obtained by writing the following reactions.

$$(1-X)III(s) = (1-X)III(\ell) \quad (1)$$

$$xV(s) = x\,V\,(\ell) \quad (2)$$

$$(1-x)III(\ell) + xV\,(\ell) = III_{1-x}\,V_x(\ell) \quad (3)$$

$$(1-x)III(s) + x\,V\,(s) = III_{1-x}\,V_x\,(\ell) \quad (4)$$

Reaction 4, which is the sum of the previous three reactions, represents the formation of a liquid solution having a composition (1-x)III and xV.

The Gibbs Free Energies of reactions 1 and 2 are simply those due to melting at T_m corrected for the temperature, T, of the solution.

$$G_1 = (1-x)\left[\, S_m^{III}(T_m^{III} - T) + \Delta C_p^{III}\left(T - T_m^{III} - T \ln \frac{T_m^{III}}{T}\right)\right] \quad (5)$$

$$G_2 = x\left[\, S_m^{V}\,(T_m^{V} - T) + \Delta C_p^{V}\left(T - T_m^{V} - T \ln \frac{T_m^{V}}{T}\right)\right] \quad (6)$$

Figure B4. Subroutine ESTMTE

```
      SUBROUTINE ESTMTE(TOTMV,TOTMS,TOTMC,FRAC,N,FRACZ,ZV,IDIM1,
     &                  V,S,C)
C
C  THIS SUBROUTINE CALCULATES AN INITIAL ESTIMATE
C  TO THE SYSTEM EQUILIBRIUM COMPOSITIONS
C
      DIMENSION TOTMC(IDIM1),FRAC(IDIM1)
      INTEGER V,S,C,VS,VS1,VSC
      REAL*8 N(IDIM1)
      VS=V+S
      VS1=VS+1
      VSC=V+S+C
      TOTMCL=TOTMV
      DO 50 I=1,VS
      IF(I.GT.V) TOTMCL=TOTMS
      N(I)=TOTMCL*FRAC(I)
   50 CONTINUE
      ZV=FRACZ*TOTMV
      IF(C.EQ.0) RETURN
      DO 60 I=VS1,VSC
      N(I)=TOTMC(I)
   60 CONTINUE
      RETURN
      END
```

Where it has been assumed that ΔC_p, the difference between the liquid and solid heat capacities, may be approximated as a constant.

The Gibbs Free Energy of reaction 3 is that due to the mixing of the group III and V liquids. This free energy consists of an ideal free energy of mixing comprised of a configurational entropy term and an excess Gibbs Free Energy term due to nonidealities. Applying a simple solution theory model for the excess Gibbs Free Energy yields [5]:

$$G_3 = RT[x\ \ell nx + (1-x)\ \ell n(1-x)] + (A_{xs} + B_{xs}T)x(1-x) \qquad (7)$$

The Gibbs Free Energy of the liquid solution represented by reaction 4 is therefore given by:

$$G_4 = G_1 + G_2 + G_3 \qquad (8)$$

Determination of the mole fraction of group V atoms in the melt, x, is accomplished by solving the implicit equation developed by Vieland [6] modified to include a simple solution rather than a regular solution model.

$$T = \frac{T_m^{IIIV}\ S_m^{IIIV} - A_{xs}\ (2x-2x^2-0.5)}{S_m^{IIIV} - R\ \ell n\ 4x(1-x) + B_{xs}(2x-2x^2-0.5)} \qquad (9)$$

The thermodynamic constants necessary for the evaluation of equations 8 and 9 are listed in Table B.3. Figures B5 and B6 demonstrate how well the theory predicts the liquidus temperatures in the Ga/As and In/P systems.

Table B.3

Thermodynamic Data for the Ga/As and In/P systems

	ΔS_m (Cal/g-mole-K)	T_m (K)	ΔC_p (Cal/g-mole-K)	A_{xs} (Cal/g-mole)	B_{xs} (Cal/g-mole-K)
Ga	4.411	302.9	-0.05		
As	4.7	1090	1.0	4666	-8.741
GaAs	16.64	1511	0		
In	1.815	429.8	-0.2		
P	0.5011	313.3	0.47	32750	-23.95
InP	10.81	1332.2	0		

Figure 35
The Ga/As System Liquidus Line
(Data refs. 7, 10,)

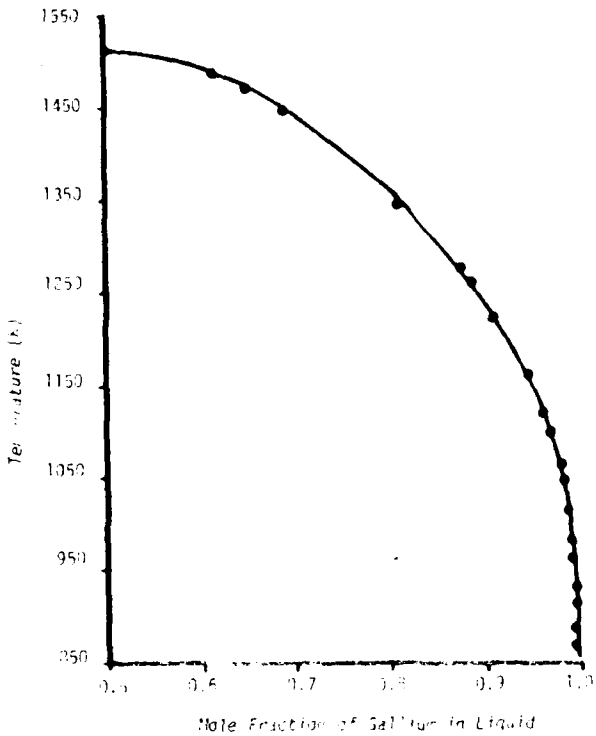
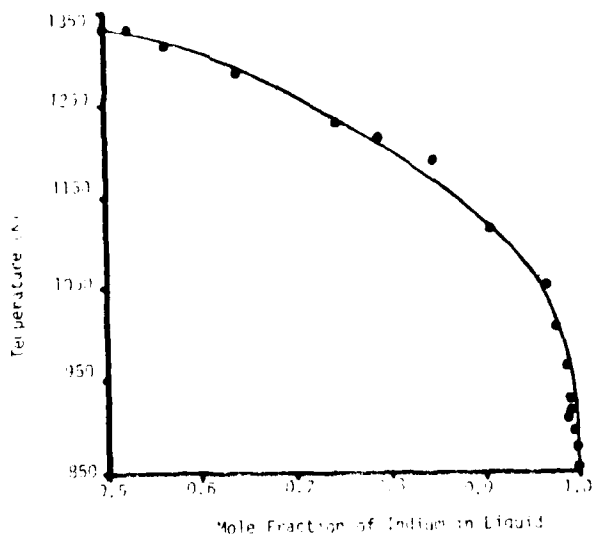


Figure 36
The In/P System Liquidus Line
(Data refs. 8, 9, 10, 11)



A listing of subroutine STEADY is shown in Figure B7. Lines 16 and 17 define a statement function which corresponds to the right hand side of equation 9. Hollerith strings are assigned to the specie identifier matrix in lines 19 through 21. The standard state chemical potentials and excess Gibbs Free Energy correlation parameters for the Ga/As and In/P systems are assigned in lines 29 through 54.

An "interval halving" root finding algorithum for solving the implicit equations is located at lines 57 through 83. The iteration is considered to have converged when the two sides of the equation differ by less than 0.01%.

The standard state chemical potential of the liquid solution is calculated in lines 86 and 91. Finally, the elemental abundance matrix is assigned the appropriate values which reflect the elemental composition of the liquid solution in lines 93 through 107.

Figure B7. Subroutine STEADY

```
      SUBROUTINE STEADY(SPEC,E,A,STOCP,ELMN,XI,T,D,V,S,C,VSC,
     &                  IDIM2,ICS,IA-T)
C
C  SUBROUTINE TO CALCULATE THE SOLID-SOLID EQUILIBRIUM
C  FOR USE IN THE STEADY-STATE APPROXIMATION IN THE SOLN PGM
C
C     ISS      SYSTEM
C       1      GA(L)-AS(L)/GA-AS (S)
C       2      IN(L)-P(L)/IN-P (S)
C
      DIMENSION A(IDIM1,IDIM2),STOCP(IDIM1)
      INTEGER SPECIE(IDIM1,3),ELMNT(IDIM2),TITLE(2),VEL(2),V,S,C,VSC,
     &        LAST/'1-X)'/,GA/'GA'/,AS/'AS'/,IN/'IN'/,P/' P'/
      DATA TITLE(1)/' GAX'/,TITLE(2)/' INA'/,
     &     VEL(1)/'-AS('/,VEL(2)/'- P('/
      THETA2(XV)=(TMIIIV*DSIIIV-AXS*(0.5-XV**2-(1.-XV)**2))/
     &        (DSIIIV-R*ALOG(4.*XV*(1.-XV))+BXS*(0.5-XV**2-(1.-XV)**2))
      VSC=V+S+C
      SPECIE(VSC,1)=TITLE(ISS)
      SPECIE(VSC,2)=VEL(ISS)
      SPECIE(VSC,3)=LAST
      DT=T-T0
      DT2=T**2-T0**2
      DTM1=1.0/T-1.0/T0
      DTM2=1.0/T**2-1.0/T0**2
      DLNT=ALOG(T/T0)
      IF(ISS.EQ.2) GO TO 50
C
C  GA-AS SYSTEM
C
      TMIII=302.9
      TMV=1090.
      TMIIIV=1511.
      DSIII=0.004411
      DSV=0.0047
      DSIIIV=0.01664
      DCIII=-0.0000
      DCV=0.001
      AXS=4.998
      BXS=-0.003741
      GO TO 60
C
C  IN-P SYSTEM
C
   50 TMIII=429.
      TMV=313.3
      TMIIIV=1343.
      DSIII=0.00141
      DSV=0.000011
      DSIIIV=0.01041
      DCIII=-0.000
      DCV=0.000472
      AXS=32.75
      BXS=-0.02
```

```
      60    CONTINUE
      C
      C  BINARY POINT FITTING ROUTINE FOR THE GROUP III & V ELEMENTS
      C
            XV=0.5
            XMIN=0.0
            XMAX=1.0
            R=0.0019872
            THETA1=T
            XOLD=0.4
            THTOLD=THETA2(XOLD)
            DO 100 I=1,50
            THET2=THETA2(XV)
            ERR=(THET2-THETA1)/THETA1
            IF(ABS(ERR).LT.0.0001) GO TO 200
            SLOPE=(THET2-THTOLD)/(XV-XOLD)
            THTOLD=THET2
            XOLD=XV
            IF(SLOPE.GT.0.AND.THET2.LT.THETA1) GO TO 80
            IF(SLOPE.LT.0.AND.THET2.GT.THETA1) GO TO 80
            XMAX=XV
            XV=0.5*(XMIN+XV)
            GO TO 100
       80   XMIN=XV
            XV=0.5*(XMAX+XV)
      100   CONTINUE
            WRITE(I*,T,120)
      120   FORMAT('0',' ***** SUBROUTINE STEADY: ITERATION FOR SOURCE ',
           &       'COMPOSITION DID NOT CONVERGE')
      200   CONTINUE
      C
      C  CALCULATE THE STANDARD CHEMICAL POTENTIAL OF THE SOURCE SOLUTION
      C
            DGA=(1.0-XV)*(DGIII*(TMIII-T)+DCIII*(T-TMIII-T*ALOG(T/TMIII)))
            DGB=XV*(DGV*(TMV-T)+DCV*(T-TMV-T*ALOG(T/TMV)))
            DGC=(AXS+BXS*T)*XV*(1.-XV)+R*T*(XV*ALOG(XV)+(1.-XV)*ALOG(1.-XV))
            STDG(VSC)=DGA+DGB+DGC
      C
      C  LOCATE THE GROUP III AND V ELEMENTS IN THE ELEMENTAL ABUNDANCE ARRAY
      C  AND INSERT THE CALCULATED ABUNDANCES INTO THIS ARRAY
      C
            IDX3=0
            IDX5=0
            DO 300 I=1,IDIM2
            IF(IGS.EQ.2) GO TO 250
            IF(ELMNT(I).EQ.GA) IDX3=I
            IF(ELMNT(I).EQ.AS) IDX5=I
            GO TO 300
      250   IF(ELMNT(I).EQ.IN) IDX3=I
            IF(ELMNT(I).EQ.SB) IDX5=I
      300   CONTINUE
            A(VSC,IDX3)=1.0-XV
            A(VSC,IDX5)=XV
            XIII=1.0-XV
      C
            RETURN
            END
```

B.4.4 TOTSI

Subroutine TOTSI, shown in Figure B8, calculates the total moles of silicon species in the vapor phase, the mole fraction of silicon species in the vapor phase and the activity of elemental silicon in a solid solution.

A character string comparison is made to determine which member of vector ELMNT is assigned the string "SI" and the moles of all vapor species with a nonzero value in their elemental abundance vectors corresponding to this position are summed. The mole fraction of silicon species in the vapor phase is then calculated from the total moles of all species in the vapor phase.

The activity of silicon in a solid solution which is in equilibrium with the vapor phase is calculated based on the silicon monomer concentration in the vapor via the reaction,

$$Si\ (s) = Si\ (v) \qquad (1)$$

The activity of silicon in a solid solution is therefore given by,

$$a_{Si} = \frac{P_{Si}}{K\ Po} \qquad (2)$$

where: P_{S_1} = partial pressure of Si(v)
Po = reference state pressure
a_{S_1} = solid solution silicon activity

The equilibrium constant K is calculated from the Gibbs Free Energy change of reaction 1 and is shown at lines 41 through 43.

B.4.5 RATIO

Subroutine RATIO, shown in Figure B9, calculates the group III/V atom ratio in the vapor phase, the activities of Ga, In, As and P in a solid solution which is in equilibrium with the vapor phase, and the saturation ratios of GaAs and InP.

The III/V atom ratio is determined at lines 20 through 45 using all of the group III and V elements in the periodic table. This results in a total III/V ratio which does not distinguish between the individual elements in each group.

Solid solution activities for Ga, In, As and P in equilibrium with the vapor phase are calculated using the same method which was applied in subroutine TOTSI for silicon. First the vapor phase monomers of each element are identified and then the activities are calculated. The thermodynamics data for each system is provided at lines 58 through 105.

Finally, the saturation ratios for GaAs and InP are calculated in order to provide a measure of the vapor phase supersaturation. The saturation ratio is defined by

$$R_{SAT} = \frac{P_{III}\ P_{V}}{K_{IIIV}\ P2_{o}} \qquad (1)$$

where the equilibrium constant, K_{IIIV}, is calculated from the Gibbs Free Energy change of the reaction

$$III\ V\ (s) = III(v) + V(v) \qquad (2)$$

Thus the saturation ratio is a comparison between the equilibrium constant for reaction 2 as calculated from the free energy change and from the vapor phase composition. A supersaturated vapor phase exists when $R_{SAT} > 1$.

B.4.6 OPTBAS

Subroutine OPTBAS, shown in Figure B10, determines the optimum set of basis species to be used in the formation reaction equations. A bubble sort is performed at lines 18 through 74 which orders arrays STDCP, A, DHO, DSO, AO, A1, A2, A3, SPECIE, PHASE, ICP and N in descending order of N. This places the species which are present in the greatest molar amounts in the first positions of the array indices. Thus, when the basis specie set is chosen using the algorithm outlined in section B.5 the optimum set of basis species will result.

Line 79 tests parameter ICHNG to determine whether the specie order has changed since the last iteration. If not (ICHNG=0) then the optimum set of basis species will not change and the remainder of this subroutine is skipped.

The set of basis species is constructed at lines 80 through 97. Subroutine TESTD checks the D matrix for linear dependencies between the rows. If a complete set of basis species cannot be found a message is written out at lines 99 and 100 and parameter ISTOP is set to unity. The iterative procedure is then halted at the next line in the main program.

B.4.7 TESTD

Subroutine TESTD tests the rows of the D matrix for linear independence by building a Gram-Schmidt orthogonalized matrix D' from D. The Gram-Schmidt orthogonalization procedure essentially subtracts away the projection of all the rows in the matrix which are above the row being orthogonalized. If the resulting orthogonalized row is composed of all zeros then this row was linearly dependent upon at least one of the above rows in the matrix. The equations used to construct matrix D' from D are presented in section B.5.

A listing of TESTD is provided in Figure B11.

Figure B8. Subroutine TOTSI

```
      SUBROUTINE TOTSI(A,ELMNT,FRAC,N,SITOT,ACTSIS,T,V,IDIM1,IDIM2,
     &                 V,E)
C
C  SUBROUTINE TO CALCULATE THE TOTAL SI IN THE VAPOR PHASE
C  AND THE ACTIVITY OF SI IN A SOLID SOLUTION
C
      DIMENSION A(IDIM1,IDIM2),FRAC(IDIM1)
      INTEGER ELMNT(IDIM2),V,E,SIVPR/'SI'/
      REAL*8 N(IDIM1)
      T0=298.15
      P0=101325.0
      RT=0.0019872*T
C
C  DETERMINE THE TOTAL AMOUNT OF SILICON IN THE VAPOR
C
      SITOT=0.0
      SIMF=0.0
      ACTSIS=0.
      DO 100 J=1,E
      KSI=J
      IF(ELMNT(J).EQ.SIVPR) GO TO 130
  100 CONTINUE
      GO TO 300
  130 CONTINUE
      DO 140 I=1,V
      IF(A(I,KSI).LT.0.001) GO TO 140
      SITOT=SITOT+N(I)
      SIMF=SIMF+FRAC(I)
  140 CONTINUE
C
C  FIND SI(V) AND CALCULATE THE ACTIVITY OF SOLID SI IN SOLUTION
C
      DO 200 I=1,V
      ICNT=0
      IF(A(I,KSI).LT.0.001) GO TO 200
      DO 150 J=1,E
      IF(A(I,J).LT.0.001) GO TO 150
      ICNT=ICNT+1
  150 CONTINUE
      IF(ICNT.GT.1) GO TO 200
      DG=108.-0.00381*(T-T0)-5.011E-7/2.*(T**2-T0**2)-147.6*(1/T-1/T0)
     &   -T*(0.035637-0.00381*ALOG(T/T0)-5.011E-7*(T-T0)
     &       -147.6/2.*(1/T**2-1/T0**2))
      ACTSIS=FRAC(I)*P0/P0*EXP(DG/RT)
      IF(N(I).LT.1.00E-1 ) ACTSIS=0.
      GO TO 300
  200 CONTINUE
  300 CONTINUE
      RETURN
      END
```

Figure B9. Subroutine RATIO

```
      SUBROUTINE RATIO(T,ELMNT,FRAC,N,STOCH,ACTGAS,ACTINS,ACTASS,
     &                 ACTPS,IIIV,PGAAS,XINP,P,TO,PO,IO,IOP1,IOP2,V,I)
C
C  THIS SUBROUTINE CALCULATES THE VAPOR III/V RATIO,
C  THE GA, IN, AS AND P SOLID SOLUTION ACTIVITIES,
C  AND THE SATURATION RATIOS OF GA-AS AND IN-P.
C
      DIMENSION A(IDIM1,IDIM2),FRAC(IDIM1),STOCH(IDIM1,11),KIII(5),KV(5)
      REAL*8 N(IDIM1)
      INTEGER ELMNT(IDIM2),ELIII(5),ELV(5),V,I
      DATA ELIII(1)/' B'/,ELIII(2)/'AL'/,ELIII(3)/'GA'/,ELIII(4)/'IN'/,
     &     ELIII(5)/'TL'/,ELV(1)/' N'/,ELV(2)/' P'/,ELV(3)/'AS'/,
     &     ELV(4)/'SB'/,ELV(5)/'BI'/
      ENDOG(T)=A0+A1*(T-T0)+A2/2.*(T**2-T0**2)-A3*(1/T-1/T0)
     &   +A4*(T*ALOG(T)-T-T0*ALOG(T0)+T0)+A5/3.*(T**3-T0**3)
     &   -T*(A0+A1*ALOG(T/T0)+A2*(T-T0)-A3/2.*(1/T**2-1/T0**2)
     &        +-4/2.*(ALOG(T)**2-ALOG(T0)**2)+A5/2.*(T**2-T0**2))
      RT=0.0019872*T
C
C  DETERMINE WHICH INDICIES CORRESPOND TO COLUMN III AND V ELEMENTS
C
      DO 100 K=1,5
      KIII(K)=0
      KV(K)=0
      DO 100 J=1,I
      IF(ELMNT(J).EQ.ELIII(K)) KIII(K)=J
      IF(ELMNT(J).EQ.ELV(K)) KV(K)=J
  100 CONTINUE
C
C  SUM-UP THE GROUP III AND V SPECIES AND CALCULATE THE RATIO
C
      SUMIII=0.0
      SUMV=0.0
      DO 200 I=1,V
      DO 200 K=1,5
      IDXIII=KIII(K)
      IDXV=KV(K)
      IF(IDXIII.EQ.0) GO TO 120
      SUMIII=SUMIII+A(I,IDXIII)*FRAC(I)
  120 CONTINUE
      IF(IDXV.EQ.0) GO TO 200
      SUMV=SUMV+A(I,IDXV)*FRAC(I)
  200 CONTINUE
      PIIIV=1.0E10
      IF(SUMV.GT.0.0) PIIIV=SUMIII/SUMV
C
C  FIND THE SPECIES:  GA(V), IN(V), P(V) AND AS(V)
C  AND CALCULATE THE ACTIVITIES FOR GA, IN, AS AND P IN THE SOLID PHASE
C
      ACTGAS=0.
      ACTINS=0.
      ACTASS=0.
      ACTPS=0.
      KGA=0
```

```
      KAS=0
      KIN=0
      KP=0
C
C  GA DATA
C
      KSPC=KIII(3)
      A1=0.023738
      A2=2.09E-6
      A3=-266.2
      A4=-0.003e12
      A5=0.
      DH=55.0
      DS=0.030617
      GO TO(245,220,230,240),IJK
C
C  INDIUM DATA
C
  220 KSPC=KIII(4)
      A1=-0.001015
      A2=-1.614E-6
      A3=0.
      A4=0.
      A5=-1.e89E-9
      DH=57.8
      DS=0.027e87
      GO TO 245
C
C  PHOSPHORUS (P) DATA
C
  230 KSPC=KV(2)
      A1=-0.000732
      A2=0.
      A3=0.
      A4=0.
      A5=0.
      DH=73.62
      DS=0.02915
      GO TO 245
C
C  ARSENIC (AS) DATA
C
  240 KSPC=KV(3)
      A1=-0.001708
      A2=-1.5E-6
      A3=15.04
      A4=0.0001957
      A5=0.
      DH=68.7
      DS=0.026001
  245 IF(KSPC.EQ.0) GO TO 300
      DO 300 I=1,4
      ICNT=0
```


Figure B17. Subroutine COEMOL

```
      IF(A(I,KS).LT.0.001) GO TO 250
      DO 260 J=1,2
      IF(A(I,J).LT.0.001) GO TO 260
      ICNT=ICNT+1
  260 CONTINUE
      IF(ICNT.GT.1) GO TO 400
      IF(A(I,KSPC).GT.1.001) GO TO 300
      DG=FNDG(T)
      ACTIV=PRAC(I)*P/P0*EXP(DG/RT)
      IF(IJK.EQ.1) ACTGAS=ACTIV
      IF(IJK.EQ.1) KGA=I
      IF(IJK.EQ.2) ACTINP=ACTIV
      IF(IJK.EQ.2) KIN=I
      IF(IJK.EQ.3) ACTPS=ACTIV
      IF(IJK.EQ.3) KP=I
      IF(IJK.EQ.4) ACTASS=ACTIV
      IF(IJK.EQ.4) KAS=I
      GO TO 400
  300 CONTINUE
  400 CONTINUE
C
C  CALCULATE THE SATURATION RATIOS FOR GA-AS AND IN-P.
C
      RGAAS=0.
      RINP=0.
C
C  GA-AS SYSTEM SATURATION RATIO
C
      A1=0.010460
      A2=2.6E-6
      A3=0.
      A4=0.
      A5=0.
      DH=-19.52
      DS=-0.002948
      KJ=KGA
      KS=KAS
      DO 500 I=1,2
      IF(KJ.EQ.0.OR.KS.EQ.0) GO TO 470
      IF(PR(KJ).LT.1.00E-30.  .OR.PR(KS).LT.1.00E-30) GO TO 470
      DG=STDGP(KJ)+STDGP(KS)-FNDG(T)/RT
      RGAT=PRAC(KJ)*PRAC(KS)**2*EXP(DG)/P0**2
      IF(I.EQ.1) RGAAS=RGAT
      IF(I.EQ.2) RINP=RGAT
C
C  IN-P SYSTEM SATURATION RATIO
C
  470 A1=0.012?7
      A2=0.
      A3=-114.3
      DH=-14.0
      DS=-0.10918
      KJ=KIN
      KS=KP
      CONTINUE
      RETURN
```

Figure B10. Subroutine OPTBAS

```
      SUBROUTINE OPTBAS(N,BESTN,A,D,OPAME,STOCP,ICP,IDIM1,PHASE,A0,A1,A2,
     &A3,SPECIE,DH0,DS0,ICP,IDIM2,ITEMP,IDIM1,IDIM2,V,S,C,E,ISTOP,ICHNG,
     &IWRT)
C
C  THIS SUBROUTINE DETERMINES THE OPTIMUM SET OF SPECIES
C
      DIMENSION A(IDIM1,IDIM2),D(IDIM2,IDIM2),IDXSAB(IDIM2),
     &          STOCP(IDIM1),A0(IDIM1),A1(IDIM1),A2(IDIM1),A3(IDIM1),
     &          DH0(IDIM1),DS0(IDIM1),ICP(IDIM1)
      REAL*8 N(IDIM1),BESTN(IDIM1),OPAME(IDIM2,IDIM2),TEMP
      INTEGER SPECIE(IDIM1,3),PHASE(IDIM1,3),ENDES(IDIM1),V,S,C,E,VSC,
     &        VSC1
      ISTOP=0
      ICHNG=0
      VSC=V+S+C
      VSCM1=VSC-1
C
C  BUBBLE SORT THE N VECTOR INTO DESCENDING ORDER
C  AND ORDER STOCP, A, DH0, DS0, A0, A1, A2, A3, SPECIE, PHASE
C  AND ICP CORRESPONDINGLY
C
      DO 300 I=1,VSCM1
      IP1=I+1
      DO 200 II=IP1,VSC
      IF(N(II).LE.N(I)) GO TO 200
      ICHNG=1
      TEMP=N(I)
      N(I)=N(II)
      N(II)=TEMP
      TEMP=BESTN(I)
      BESTN(I)=BESTN(II)
      BESTN(II)=TEMP
      TEMP=STOCP(I)
      STOCP(I)=STOCP(II)
      STOCP(II)=TEMP
      TEMP=A0(I)
      A0(I)=A0(II)
      A0(II)=TEMP
      TEMP=A1(I)
      A1(I)=A1(II)
      A1(II)=TEMP
      TEMP=A2(I)
      A2(I)=A2(II)
      A2(II)=TEMP
      TEMP=A3(I)
      A3(I)=A3(II)
      A3(II)=TEMP
      TEMP=DH0(I)
      DH0(I)=DH0(II)
      DH0(II)=TEMP
      TEMP=DS0(I)
      DS0(I)=DS0(II)
      DS0(II)=TEMP
      ITEMP=ENDES(I)
```

```
      BGUESS(I)=BGUESS(II)
      BGUESS(II)=ITEMP
      ITEMP=ICP(I)
      ICP(I)=ICP(II)
      ICP(II)=ITEMP
      DO 50 J=1,3
      ITEMP=SPECIE(I,J)
      SPECIE(I,J)=SPECIE(II,J)
      SPECIE(II,J)=ITEMP
      ITEMP=PHASE(I,J)
      PHASE(I,J)=PHASE(II,J)
      PHASE(II,J)=ITEMP
   50 CONTINUE
      DO 100 J=1,E
      TEMP=A(I,J)
      A(I,J)=A(II,J)
      A(II,J)=TEMP
  100 CONTINUE
  200 CONTINUE
  300 CONTINUE
C
C  IF THE PREVIOUSLY USED BASIS IS STILL THE OPTIMUM BASIS
C  SKIP THE REST OF THIS SUBROUTINE AND CONTINUE WITH THE CALCULATIONS
C
      IF(ITER.GT.1.AND.ICHNG.EQ.0) GO TO 480
C
C  BUILD THE D MATRIX WHICH WILL CONTAIN THE OPTIMUM BASIS
C
      DO 320 J=1,E
      DPRME(1,J)=A(1,J)
  320 CONTINUE
      MA=0
      DO 400 MD=1,E
  340 MA=MA+1
      IF(MA.GT.VSC) GO TO 450
      DO 350 J=1,E
      D(MD,J)=A(MA,J)
  350 CONTINUE
      IDX&AS(MD)=MA
      IF(MD.EQ.1) GO TO 400
      CALL TESTD(D,DPRME,MD,E,IDIM2,.TST)
      IF(ITST.EQ.0) GO TO 340
  400 CONTINUE
      GO TO 480
  450 WRITE(IWRT,460) ITER
  460 FORMAT('0','***** ITERATION ',I5,' AN OPTIMUM SET OF BASIS ',
     &'SPECIES COULD NOT BE FOUND FOR THIS SYSTEM IN SUBROUTINE OPTIM')
      ISTOP=1
  480 RETURN
      END
```

Figure B11. Subroutine TESTD

```
      SUBROUTINE TESTD(D,DPRME,MD,E,IDIM2,ITST)
C
C  THIS SUBROUTINE TESTS THE D MATRIX FOR LINEAR DEPENDENCE
C  USING A GRAM-SCHMIDT ORTHOGONALIZATION ALGORITHM
C
      DIMENSION D(IDIM2,IDIM2)
      REAL*8 DPRME(IDIM2,IDIM2),ANUM,DENOM
      INTEGER E
      ITST=0
      DO 100 J=1,E
      DPRME(MD,J)=D(MD,J)
  100 CONTINUE
      MDM1=MD-1
      DO 400 L=1,MDM1
      ANUM=0.0
      DENOM=0.0
      DO 200 K=1,E
      ANUM=ANUM+D(MD,K)*DPRME(L,K)
      DENOM=DENOM+DPRME(L,K)**2
  200 CONTINUE
      DO 300 J=1,E
      DPRME(MD,J)=DPRME(MD,J)-DPRME(L,J)*ANUM/DENOM
  300 CONTINUE
  400 CONTINUE
C
C  TEST FOR "ZEROS" ON THE NEW ROW
C
      DO 500 J=1,E
      IF(DABS(DPRME(MD,J)).GT.1.0D-5) ITST=ITST+1
  500 CONTINUE
      RETURN
      END
```

B.4.8 EQCON

Subroutine EQCON, shown in Figure B12, calculates the equilibrium constants for each of the formation reactions from the Gibbs Free Energy change of the reaction. Array D, which contains the optimum set of basis species, is inverted at line 26 using IMSL subroutine LINVIF. A message is written out at lines 27, 28 and 29 if the inverted matrix has less than four significant figures. If array D appears to be algorithmically singular to LINVIF a message is written out at lines 30 through 32, parameter ISTOP is set to unity and the iterative process is halted in the main program.

Lines 35 through 45 calculate the stoichiometric coefficients for the formation reactions using equation 4 from section B.5. The equilibrium constants for these reactions are then calculated at lines 46 through 57.

B.4.9 ACTCOF

A listing of subroutine ACTCOF, which calculates the activity coefficients for each specie, is shown in Figure B13. Initially all of the activity coefficients are set to unity. The iteration process for the equilibrium composition proceeds under this assumption of an ideal system until RELMAX, the convergence test parameter, becomes less than 0.1. At this point three options become available for the solution phase. The first option (IXSCOR=0) simply assumes an ideal solution phase. The second option (IXSCOR=1) treats the solution phase using simple solution theory and is appicable to binary solutions only. The activity coefficient for specie i is given by:

$$\gamma_i = \exp\left[(A_{xs} + B_{xs}\, T)(1-X_i)^2/RT\right] \qquad (1)$$

The third option (IXSCOR2=2) allows the first specie in the solution phase to have an activity coefficient described by Henry's constant, H.

$$\gamma_{V+1} = H = A_{xs} \exp[B_{xs}/T] \qquad (2)$$

The vapor phase is always assumed to be ideal.

B.4.10 CALCQ

A listing of CALCQ is shown in Figure B14. This subroutine calculates the "equilibrium constants" for each of the formation reactions based on the current estimate to the equilibrium composition. These equilibrium constants are calculated by the following relationship.

$$Q_i = \gamma_i X_i P_{pi} \Big/ \prod_{k=1}^{E} (\gamma_k X_k P_{pk})^{\nu_{ik}} \qquad (1)$$

where: γ_i = activity coefficient

X_i = mole fraction

ν_{ik} = stoichiometric coefficient

$P_{pi} = \begin{cases} P/Po & \text{vapor species} \\ 1 & \text{condensed phases} \end{cases}$

Figure B12. Subroutine EQCON

```
      SUBROUTINE EQCON(A,D,DD,DINV,DG,GNU,STOCP,KEG,IDXBAS,WKA,
     &                 RT,ITER,IDIM1,IDIM2,V,S,C,E,ISTOP,IWRT)
C
C  THIS SUBROUTINE CALCULATES THE REACTION COEFFICIENT MATRIX
C  AND THE EQUILIBRIUM CONSTANTS FOR THE FORMATION REACTIONS
C
      DIMENSION A(IDIM1,IDIM2),D(IDIM2,IDIM2),DD(IDIM2,IDIM2),
     &          DINV(IDIM2,IDIM2),DG(IDIM1),GNU(IDIM1,IDIM2),
     &          IDXBAS(IDIM2),STOCP(IDIM1),WKA(IDIM2)
      DOUBLE PRECISION DD,DINV,WKA
      INTEGER V,S,C,E,VSC
      REAL KEG(IDIM1)
      VSC=V+S+C
      ISTOP=0
C
C  STORE ARRAY D IN ARRAY DD AND USE ARRAY DD IN THE CALL TO LINVIF
C
      DO 100 I=1,E
      DO 100 J=1,E
      DD(I,J)=D(I,J)
  100 CONTINUE
C
C  INVERT MATRIX DD USING IMSL SUBROUTINE LINVIF
C
      IDGT=4
      CALL LINVIF(DD,E,IDIM2,DINV,IDGT,WKA,IER)
      IF(IER.EQ.34) WRITE(IWRT,110) ITER,IDGT
  110 FORMAT('0',' ***** ITERATION ',I5,' ACCURACY TEST FAILED IN ',
     &'SUBROUTINE LINVIF DURING MATRIX INVERSION..... IDGT=',I2)
      IF(IER.EQ.129) WRITE(IWRT,120) ITER
  120 FORMAT('0',' ***** ITERATION ',I5,' MATRIX D IS SINGULAR',
     &       ' IN SUBROUTINE EQCON')
      IF(IER.EQ.129) ISTOP=1
      IF(ISTOP.EQ.1) GO TO 600
C
C  CALCULATE THE REACTION COEFFICIENT MATRIX
C
      DO 300 I=1,VSC
      DO 300 J=1,E
      TEMP=0.0
      DO 200 JJ=1,E
      TEMP=TEMP+A(I,JJ)*DINV(JJ,J)
  200 CONTINUE
      GNU(I,J)=TEMP
  300 CONTINUE
C
C  CALCULATE THE EQUILIBRIUM CONSTANTS FOR THE FORMATION REACTIONS
C
      DO 500 I=1,VSC
      ARG=(-1.0)*STOCP(I)
      DO 400 K=1,E
      IDXE=IDXBAS(K)
      ARG=ARG+GNU(I,K)*STOCP(IDXE)
  400 CONTINUE
```

```
      DG(I)=(-1.0)*ARG*RT
      KEQ(I)=EXP(ARG)
500   CONTINUE
600   RETURN
      END
```

Figure B13. Subroutine ACTCOF

```
      SUBROUTINE ACTCOF(FRAC,ACOEF,ISPCE,SPECIE,INDEX,IDIM1,RELMAX,
     &                  IXSCOR,AXS,BXS,T,IACFF,V,S,C,IWRT)
C
C  SUBROUTINE TO CALCULATE ACTIVITY COEFFICIENTS FOR THE SOLUTION PHASE
C
C  IXSCOR  ALGORITHUM
C        1  BINARY SIMPLE SOLUTION THEORY  GE=(AXS+BXS*T)*X1*X2
C        2  HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE  H=AXS*EXP(BXS/
C
      DIMENSION ACOEF(IDIM1),FRAC(IDIM1),INDEX(IDIM1)
      INTEGER ISPCE(IDIM1,3),SPECIE(IDIM1,3),V,S,C,VSC
      VSC=V+S+C
      DO 100 I=1,VSC
      ACOEF(I)=1.0
  100 CONTINUE
      IF(ABS(RELMAX).LT.0.1) IACFF=1
      IF(IXSCOR.EQ.2) IACFF=1
      IF(IXSCOR.LT.1.OR.IXSCOR.GT.2.OR.S.LE.1) IACFF=1
      IF(IACFF.EQ.0) GO TO 500
      RT=0.0019872*T
C
C  IDENTIFY THE SOLUTION SPECIES
C
      DO 150 J=1,S
      K=V+J
      DO 150 I=1,VSC
      IF(SPECIE(I,1).EQ.ISPCE(K,1).AND.
     &   SPECIE(I,2).EQ.ISPCE(K,2).AND.
     &   SPECIE(I,3).EQ.ISPCE(K,3)) INDEX(J)=I
  150 CONTINUE
      ITEST=1
      DO 155 J=1,S
      IF(INDEX(J).LT.1.OR.INDEX(J).GT.VSC) ITEST=0
  155 CONTINUE
      IF(ITEST.EQ.0) WRITE(IWRT,160)
  160 FORMAT('0','***** THE SOLUTION SPECIES COULD NOT BE IDENTIFIED',
     &       ' IN SUBROUTINE ACTCOF')
      IF(IXSCOR.EQ.2) GO TO 200
C
C  BINARY SIMPLE SOLUTION THEORY
C
      IDX1=INDEX(1)
      IDX2=INDEX(2)
      X1=FRAC(IDX1)
      X2=1.0-X1
      ARG1=(AXS+BXS*T)*X2**2/RT
      ARG2=(AXS+BXS*T)*X1**2/RT
      ACOEF(IDX1)=EXP(ARG1)
      ACOEF(IDX2)=EXP(ARG2)
      GO TO 500
C
C  HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE
C
  200 IDX1=INDEX(1)
      ACOEF(IDX1)=AXS*EXP(BXS/T)
  500 RETURN
      END
```

Figure B14. Subroutine CALCQ

```
      SUBROUTINE CALCQ(GNU,N,ACCEF,FRAC,PHASE,VAPCR,SCLN,IDXBAS,Q,
     &                 ZV,FRACZ,P,PO,V,S,C,E,IDIM1,IDIM2,IWRT)
C
C  SUBROUTINE TO CALCULATE EQUILIBRIUM CONSTANTS FROM COMPOSITION
C
      DIMENSION GNU(IDIM1,IDIM2),ACCEF(IDIM1),FRAC(IDIM1),IDXBAS(IDIM2),
     &          Q(IDIM1)
      INTEGER V,S,C,E,VSC,PHASE(IDIM1,3),VAPCR(3),SCLN(3)
      REAL*8 N(IDIM1),NV,NS
      VSC=V+S+C
C
C  CALCULATE THE TOTAL NUMBER OF MOLES IN EACH PHASE
C
      NS=0.0
      NV=ZV
      DO 100 I=1,VSC
      IF(PHASE(I,1).EQ.VAPCR(1)) NV=NV+N(I)
      IF(PHASE(I,1).EQ.SCLN(1)) NS=NS+N(I)
  100 CONTINUE
C
C  CALCULATE THE MOLE FRACTIONS
C
      DO 200 I=1,VSC
      FRAC(I)=1.0
      IF(PHASE(I,1).EQ.VAPCR(1)) FRAC(I)=N(I)/NV
      IF(PHASE(I,1).EQ.SCLN(1)) FRAC(I)=N(I)/NS
  200 CONTINUE
      FRACZ=ZV/NV
C
C  CALCULATE THE EQUILIBRIUM CONSTANTS
C
      DO 400 I=1,VSC
      PPO=1.0
      IF(PHASE(I,1).EQ.VAPCR(1)) PPO=P/PO
      Q(I)=ACCEF(I)*FRAC(I)*PPO
      DO 300 J=1,E
      K=IDXBAS(J)
      PPO=1.0
      IF(PHASE(K,1).EQ.VAPCR(1)) PPO=P/PO
      Q(I)=Q(I)/(ACCEF(K)*FRAC(K)*PPO)**GNU(I,J)
  300 CONTINUE
  400 CONTINUE
      RETURN
      END
```

The product in the denominator is taken over the basis species in the system.

B.4.11 ADJEXT

Subroutine ADJEXT, shown in Figure B15, adjusts the extents of each formation reaction using equation 8 from section B.5. The predicted change in each reaction extent is calculated in lines 11 through 31. The $\Delta\xi_j$ values are set to zero in lines 28 and 29 for species which are present in only very small amounts. Nonnegativity of the basis species molar amounts is assured by application of equations 10 and 11 in section B.5 in lines 32 through 51.

B.4.12 CNVFRC and DGDLAM

Listings of subroutine CNVFRC and function subprogram DGDLAM are shown in Figure B16. Subroutine CNVFRC calculates a convergence forcer, λ, using equation 14 from section B.5.

At line 20 subroutine CORMOL is called to determine the molar amounts which would be present if $\lambda = 1$ and the derivative is evaluated in line 21. The derivative is evaluated for $\lambda = 0$ at line 27 and line 30. Lines 31 and 32 limit the maximum and minimum values of the convergence forcer to 1.0 and RLXMIN respectively.

Function subroutine DGDLAM calculates the derivative of the system Gibbs Free Energy with respect to the convergence forcer using the following relation from Smith and Missen [2].

$$\frac{dG}{d\lambda} = RT \sum_{i=1}^{vsc} (n_i' - n_i)[\mu_i^o + \ln(\Sigma_i n_i' P_{pi}/n_T)] \qquad (1)$$

where: n_T = total moles in the phase

n_i = equations 9 and 10 section B.5

$P_{pi} = \begin{cases} P/Po & \text{vapor phase} \\ 1 & \text{condensed phases} \end{cases}$

B.4.13 CORMOL

Subroutine CORMOL, shown in Figure B17, corrects the molar amounts of each specie to reflect the adjusted extents of the formation reactions using equations 9 and 10 in section B.5. The minimum molar amount any specie may attain is set to 1.65×10^{-24} moles (one molecule).

Figure B15. Subroutine ADJEXT

```
      SUBROUTINE ADJEXT(N,KEQ,G,GNU,DZETA,IDXBAS,COND,PHASE,IDIM1,IDIM2,
     &                  V,S,C,E,IART)
C
C  SUBROUTINE TO ADJUST THE EXTENTS OF REACTION
C
      DIMENSION IDXBAS(IDIM2),G(IDIM1),GNU(IDIM1,IDIM2)
      INTEGER COND(3),PHASE(IDIM1,3),V,S,C,E,VSC
      REAL KEQ(IDIM1)
      REAL*8 N(IDIM1),DZETA(IDIM1),DENOM,TOTON
      VSC=V+S+C
C
C  CALCULATE THE CHANGE IN REACTION EXTENT FOR EACH REACTION
C
      DO 200 I=1,VSC
      DELI=1.0
      IF(PHASE(I,1).EQ.COND(1)) DELI=0.0
      DENOM=DELI/N(I)
      DZETA(I)=0.0
      DO 100 J=1,E
      K=IDXBAS(J)
      IF(I.EQ.K) GO TO 200
      DELK=1.0
      IF(PHASE(K,1).EQ.COND(1)) DELK=0.0
      DENOM=DENOM-DELK*GNU(I,J)**2/N(K)
  100 CONTINUE
      IF(DENOM.EQ.0.0) DENOM=ALOG(KEQ(I))-ALOG(G(I))
      DZETA(I)=(ALOG(KEQ(I))-ALOG(G(I)))/DABS(DENOM)
      IF(N(I).LT.1.66E-24.AND.DZETA(I).LT.0.0) DZETA(I)=0.0
      IF(DZETA(I).LT.0.0.AN .DABS(DZETA(I)).GT.N(I))
     &                                  DZETA(I)=(-1.0)*N(I)
  200 CONTINUE
C
C  LIMIT THE MAXIMUM ALLOWABLE DZETA VALUES
C  BASED ON NON-NEGATIVITY OF THE BASIS SPECIES
C
      AKAPA=1.0
      DO 400 J=1,E
      K=IDXBAS(J)
      TOTON=0.0
      DO 300 I=1,VSC
      TOTON=TOTON-GNU(I,J)*DZETA(I)
  300 CONTINUE
      TEST=N(K)+TOTON*AKAPA
      IF(TEST.LT.0.0.AND.N(K).GT.1.66E-24) AKAPA=(-1.0)*N(K)/TOTON
  400 CONTINUE
      DO 500 I=1,VSC
      DO 450 J=1,E
      IF(I.EQ.IDXBAS(J)) GO TO 500
  450 CONTINUE
      DZETA(I)=DZETA(I)*AKAPA
  500 CONTINUE
      RETURN
      END
```

Figure B16. Subroutine CNVFRC

```
      SUB-ROUTINE CNVFRC(N,NTEMP,STOCP,ACCEF,DZETA,GNU,IDXMAS,VAPCH,
     &                   CCNU,SCLN,PHASE,ZV,ZT,P,PO,FLXMIN,LAMBDA,IDIM1,
     &                   IDIM2,V,S,C)
C
C  SUBROUTINE TO CALCULATE THE CONVERGENCE FUNCTION LAMBDA
C
      DIMENSION IDXMAS(IDIM2),GNU(IDIM1,IDIM2),
     &          STOCP(IDIM1),ACCEF(IDIM1)
      INTEGER VAPCH(3),CCNU(3),SCLN(3),PHASE(IDIM1,3),V,S,C,D,VSC
      REAL LAMBDA
      REAL*8 N(IDIM1),NTEMP(IDIM1),DZETA(IDIM1)
      VSC=V+S+C
C
C  CALCULATE DG/DLAMBDA AT LAMBDA=1.0
C
      LAMBDA=1.0
      DO 100 I=1,VSC
      NTEMP(I)=N(I)
  100 CONTINUE
      CALL CCRMOL(NTEMP,DZETA,GNU,IDXMAS,IDIM1,IDIM2,LAMBDA,VSC,T)
      DGDL1=DGDLAM(N,NTEMP,STOCP,ACCEF,PHASE,VAPCH,SCLN,ZV,ZT,P,PO,
     &             IDIM1,VSC)
      IF(DGDL1.LE.0.0) GO TO 500
C
C  CALCULATE DG/DLAMBDA AT LAMBDA=0.0
C
      DGDL0=(-1.0)*DGDLAM(NTEMP,N,STOCP,ACCEF,PHASE,VAPCH,SCLN,ZV,
     &                    ZT,P,PO,IDIM1,VSC)
      IF(DGDL0.EQ.DGDL1) DGDL1=0.0
      LAMBDA=DGDL0/(DGDL0-DGDL1)
      IF(LAMBDA.GT.1.0) LAMBDA=1.0
      IF(LAMBDA.LT.0.0) LAMBDA=FLXMIN
  500 CONTINUE
      RETURN
      END
      FUNCTION DGDLAM(N1,N2,STOCP,ACCEF,PHASE,VAPCH,SCLN,ZV,ZT,P,PO,
     &                IDIM1,VSC)
C
C  SUBPROGRAM TO CALCULATE DG/DLAMBDA
C
      DIMENSION ACCEF(IDIM1),STOCP(IDIM1)
      INTEGER PHASE(IDIM1,3),VAPCH(3),SCLN(3),VSC
      REAL*8 N1(IDIM1),N2(IDIM1),NV,NS
C
C  CALCULATE THE TOTAL NUMBER OF MOLES IN THE SOLUTION AND VAPOR PHASES
C
      NS=0.0
      NV=ZV
      DO 100 I=1,VSC
      IF(PHASE(I,1).EQ.VAPCH(1)) NV=NV+N2(I)
      IF(PHASE(I,1).EQ.SCLN(1)) NS=NS+N2(I)
  100 CONTINUE
C
C  CALCULATE DG/DLAMBDA
```

```
C
      DGDL=0.0
      DO 200 I=1,VBC
      ARG=1.0
      IF(PHASE(I,1).EQ.VAPOR(1)) ARG=ACCEF(I)*N2(I)*P/PSAT
      IF(PHASE(I,1).EQ.SOLN(1)) ARG=ACCEF(I)*N2(I)/NS
      DGDL=DGDL+(N2(I)-N1(I))*(STDGP(I)+RLOG(ARG))
  200 CONTINUE
      DGDLAM=DGDL*RT
      RETURN
      END
```

Figure B17. Subroutine CORMOL

```
      SUBROUTINE CORMOL(N,DZETA,GNU,IDXBAS,IDIM1,IDIM2,LAMBDA,VSC,E)
C
C  SUBROUTINE TO CORRECT THE MOLAR AMOUNTS OF EACH SPECIE
C
      DIMENSION GNU(IDIM1,IDIM2),IDXBAS(IDIM2)
      REAL LAMBDA
      REAL*8 N(IDIM1),DZETA(IDIM1)
      INTEGER VSC,E
C
C  CORRECT EACH NONBASIS SPECIE
C
      DO 200 I=1,VSC
      DO 100 J=1,E
      IF(I.EQ.IDXBAS(J)) GO TO 200
  100 CONTINUE
      N(I)=N(I)+DZETA(I)*LAMBDA
      IF(N(I).LT.1.65E-24) N(I)=1.65E-24
  200 CONTINUE
C
C  CORRECT EACH BASIS SPECIE
C
      DO 400 J=1,E
      K=IDXBAS(J)
      DO 300 I=1,VSC
      N(K)=N(K)-GNU(I,J)*DZETA(I)*LAMBDA
  300 CONTINUE
      IF(N(K).LT.1.65E-24) N(K)=1.65E-24
  400 CONTINUE
      RETURN
      END
```

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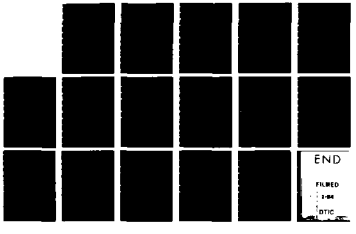

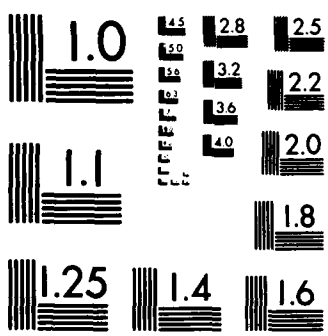

B.4.14 ORDER

A listing of subroutine ORDER is shown in Figure B18. Subroutine ORDER places arrays N, STOCP, AO, AI, A2, A3, DHO, DSO, ICP, DZETA, CHMPT, ACOEF, FRAC, DG, Q, KEQ, SPECIE, PHASE and A into the specie order of the original problem statement. This makes the output readily accessable and also is necessary for the correct operation of the composition looping option (IOPT=3).

B.4.15 WRAPUP

Subroutine WRAPUP, shown in Figure B19 writes a wrap-up file to logical unit designator IFILE. This subroutine is accessed when parameter IWRAP>0. For IWRAP=1 or 2 the value of IFILE is set at 2. For IWRAP=3 IFILE is set equal to IWRT which is the line printer logical unit designator. This subroutine provides concise data output and is quite useful when the input data set has been verified to be correct and parametric studies are desired.

B.4.16 DEBUG

Subroutine DEBUG is accessed when parameter IDEBUG>1. This subroutine provides an output of the convergence forcer, system Gibbs Free Energy, the relative state of convergence, specie molar amounts and changes in the reaction extents. A listing of DEBUG is shown in Figure B20.

B.4.17 GIBBS

Subroutine GIBBS, shown in Figure B21, calculates the total system Gibbs Free Energy using the relation

$$G = RT \sum_{i=1}^{vsc} n_i \left[\mu_i^o + \ln \left(\gamma_i \, X_i \, P_{pi} \right) \right] \qquad (1)$$

where: γ_i = activity coefficient

X_i = mole fraction of i

$$P_{pi} = \begin{cases} P/P_o & \text{vapor phase} \\ 1 & \text{condensed phases} \end{cases}$$

B.4.18 PMAT, DPMAT, PVEC, and IPVEC

Subroutines PMAT, DPMAT, PVEC and IPVEC are used to write out single precision, double precision matricies, and single precision and integer vectors when the debugging option is active. Listings of these subroutines are shown in Figure B22 through B25.

Figure B18. Subroutine ORDER

```
      SUBROUTINE ORDER(ISPCE,SPECIE,PHASE,N,A,STDCP,A0,A1,A2,A3,DH0,
     &DS0,DZETA,CHMPT,ACOEF,FRAC,QUES,DG,Q,KEQ,ICP,IDIM1,IDIM2,E,VSC,
     &IWRT)
C
C  SUBROUTINE TO ORDER THE ARRAYS BACK TO THE ORIGINAL ORDER
C  OF THE PROBLEM STATEMENT
C
      DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1),A0(IDIM1),A1(IDIM1),
     &A2(IDIM1),A3(IDIM1),CHMPT(IDIM1),ACOEF(IDIM1),DH0(IDIM1),
     &DS0(IDIM1),FRAC(IDIM1),DG(IDIM1),Q(IDIM1),ICP(IDIM1)
      INTEGER QUES(IDIM1),ISPCE(IDIM1,3),SPECIE(IDIM1,3),
     &        PHASE(IDIM1,3),E,VSC,VSCM1
      REAL KEQ(IDIM1)
      REAL*8 N(IDIM1),DZETA(IDIM1),TEMP
      VSCM1=VSC-1
      DO 300 I=1,VSCM1
      IP1=I+1
      DO 200 II=IP1,VSC
      IF(ISPCE(I,1).EQ.SPECIE(II,1).AND.
     &   ISPCE(I,2).EQ.SPECIE(II,2).AND.
     &   ISPCE(I,3).EQ.SPECIE(II,3)) GO TO 50
      GO TO 200
   50 TEMP=N(I)
      N(I)=N(II)
      N(II)=TEMP
      TEMP=STDCP(I)
      STDCP(I)=STDCP(II)
      STDCP(II)=TEMP
      TEMP=A0(I)
      A0(I)=A0(II)
      A0(II)=TEMP
      TEMP=A1(I)
      A1(I)=A1(II)
      A1(II)=TEMP
      TEMP=A2(I)
      A2(I)=A2(II)
      A2(II)=TEMP
      TEMP=A3(I)
      A3(I)=A3(II)
      A3(II)=TEMP
      TEMP=DH0(I)
      DH0(I)=DH0(II)
      DH0(II)=TEMP
      TEMP=DS0(I)
      DS0(I)=DS0(II)
      DS0(II)=TEMP
      ITEMP=ICP(I)
      ICP(I)=ICP(II)
      ICP(II)=ITEMP
      TEMP=DZETA(I)
      DZETA(I)=DZETA(II)
      DZETA(II)=TEMP
      TEMP=CHMPT(I)
      CHMPT(I)=CHMPT(II)
```

```
      CHMPT(II)=TEMP
      TEMP=ACOEF(I)
      ACOEF(I)=ACOEF(II)
      ACOEF(II)=TEMP
      TEMP=FRAC(I)
      FRAC(I)=FRAC(II)
      FRAC(II)=TEMP
      ITEMP=QUES(I)
      QUES(I)=QUES(II)
      QUES(II)=ITEMP
      TEMP=DG(I)
      DG(I)=DG(II)
      DG(II)=TEMP
      TEMP=C(I)
      Q(I)=Q(II)
      Q(II)=TEMP
      TEMP=KEQ(I)
      KEQ(I)=KEQ(II)
      KEQ(II)=TEMP
      DO 60 J=1,3
      ITEMP=SPECIE(I,J)
      SPECIE(I,J)=SPECIE(II,J)
      SPECIE(II,J)=ITEMP
      ITEMP=PHASE(I,J)
      PHASE(I,J)=PHASE(II,J)
      PHASE(II,J)=ITEMP
   60 CONTINUE
      DO 100 J=1,E
      TEMP=A(I,J)
      A(I,J)=A(II,J)
      A(II,J)=TEMP
  100 CONTINUE
  200 CONTINUE
  300 CONTINUE
      RETURN
      END
```

Figure B19. Subroutine WRAPUP

```
      SUBROUTINE WRAPUP(TITLE,SPECIE,INERT,N,FRAC,GUESS,ZV,ZAC,ZIT,T,
     &    SIMF,ACTSIS,ACTGAS,ACTINS,ACTPS,ACTASS,RIIIV,RGAAS,RINP,
     &   BSTCVG,ITBST,RELMAX,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE,V,VSC)
C
C  SUBROUTINE TO WRITE-OUT A SUMMARY OF THE RESULTS TO A FILE
C
      DIMENSION INERT(3),FRAC(IDIM1)
      INTEGER TITLE(20),SPECIE(IDIM1,3),GUESS(IDIM1),V,VSC,
     &        EL(5)/'SI','GA','IN',' P','AS'/
      REAL*8 N(IDIM1)
      IF(IDATA.EQ.0) WRITE(IFILE,50) (TITLE(K),K=1,20)
   50 FORMAT(20A4)
      WRITE(IFILE,55) T,P
   55 FORMAT('TEMPERATURE = ',F7.1,' K',/,'PRESSURE = ',1PE12.5,' PA')
      IF(ABS(RELMAX).GT.CNVG.AND.IDATA.NE.0)WRITE(IFILE,58) RELMAX,
     & CNVG,ESTCVG,ITBST
   58 FORMAT(66('*'),/,'*',5X,'ITERATION FOR EQUILIBRIUM COMPOSITION ',
     &       'DID NOT CONVERGE',5X,'*',/,'*',1X,'MAXIMUM ERROR=',
     &       E12.5,2X,'CONVERGENCE CRITERION=',E12.5,1X,'*',
     &/,'*',9X,'BEST CONVERGENCE=',E12.5,' AT ITERATION ',I4,8X,'*',
     &/,'*',12X,'THE BEST OBTAINED RESULTS ARE SHOWN BELOW',11X,'*',
     &       /,66('*'))
      IF(IDATA.EQ.0) WRITE(IFILE,60)
   60 FORMAT(13X,'INITIAL COMPOSITIONS')
      IF(IDATA.EQ.1) WRITE(IFILE,70)
   70 FORMAT(13X,'EQUILIBRIUM COMPOSITIONS')
      IF(IDATA.EQ.0) WRITE(IFILE,80)
   80 FORMAT('SPECIE',7X,'MOLE FRACTION',4X,'GRAM MOLES')
      DO 200 I=1,VSC
      WRITE(IFILE,100) (SPECIE(I,K),K=1,3),FRAC(I),N(I),GUESS(I)
      IF(I.NE.V) GO TO 200
      WRITE(IFILE,100) (INERT(K),K=1,3),FRACZ,ZV
  100 FORMAT(3A4,2X,E12.5,2X,E12.5,1X,A4)
      IF(RIIIV.GT.0.AND.RIIIV.LT.1.0E6) WRITE(IFILE,105) RIIIV
  105 FORMAT('VAPOR III/V ',10X,F9.4)
      IF(SITOT.GT.0) WRITE(IFILE,110) SIMF,SITOT
  110 FORMAT('SI IN VAPOR ',2X,E12.5,2X,E12.5)
      IF(ACTSIS.GT.0) WRITE(IFILE,120) EL(1),ACTSIS
  120 FORMAT(1A2,' ACTIVITY',13X,E12.5)
      IF(ACTGAS.GT.0) WRITE(IFILE,120) EL(2),ACTGAS
      IF(ACTINS.GT.0) WRITE(IFILE,120) EL(3),ACTINS
      IF(ACTPS.GT.0) WRITE(IFILE,120) EL(4),ACTPS
      IF(ACTASS.GT.0) WRITE(IFILE,120) EL(5),ACTASS
      IF(RGAAS.GT.0) WRITE(IFILE,130) RGAAS
  130 FORMAT('GA-AS SATURATION RATIO  ',E12.5)
      IF(RINP.GT.0) WRITE(IFILE 135) RINP
  135 FORMAT(' IN-P SATURATION RATIO  ',E12.5)
  200 CONTINUE
      IF(ISS.GT.0) WRITE(IFILE,205) XIII
  205 FORMAT(3X,'X=',F6.4)
      WRITE(IFILE,210)
  210 FORMAT('      ')
      IDATA=1
      RETURN
      END
```

Figure B20. Subroutine DEBUG

```
      SUBROUTINE DEBUG(N,DZETA,VSC,ICIM1,ITER,ALMBDA,GFE,
     &                 RMX,IWRT)
C
C  ROUTINE TO WRITE-OUT N, DZETA, ALMBDA DURING THE ITERATION PROCESS
C
      REAL*8 N(ICIM1),DZETA(ICIM1)
      INTEGER VSC
      WRITE(IWRT,10) ITER,ALMBDA,GFE,RMX
   10 FORMAT('0','ITERATION = ',I5,5X,'LAMBDA = ',E14.7,
     &       5X,'GIBBS FREE ENERGY = ',E14.7,' KCAL',
     &       5X,'RELATIVE ERROR = ',E12.5,/,1X,
     &       'N-VALUES',T20,'DELTA-ZETA VALUES')
      DO 50 I=1,VSC
      WRITE(IWRT,20) N(I),DZETA(I)
   20 FORMAT(1X,E14.7,T20,E14.7)
   50 CONTINUE
      RETURN
      END
```

Figure B21. Subroutine GIBBS

```
      SUBROUTINE GIBBS(N,STDCP,STDCPZ,ACCEF,FRAC,ZV,FRACZ,COND,SCLN,
     &                 PHASE,FT,P,PO,IDIM1,V,S,C,GFE)
C
C  SUBROUTINE TO CALCULATE THE GIBBS FREE ENERGY OF THE SYSTEM
C
      DIMENSION STDCP(IDIM1),FRAC(IDIM1),ACCEF(IDIM1)
      REAL*8 N(IDIM1)
      INTEGER COND(3),SCLN(3),PHASE(IDIM1,3),V,S,C,VSC
      VSC=V+S+C
C
C  GAS CONSTANT IS IN UNITS OF: KCAL/G-MOLE-K
C
      ARG=1.0
      IF(FRACZ.GT.0.0) ARG=FRACZ*P/PO
      GSTAR=ZV*(STDCPZ+ALOG(ARG))
      DO 150 I=1,VSC
      ARG=ACCEF(I)*FRAC(I)*P/PO
      IF(PHASE(I,1).EQ.COND(1)) ARG=1
      IF(PHASE(I,1).EQ.SCLN(1)) ARG=ACCEF(I)*FRAC(I)
      GSTAR=GSTAR+N(I)*(STDCP(I)+ALOG(ARG))
  150 CONTINUE
      GFE=GSTAR*RT
      RETURN
      END
```

Figure B22. Subroutine PMAT

```
      SUBROUTINE PMAT(MATRIX,NDIM1,NDIM2,L1,L2,NAME,IWRT)
C
C  SUBROUTINE TO WRITE-OUT REAL MATRICIES
C
      INTEGER*2 NAME(3)
      REAL MATRIX(NDIM1,NDIM2)
      WRITE(IWRT,10) (NAME(J),J=1,3)
   10 FORMAT('0','MATRIX ',3A2)
      DO 100 I=1,L1
      WRITE(IWRT,20) (MATRIX(I,J),J=1,L2)
   20 FORMAT(1X,10(E11.4,2X))
  100 CONTINUE
      RETURN
      END
```

Figure B23 Subroutine DPMAT

```
      SUBROUTINE DPMAT(DMTRIX,NDIM1,NDIM2,L1,L2,NAME,IWRT)
C
C  SUBROUTINE TO WRITE-OUT DOUBLE PRECISION REAL MATRICIES
C
      DOUBLE PRECISION DMTRIX(NDIM1,NDIM2)
      INTEGER*2 NAME(3)
      WRITE(IWRT,10) (NAME(J),J=1,3)
   10 FORMAT('0','MATRIX ',3A2)
      DO 100 I=1,L1
      WRITE(IWRT,20) (DMTRIX(I,J),J=1,L2)
   20 FORMAT(1X,10(D11.4,2X))
  100 CONTINUE
      RETURN
      END
```

Figure B24. Subroutine PVEC

```
      SUBROUTINE PVEC(VECTOR,NDIM,L,NAME,IWRT)
C
C  SUBROUTINE TO WRITE-OUT REAL VECTORS
C
      DIMENSION VECTOR(NDIM)
      INTEGER*2 NAME(3)
      WRITE(IWRT,10) (NAME(J),J=1,3)
   10 FORMAT('0','THE TRANSPOSED ',3A2,' VECTOR IS:')
      WRITE(IWRT,20) (VECTOR(J),J=1,L)
   20 FORMAT(1X,10(E11.4,2X))
      RETURN
      END
```

Figure B25. Subroutine IPVEC

```
      SUBROUTINE IPVEC(IVCTOR,NDIM,L,NAME,IWRT)
C
C  SUBROUTINE TO WRITE-OUT INTEGER VECTORS
C
      DIMENSION IVCTOR(NDIM)
      INTEGER*2 NAME(3)
      WRITE(IWRT,10) (NAME(J),J=1,3)
   10 FORMAT('0','THE TRANSPOSED ',3A2,' VECTOR IS:')
      WRITE(IWRT,20) (IVCTOR(J),J=1,L)
   20 FORMAT(1X,10(I11,2X))
      RETURN
      END
```

B.4.19 IMSL Subroutines LINVIF, LEQTIF LUELMF, and LUDATF.

The calling sequence of the IMSL subroutines is shown in Figure B26 and listings of these subroutines are provided in Figure B27. Subroutine LINVIF inverts matricies by placing ones on the diagonal of matrix B and then calling LEQTIF to solve the matrix problem

$$A\ X = B \qquad (1)$$

for matrix X, the inverse of A.

Double precision arithmetic is used and the routines test to see that IDGT significant figures are present in the result. If less than IDGT significant figures are present parameter IER is set to 34. Parameter IER is set to 129 if matrix A is found to be algorithmically singular.

Figure 32

IMSL Subroutine Calling Sequence

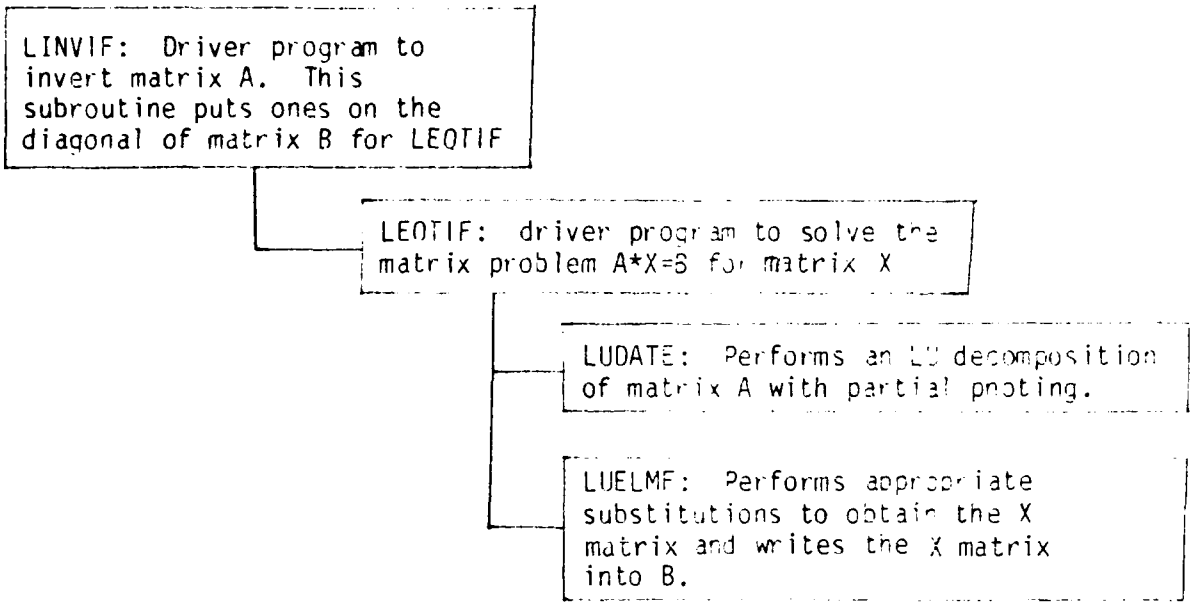

Figure B27 IMSL Subroutines LINVIF, LEQTIF, LUDATF and LUELMF

```
      SUBROUTINE LINVIF (A,N,IA,AINV,IDGT,WKAREA,IER)
C
C  IMSL SUBROUTINE FOR INVERTING REAL MATRICIES
C
      DOUBLE PRECISION A(IA,N),AINV(IA,N),WKAREA(1),ZERO,ONE
      DATA                 ZERO/0.0D0/,ONE/1.0D0/
      IER=0
      DO 10 I=1,N
         DO 5 J=1,N
            AINV(I,J) = ZERO
    5    CONTINUE
         AINV(I,I) = ONE
   10 CONTINUE
      CALL LEQTIF (A,N,N,IA,AINV,IDGT,WKAREA,IER)
      IF (IER .EQ. 0) GO TO 9005
 9000 CONTINUE
 9005 RETURN
      END
```

```
      SUBROUTINE LEQTIF (A,M,N,IA,B,IDGT,WKAREA,IER)
C
C  IMSL SUBROUTINE LEQTIF FOR SOLVING THE MATRIX PROBLEM A*X=B
C
      DIMENSION          A(IA,1),B(IA,1),WKAREA(1)
      DOUBLE PRECISION   A,B,WKAREA,D1,D2,WA
C                                     INITIALIZE IER
C                                     FIRST EXECUTABLE STATEMENT
      IER=0
C                                     DECOMPOSE A
      CALL LUDATF (A,A,N,IA,IDGT,D1,D2,WKAREA,WKAREA,WA,IER)
      IF (IER .GT. 128) GO TO 9005
C                                     CALL ROUTINE LUELMF (FORWARD AND
C                                     BACKWARD SUBSTITUTIONS)
      DO 10 J=1,M
         CALL LUELMF (A,B(1,J),WKAREA,N,IA,B(1,J))
   10 CONTINUE
 9005 RETURN
      END
```

```
      SUBROUTINE LUDATF (A,LU,N,IA,IDGT,D1,D2,IPVT,EQUIL,WA,IER)
C
C  THIS SUBROUTINE IS USED WITH SUBROUTINE LEQTIF
C
      DIMENSION          A(IA,1),LU(IA,1),IPVT(1),EQUIL(1)
      DOUBLE PRECISION   A,LU,D1,D2,EQUIL,WA,ZERO,ONE,FOUR,SIXTN,SIXTH,
     *                   RN,WREL,BIGA,BIG,P,SUM,AI,WI,T,TEST,C
      DATA               ZERO,ONE,FOUR,SIXTN,SIXTH/0.D0,1.D0,4.D0,
     *                   16.D0,.0625D0/
C                                     FIRST EXECUTABLE STATEMENT
C                                     INITIALIZATION
      IER = 0
      RN = N
      WREL = ZERO
      D1 = ONE
      D2 = ZERO
      BIGA = ZERO
      DO 10 I=1,N
         BIG = ZERO
         DO 5 J=1,N
            P = A(I,J)
            LU(I,J) = P
            P = DABS(P)
            IF (P .GT. BIG) BIG = P
    5    CONTINUE
         IF (BIG .GT. BIGA) BIGA = BIG
         IF (BIG .EQ. ZERO) GO TO 110
         EQUIL(I) = ONE/BIG
   10 CONTINUE
      DO 105 J=1,N
         JM1 = J-1
         IF (JM1 .LT. 1) GO TO 40
C                                     COMPUTE U(I,J), I=1,...,J-1
         DO 35 I=1,JM1
            SUM = LU(I,J)
            IM1 = I-1
            IF (IDGT .EQ. 0) GO TO 25
C                                     WITH ACCURACY TEST
            AI = DABS(SUM)
            WI = ZERO
            IF (IM1 .LT. 1) GO TO 20
            DO 15 K=1,IM1
               T = LU(I,K)*LU(K,J)
               SUM = SUM-T
               WI = WI+DABS(T)
   15       CONTINUE
            LU(I,J) = SUM
   20       WI = WI+DABS(SUM)
            IF (AI .EQ. ZERO) AI = BIGA
            TEST = WI/AI
            IF (TEST .GT. WREL) WREL = TEST
            GO TO 35
C                                     WITHOUT ACCURACY
   25       IF (IM1 .LT. 1) GO TO 35
```

```
      DO 30 K=1,IM1
         SUM = SUM-LU(I,K)*LU(K,J)
30    CONTINUE
      LU(I,J) = SUM
35  CONTINUE
40  P = ZERO
C                                   COMPUTE U(J,J) AND L(I,J), I=J+1,...
    DO 70 I=J,N
      SUM = LU(I,J)
      IF (IDGT .EQ. 0) GO TO 55
C                                   WITH ACCURACY TEST
      AI = DABS(SUM)
      WI = ZERO
      IF (JM1 .LT. 1) GO TO 50
      DO 45 K=1,JM1
         T = LU(I,K)*LU(K,J)
         SUM = SUM-T
         WI = WI+DABS(T)
45    CONTINUE
      LL(I,J) = SUM
50    WI = WI+DABS(SUM)
      IF (AI .EQ. ZERO) AI = EIGA
      TEST = WI/AI
      IF (TEST .GT. WREL) WREL = TEST
      GO TO 65
C                                   WITHOUT ACCURACY TEST
55    IF (JM1 .LT. 1) GO TO 65
      DO 60 K=1,JM1
         SUM = SUM-LU(I,K)*LU(K,J)
60    CONTINUE
      LU(I,J) = SUM
65    Q = EQUIL(I)*DABS(SUM)
      IF (P .GE. Q) GO TO 70
      P = Q
      IMAX = I
70  CONTINUE
C                                   TEST FOR ALGORITHMIC SINGULARITY
    IF (RN+P .EQ. RN) GO TO 110
    IF (J .EQ. IMAX) GO TO 80
C                                   INTERCHANGE ROWS J AND IMAX
    D1 = -D1
    DO 75 K=1,N
      P = LU(IMAX,K)
      LU(IMAX,K) = LU(J,K)
      LU(J,K) = P
75  CONTINUE
    EQUIL(IMAX) = EQUIL(J)
80  IPVT(J) = IMAX
    D1 = D1*LU(J,J)
85  IF (DABS(D1) .LE. ONE) GO TO 90
    D1 = D1*SIXTH
    D2 = D2+FOUR
    GO TO 85
90  IF (DABS(D1) .GE. SIXTH) GO TO 95
```

```
      D1 = D1*SIXTN
      D2 = D2-FOUR
      GO TO 90
   95 CONTINUE
      JP1 = J+1
      IF (JP1 .GT. N) GO TO 105
C                                        DIVIDE BY PIVOT ELEMENT U(J,J)
      P = LU(J,J)
      DO 100 I=JP1,N
         LU(I,J) = LU(I,J)/P
  100 CONTINUE
  105 CONTINUE
C                                        PERFORM ACCURACY TEST
      IF (IDGT .EQ. 0) GO TO 9005
      P = 3*N+3
      WA = P*WREL
      IF (WA+10.D0**(-IDGT) .NE. WA) GO TO 9005
      IER = 34
      GO TO 9005
C                                        ALGORITHMIC SINGULARITY
  110 IER = 129
      D1 = ZERO
      D2 = ZERO
 9005 RETURN
      END
```

```
      SUBROUTINE LUELMF (A,B,IPVT,N,IA,X)
C
C  THIS SUBROUTINE IS USED WITH SUBROUTINE LEQTIF
C
      DIMENSION          A(IA,1),B(1),IPVT(1),X(1)
      DOUBLE PRECISION   A,B,X,SUM
C                                        FIRST EXECUTABLE STATEMENT
C                                        SOLVE LY = B FOR Y
      DO 5 I=1,N
    5 X(I) = B(I)
      IM = 0
      DO 20 I=1,N
         IP = IPVT(I)
         SUM = X(IP)
         X(IP) = X(I)
         IF (IM .EQ. 0) GO TO 15
         IM1 = I-1
         DO 10 J=IM,IM1
            SUM = SUM-A(I,J)*X(J)
   10    CONTINUE
         GO TO 20
   15    IF (SUM .NE. 0.D0) IM = I
   20 X(I) = SUM
C                                        SOLVE UX = Y FOR X
      DO 30 IB=1,N
         I = N+1-IB
         IP1 = I+1
         SUM = X(I)
         IF (IP1 .GT. N) GO TO 30
         DO 25 J=IP1,N
            SUM = SUM-A(I,J)*X(J)
   25    CONTINUE
   30 X(I) = SUM/A(I,I)
      RETURN
      END
```

B.5 Theoretical Development of the Stoichiometric Algorithm

The stoichiometric algorithms employed by Cruise [1] and Smith and Missen [2] may be extended to include a solution phase in addition to vapor and pure condensed phases. A stoichiometric algorithm is one in which a set of formation reaction equations are used to provide a driving force in the numerical solution of the equilibrium problem. The formation reaction for any specie i in a system containing E elements is written as

$$S_i = \sum_{k=1}^{E} \nu_{ik} S_k^b \qquad (1)$$

The reactants in equation 1 are called the basis species (thus the superscript "b") and form a linearly independent set of species from within the system which represent all of the elements present in the system. The stoichiometric coefficient ν_{ik} describes the number of molecules of basis specie k which are required in the formation of specie i.

The technique used in this stoichiometric algorithm to calculate the equilibrium composition of the system is as follows. First, the equilibrium constants for the formation reactions in equation 1 are calculated from the Gibbs Free Energy change of the reactions. Next, the current compositions for each of the species present are used to calculate another "equilibrium constant". The values of the two constants are then used in finite difference equations which approximate derivatives of the equilibrium constants with respect to the reaction extents. These equations predict changes in the reaction extents which will yield an improved approximation to the equilibirum composition of the system.

The discrete formulation of this algorithm, applied to a system consisting of a vapor phase have V speices, a solution phase have S species and C pure condensed phases, starts with the definitions of the elemental abundance matrix, a vector representing the molar amount of each specie and a vector containing the total moles of each element present in the system.

$$\underline{A} = \begin{pmatrix} a_{11} & \cdots & a_{iE} \\ a_{vsc,1} & \cdots & a_{vsc,E} \end{pmatrix}$$

$$\underline{N}^T = (n_1 \ \ldots \ n_{vsc})$$

$$\underline{B}^T = (b_1 \ \ldots \ b_E)$$

where: a_{ij} = number of atoms of element j in specie i

n_i = moles of specie i in the system

b_j = moles of element j in the system

VSC = V+S+C

E = number of elements in the system

These definitions result in the following relationship which describes the system mass balance.

$$A^T N = B \qquad (2)$$

In order to construct a set of formation reactions, as in equation 1, a set of basis species which are linearly independent from each other yet represent all of the elements present in the system must be found. A further restriction is placed upon the set of basis species when the convergence rate of the algorithm is considered. Obviously, the molar amounts of each specie must be nonnegative for a physically realistic situation to exist. If a basis specie which has a very small initial composition is chosen, and the formation of another specie requires the consumption of this basis specie, then the rate of convergence will be slow in order to prevent the molar amount of the basis specie from becoming negative. Thus, a rapidly converging algorithm will employ an optimum set of basis species which, in addition to the two previously mentioned requirements, are present in the greatest molar amounts available. Also, since the molar amounts of each specie change after each iteration, this optimum set of basis species may need to be rechosen at each iteration.

The optimum set of basis species is chosen by first sorting vector N into descending order ($n_1 > n_2 > \ldots n$) and ordering the rows of A correspondingly. The first row of A is then transferred into the first row of a new matrix D. The second row of A is then transferred into the next row of D and tested for linear independence. If it is linearly independent the row is kept and the process continues. If not the next row in A is tried. This process in continued until D is filled. For a system comprised of E elements there will be E basis species, therefore matrix D will always be square.

An efficient method of testing for linear independence between the rows of the D matrix is to build the Gram-Schmidt orthogonalized matrix D' using the formulation [4]

$$d'_{1j} = d_{1j}$$

$$d'_{ij} = d_{ij} - \sum_{\ell=1}^{i-1} d'_{\ell j} \left[\frac{\sum_{k=1}^{E} d_{ik}\, d'_{\ell k}}{\sum_{k=1}^{E} (d'_{\ell k})^2} \right] \qquad (3)$$

where: $i = 2,3,\ldots md$

$j = 1,2\ldots E$

md = current row in matrix D

A linear dependence between row md of D and the remaining rows in D exists if row md of D' contains all zeros.

The matrix containing the stoichiometric coefficients for all of the formation reactions is given by:

$$N = \begin{pmatrix} \nu_{11} & \cdots & \nu_{iE} \\ \vdots & & \\ \nu_{vsc,1} & \cdots & \nu_{vsc,E} \end{pmatrix} = A\, D^{-1} \qquad (4)$$

Equilibrium constants may now be calculated for each of the formation reaction equations using the Gibbs Free Energy change of each reaction.

$$\ell n\, K_{eqi} = \frac{1}{RT} \left(\sum_{k=1}^{E} \nu_{ik}\, \mu_k^\circ - \mu_i^\circ \right) \qquad (5)$$

where: μ_i° = standard chemical potential of specie i

μ_k° = standard chemical potential of basis specie k

An "equilibrium constant" for each formation reaction may also be calculated from the current estimate to the equilibrium composition.

$$\ell n\, Q_i = \ell n\, a_i - \sum_{k=1}^{E} \nu_{ik}\, \ell n\, a_k \qquad (6)$$

where: $a_i = \gamma_i\, n_i\, P_{pi}/n_T$ (activity of speice i)

γ_i = activity coefficient

n_T = total moles of species in the same phase as specie i

$$P_{pi} = \begin{cases} P/Po & \text{vapor species} \\ 1 & \text{nonvapor species} \end{cases}$$

Defining the extent of reaction, ξ_i, as

$$\xi_i = (n'_j - n_j)/\nu_{ij}$$

where: n'_j = composition of specie j at reaction extent ξ_i

the "equilibrium constant" as calculated from the current composition may be written as

$$\ell n\ Q_i = \ell n\ [\beta_i(n_i + \xi_i)] - \sum_{k=1}^{E} \gamma_{ik}\ \ell n\ [\beta_i(n_k + \nu_{ik}\xi_i)] \qquad (7)$$

where: $\beta_i = \gamma_i\ P_{pi}/n_T$

As an approximation assume that β_i and β_k are constant for small changes in ξ_i. Introducing a function δ_i to account for nonvapor phases, a finite difference approximation which relates changes in the extent of reaction to the difference between the actual equilibrium constant and the "equilibrium constant" calculated from the current composition is obtained by differentiation of equation 7.

$$\frac{\ell n\ K_{eqi} - \ell n\ Q_i}{\Delta\xi_i} \approx \frac{d\ \ell n\ Q_i}{d\xi_i} \approx \frac{\delta_i}{n_i} - \sum_{k=1}^{E} \frac{\delta_k\ \nu_{ik}^2}{n_k} \qquad (8)$$

where: $\delta_i,\ \delta_k = \begin{cases} 1 \text{ vapor phase} \\ 0 \text{ nonvpaor phases} \end{cases}$

Thus the difference between the equilibrium constant for formation reaction i as calculated from the Gibbs Free Energy (K_{eqi}) and as calculated from the current approximation to the equilibrium composition (Q_i) results in a prediction of $\Delta\xi_i$ which will yield a better approximation to the system equilibrium composition.

In order to prevent the occurance of negative molar amounts the effect of $\Delta\xi_i$ on the new composition must be tested. Thus, for the nonbasis species:

$$n'_i = n_i\ \Delta\xi'_i \qquad (9)$$

and for the basis species

$$n'_k = n_k - \sum_{i=1}^{vsc} \nu_{ik}\ \Delta\xi_i \qquad (10)$$

$$\text{where: } \Delta\xi'_i = \kappa\,\Delta\xi_i \qquad (11)$$

In order to assure that nonbasis species remain positive $\Delta\xi_i$ is set equal to $-n_i$ if $\Delta\xi_i<0$ and $|\Delta\xi_i| > n_i$. Nonnegativity of the basis species is assured by applying the relation

$$\kappa = -n_k \Big/ \sum_{i=1}^{vsc} (-\nu_{ik}\,\Delta\xi_i) \qquad (12)$$

to each of the basis species in the system and choosing the smallest positive value of κ which results while κ is constrained to be no greater than unity.

In order to assure convergence of the numerical scheme it is necessary to apply a convergence forcer. The Gibbs Free Energy of the system is given by

$$G = \sum_{i=1}^{vsc} n_i \left[\mu_i^\circ + RT \ln a_i\right] \tag{11}$$

The procedure used for determining the value of the convergence forcer, λ, is as follows.

1) Evaluate the derivative:

$$\left(\frac{dG}{d\lambda}\right)_{\lambda=1} = \sum_{i=1}^{vsc} \Delta n_i \left[\mu_i^\circ + \ln a_i'\right] \tag{12}$$

where: $a_i' = \beta_i n_i'$

$$\Delta n_i = n_i' - n_i$$

If $\left(\frac{dG}{d\lambda}\right)_{\lambda=1} \leq 0$ then set $\lambda = 1$.

2) If $\left(\frac{dG}{d\lambda}\right)_{\lambda=1} > 0$ then evaluate:

$$\left(\frac{dG}{d\lambda}\right)_{\lambda=0} = \sum_{i=1}^{vsc} \Delta n_i \left[\mu_i^\circ + \ell n\ a_i\right] \tag{13}$$

The optimum value of λ is then approximated by:

$$\lambda = \frac{\left(dG/d\lambda\right)_{\lambda=0}}{\left(\frac{dG}{d\lambda}\right)_{\lambda=0} - \left(\frac{dG}{d\lambda}\right)_{\lambda=1}} \tag{14}$$

Equation 14 represents a single step of a Regula-Falsi root finding algorithm which yields a sufficiently accurate estimate to the optimum value of the convergence forcer. Infrequently, equation 14 will predict a negative value for λ and in this case λ is set to 0.05 in order to allow the iterative solution to continue.

B.6 Example Calculation: The GaAs Chloride System Source Zone

The results of an equilibrium calculation for the GaAs chloride system source zone are shown in Figure B28. The wrap-up file of these results and the data file which yielded them are shown in Figures B29 and B30 respectively. This calculation determines the gas phase composition leaving the source zone of a chloride system CVD reactor at a temperature of 700C and 1 atm pressure. The inlet gas composition was 1% $AsCl_3$ and 99% H_2. The steady state liquid option (ISS=1) was active and excess solid SiO_2 was assumed present in order to determine the amount of silicon which would be present in the vapor.

Figure B28. The GaAs Chloride System Source Zone

STOICHIOMETRIC FORMULATION FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS CHLORIDE SYSTEM SOURCE ZONE A TEST OF MOMPEC S101C PAGE 1

TEMPERATURE = 923.2 K PRESSURE = 0.10133E 06 PA

SPECIE SYMBOL	ENTHALPY OF FORMATION 298 (KCAL/G-MOLE)	ENTROPY OF FORMATION 298 (KCAL/G-MOLE-K)	HEAT CAPACITY CORRELATION COEFFICIENTS ICP=0 CP = A0 + A1*T + A2/T**2 + A3*LN(T) ICP=1 CP = A0 + A1*T + A2*T**2 + A3*T**3 A0 (KCAL/G-MOLE-K)	A1 (KCAL/G-MOLE-K**2)	A2 ( )	A3 ( )	ICP (-)
AS (V)	55.560	0.033951	0.003761	0.0	0.0	0.0	0
AS2 (V)	45.760	0.049486	0.007530	-0.16900E-06	-0.37080E 02	0.21130E-03	0
AS3 (V)	52.200	0.048531	0.010836	-0.13650E-06	-0.50890E 02	0.17200E-03	0
AS4 (V)	57.700	0.044112	0.013616	-0.17560E-06	-0.11120E 03	0.21800E-03	0
AS-CL (V)	-17.400	0.031069	0.008471	0.45300E-07	-0.94150E 02	0.0	0
AS-CL2 (V)	-14.500	0.040420	0.013790	0.85650E-07	-0.35240E 02	0.0	0
AS-CL3 (V)	-52.700	0.048495	0.017760	0.77600E-07	-0.15766E 03	0.0	0
AS-H (V)	58.000	0.025367	0.005400	0.14320E-05	-0.10800E 02	0.0	0
AS-H2 (V)	16.500	-0.003120	0.010070	0.54290E-05	-0.22000E 03	0.0	0
CL (V)	28.990	0.039809	0.005779	-0.40830E-06	-0.18679E 02	0.0	0
CL2 (V)	0.0	0.0	0.006800	0.20600E-06	-0.67040E 02	0.0	0
GA (V)	65.720	0.030617	0.030138	0.20900E-05	-0.26500E 03	-0.38120E-02	0
GA-CL (V)	-17.400	0.020757	0.008920	0.10210E-07	-0.39450E 02	0.0	0
GA-CL2 (V)	-59.400	0.009042	0.013840	0.51750E-07	-0.86440E 02	0.0	0
GA-CL3 (V)	-107.200	-0.004763	0.018740	0.74750E-07	-0.16900E 03	0.0	0
GA-CL6 (V)	-225.500	0.041406	0.043060	0.42760E-06	-0.49220E 03	0.0	0
H (V)	52.103	0.011708	0.004968	0.0	0.0	0.0	0
H2 (V)	0.0	0.0	0.015696	0.21200E-05	-0.59060E 02	-0.14620E-02	0
HCL (V)	-22.063	0.002394	0.006524	0.12900E-05	-0.32510E 02	0.0	0
HCL3 (V)	-97.790	0.010604	0.009439	0.24400E-05	0.57900E 02	0.16320E-03	0
N (V)	59.550	0.013925	0.005542	0.51030E-07	0.13680E 02	-0.89900E-04	0
N2 (V)	0.0	0.0	0.007902	-0.11500E-05	0.88770E 02	0.25045E-02	0
NH (V)	85.420	0.007374	0.011411	0.18800E-05	0.26700E 01	-0.70700E-03	0
NH2 (V)	39.500	0.004617	0.004650	0.18000E-06	0.42000E 02	0.0	0
NH3 (V)	-17.900	0.044869	0.008870	0.13370E-06	-0.53000E 02	0.0	0
NH4CL (V)	-75.000	0.022924	0.011763	0.20400E-06	-0.11050E 03	0.40610E-03	0
NH4CL2 (V)	-132.300	0.006751	0.012777	0.76200E-06	-0.17605E 03	0.11170E-02	0
NH4CL3 (V)	-189.600	-0.031996	0.014511	0.17190E-05	-0.24150E 03	0.17780E-02	0
NH4 (V)	70.000	0.027217	0.006630	0.14230E-05	-0.98840E 01	0.0	0
NH4CL	-71.000	0.018010	-0.000824	-0.14200E-05	0.33290E 03	0.14597E-01	0
NH4CL3	-117.900	-0.025100	-0.007910	-0.24200E-05	-0.15350E 03	0.49330E-02	0
SI2H2CL2	-79.900	-0.020452	-0.031507	-0.38500E-05	-0.34460E 02	0.84077E-02	0
SIH2CL	-43.700	-0.013043	-0.050376	-0.50400E-05	0.12480E 03	0.11534E-01	0
SIH3 (V)	-11.000	0.027100	0.006471	-0.13900E-05	0.47550E 02	0.23680E-02	0
SIH2 (V)	31.000	0.031009	-0.014368	-0.27000E-05	0.95000E 01	0.44804E-02	0
SIH3CL (V)	-18.200	0.029847	0.042150	-0.10300E-05	0.84600E 01	0.0	0
SIH4 (V)	12.500	0.049593	0.002947	0.38201E-04	-0.11049E 07	0.0	1
SIH4 (V)	0.0	0.0	0.0	0.0	0.0	0.0	0
SI (V)	0.0	0.0	0.005730	0.63110E-06	-0.10560E 03	0.0	0
SICL4 (V)	-157.700	-0.033581	0.031883	0.14140E-04	-0.36070E 03	-0.17030E-02	0
GAAS(CRYS)	0.0	0.0	0.0	0.0	0.0	0.0	0

THE ENTHALPY AND ENTROPY OF FORMATION REFERENCE TEMPERATURE AND PRESSURE ARE TO = 298.2 K PO = 101325.0 PA

MAXIMUM NUMBER OF ITERATIONS ALLOWED = 1000

CONVERGENCE CRITERION = 0.1000E-03

OUTPUT PARAMETER IDEBUG = 0

[illegible] THE III-V LIQUID SOLUTION IS AT EQUILIBRIUM WITH THE III-V STOICHIOMETRIC SOLID

STOICIOMETRIC FORMULATION FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS CHLORIDE SYSTEM SOURCE ZONE. A TEST OF MCMPEC. STOIC

TEMPERATURE = 973.2 K PRESSURE = 0.10133E 06 PA

INPUT DATA AND INITIAL COMPOSITION ESTIMATES

SPECIE SYMBOL	PHASE	INITIAL COMPOSITION ESTIMATE (G MOLES)	STANDARD CHEMICAL POTENTIAL (KCAL/G-MOLE)	ELEMENTAL ABUNDANCE MATRIX H	O	CL	SI	GA	AS
AS (V)	VAPOR	0.10000000D-19	34.140	0.0	0.0	0.0	0.0	0.0	1.000
AS2 (V)	VAPOR	0.10000000D-19	2.436	0.0	0.0	0.0	0.0	0.0	2.000
AS3 (V)	VAPOR	0.10000000D-19	-1.934	0.0	0.0	0.0	0.0	0.0	3.000
AS4 (V)	VAPOR	0.10000000D-19	-14.549	0.0	0.0	0.0	0.0	0.0	4.000
AS-CL (V)	VAPOR	0.10000000D-19	-6.669	0.0	0.0	1.000	0.0	0.0	1.000
AS-CL2 (V)	VAPOR	0.10000000D-19	-1.807	0.0	0.0	2.000	0.0	0.0	1.000
AS-CL3 (V)	VAPOR	0.99999999D-02	-61.496	0.0	0.0	3.000	0.0	0.0	1.000
AS-H (V)	VAPOR	0.10000000D-19	28.451	1.000	0.0	0.0	0.0	0.0	1.000
AS-H3 (V)	VAPOR	0.10000000D-19	12.613	3.000	0.0	0.0	0.0	0.0	1.000
CL (V)	VAPOR	0.10000000D-19	13.970	0.0	0.0	1.000	0.0	0.0	0.0
CL2 (V)	VAPOR	0.10000000D-19	-4.061	0.0	0.0	2.000	0.0	0.0	0.0
GA (V)	VAPOR	0.10000000D-19	32.200	0.0	0.0	0.0	0.0	1.000	0.0
GA-CL (V)	VAPOR	0.10000000D-19	-41.543	0.0	0.0	1.000	0.0	1.000	0.0
GA-CL2 (V)	VAPOR	0.10000000D-19	-74.373	0.0	0.0	2.000	0.0	1.000	0.0
GA-CL3 (V)	VAPOR	0.10000000D-19	-106.769	0.0	0.0	3.000	0.0	1.000	0.0
GA2-CL6 (V)	VAPOR	0.10000000D-19	-204.797	0.0	0.0	6.000	0.0	2.000	0.0
H (V)	VAPOR	0.10000000D-19	58.266	1.000	0.0	0.0	0.0	0.0	0.0
H2 (V)	VAPOR	0.99999999D 00	-3.326	2.000	0.0	0.0	0.0	0.0	0.0
H-CL (V)	VAPOR	0.10000000D-19	-27.738	1.000	0.0	1.000	0.0	0.0	0.0
H2-O (V)	VAPOR	0.10000000D-19	-51.471	2.000	1.000	0.0	0.0	0.0	0.0
O (V)	VAPOR	0.10000000D-19	43.528	0.0	1.000	0.0	0.0	0.0	0.0
O2 (V)	VAPOR	0.10000000D-19	0.513	0.0	2.000	0.0	0.0	0.0	0.0
O-H (V)	VAPOR	0.10000000D-19	9.340	1.000	1.000	0.0	0.0	0.0	0.0
SI (V)	VAPOR	0.10000000D-19	70.874	0.0	0.0	0.0	1.000	0.0	0.0
SI-CL (V)	VAPOR	0.10000000D-19	10.791	0.0	0.0	1.000	1.000	0.0	0.0
SI-CL2 (V)	VAPOR	0.10000000D-19	-55.030	0.0	0.0	2.000	1.000	0.0	0.0
SI-CL3 (V)	VAPOR	0.10000000D-19	-93.970	0.0	0.0	3.000	1.000	0.0	0.0
SI-CL4 (V)	VAPOR	0.10000000D-19	-138.446	0.0	0.0	4.000	1.000	0.0	0.0
SI-H (V)	VAPOR	0.10000000D-19	60.056	1.000	0.0	0.0	1.000	0.0	0.0
SI-H4 (V)	VAPOR	0.10000000D-19	19.295	4.000	0.0	0.0	1.000	0.0	0.0
SI-H-CL3	VAPOR	0.10000000D-19	-104.369	1.000	0.0	3.000	1.000	0.0	0.0
SI-H2-CL2	VAPOR	0.10000000D-19	-64.142	2.000	0.0	2.000	1.000	0.0	0.0
SI-H3-CL	VAPOR	0.10000000D-19	-22.546	3.000	0.0	1.000	1.000	0.0	0.0
SI-O (V)	VAPOR	0.10000000D-19	-48.611	0.0	1.000	0.0	1.000	0.0	0.0
SI-O2 (V)	VAPOR	0.10000000D-19	-79.090	0.0	2.000	0.0	1.000	0.0	0.0
SI2-CL6 (V)	VAPOR	0.10000000D-19	-188.093	0.0	0.0	6.000	2.000	0.0	0.0
SI2-O (V)	VAPOR	0.10000000D-19	40.364	0.000	0.0	0.0	2.000	0.0	0.0
[illegible]	[illegible]	0.0	0.0						
SI (L)	CONDENSED	0.10000000D-19	-2.605	0.0	0.0	0.0	1.000	0.0	0.0
SI-O2 (S)	CONDENSED	0.10000000D 01	-181.795	0.0	2.000	0.0	1.000	0.0	0.0
GA-AS (L-E)	CONDENSED	0.10000000D 01	-3.011	0.0	0.0	0.0	0.0	0.994	0.006
[illegible]									

TOTAL GRAM-MOLES OF EACH ELEMENT FROM INPUT DATA AND AS CALCULATED FROM THE INITIAL COMPOSITION ESTIMATES

	INPUT DATA	CALCULATED		INPUT DATA	CALCULATED		INPUT DATA	CALCULATED		INPUT DATA	CALCULATED
H	0.19800E 01	0.19800E 01	O	0.20000E 01	0.20000E 01	CL	0.30000E-01	0.30000E-01	SI	0.10000E 01	0.10000E 01
GA	0.99353E 00	0.99353E 00	AS	0.16470E-01	0.16470E-01						

STOICIOMETRIC FORMULATION FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS CHLORIDE SYSTEM SOURCE ZONE. A TEST OF MCMPEC.STOIC.

TEMPERATURE = 973.2 K PRESSURE = 0.10133E+06 PA

EXECUTION DIAGNOSTICS

TEMPERATURE = 973.2 K PRESSURE = 0.10133E+05 PA

EQUILIBRIUM COMPOSITIONS AFTER 301 ITERATIONS

SYSTEM GIBBS FREE ENERGY = -0.1895892E+03 (KCAL)

RELATIVE ERROR = 0.24542E-04 CONVERGENCE CRITERION = 0.10000E-03 RELAXATION PARAMETER AT LAST ITERATION = 0.50000E-01

SPECIE SYMBOL	PHASE	EQUILIBRIUM MOLE FRACTION	EQUILIBRIUM COMPOSITION (G-MOLES)	ESTIMATED COMPOSITION UNCERTAINTY (G-MOLES)	CHEMICAL POTENTIAL (KCAL/G-MOLE)	ACTIVITY COEFFICIENT
[illegible] (V)	VAPOR	0.71626E-09	0.73249020-09	0.0	-6.583	0.10000E+01
[illegible]2 (V)	VAPOR	0.31360E-03	0.32071220-03	0.0	-13.166	0.10000E+01
[illegible]3 (V)	VAPOR	0.99865E-04	0.10212870-03	0.0	-19.749	0.10000E+01
[illegible]4 (V)	VAPOR	0.22596E-02	0.23108330-02	0.0	-26.331	0.10000E+01
[illegible]-CL (V)	VAPOR	0.67099E-10	0.68619730-10	0.0	-51.972	0.10000E+01
GA-CL2 (V)	VAPOR	0.34839E-21	0.35629020-21	0.0	-97.361	0.10000E+01
GA-CL3 (V)	VAPOR	0.56670E-18	0.57965650-18	0.0	-142.749	0.10000E+01
AS-H (V)	VAPOR	0.56510E-09	0.57790300-09	0.0	-8.277	0.10000E+01
AS-H3 (V)	VAPOR	0.35296E-05	0.36095810-05	0.0	-11.666	0.10000E+01
CL (V)	VAPOR	0.46795E-13	0.47855420-13	0.0	-45.389	0.10000E+01
CL2 (V)	VAPOR	0.33612E-19	0.34374010-19	0.0	-90.778	0.10000E+01
GA (V)	VAPOR	0.12531E-07	0.12815350-07	0.0	-2.788	0.10000E+01
GA-CL (V)	VAPOR	0.29201E-01	0.29863230-01	0.0	-48.377	0.10000E+01
GA-CL2 (V)	VAPOR	0.44176E-04	0.45176900-04	0.0	-93.766	0.10000E+01
GA-CL3 (V)	VAPOR	0.53388E-07	0.54597860-07	0.0	-139.155	0.10000E+01
GA2-CL6 (V)	VAPOR	0.31041E-16	0.31744810-16	-0.33907300-20	-279.309	0.10000E+01
H (V)	VAPOR	0.10628E-08	0.10868760-08	0.0	-1.694	0.10000E+01
H2 (V)	VAPOR	0.96803E+00	0.98997150+00	0.0	-3.389	0.10000E+01
H-CL (V)	VAPOR	0.45221E-04	0.46246170-04	0.0	-47.083	0.10000E+01
HCL2 (V)	VAPOR	0.63506E-08	0.64944830-08	0.0	-97.974	0.10000E+01
[illegible] (V)	VAPOR	0.16134E-23	0.16500000-23	0.0	-62.421	0.10000E+01
[illegible] (V)	VAPOR	0.16134E-23	0.16500000-23	0.0	-109.462	0.10000E+01
[illegible] (V)	VAPOR	0.11915E-19	0.12185540-19	0.0	-86.290	0.10000E+01
CL (V)	VAPOR	0.17775E-13	0.18173100-13	0.0	-12.624	0.10000E+01
CL-CL (V)	VAPOR	0.75562E-17	0.77273080-17	0.0	-58.013	0.10000E+01
CL-CL2 (V)	VAPOR	0.20754E-10	0.21223920-10	0.0	-103.402	0.10000E+01
CL-CL3 (V)	VAPOR	0.48893E-13	0.50000830-13	0.0	-148.791	0.10000E+01
CL-CL4 (V)	VAPOR	0.30475E-12	0.31159350-12	0.0	-194.180	0.10000E+01
CL-H (V)	VAPOR	0.19851E-15	0.20300300-15	0.0	-14.319	0.10000E+01
CL-H4 (V)	VAPOR	0.20422E-08	0.20884650-08	0.0	-19.402	0.10000E+01
CL-H CL3	VAPOR	0.57641E-10	0.58947730-10	0.0	-150.485	0.10000E+01
CL-H2-CL2	VAPOR	0.26166E-09	0.26760270-09	0.0	-196.791	0.10000E+01
CL-H3-CL	VAPOR	0.75315E-09	0.77008530-09	0.0	-63.096	0.10000E+01
CL-H (V)	VAPOR	0.12201E-10	0.12477100-10	0.0	-27.210	0.10000E+01
CL2 (V)	VAPOR	0.12725E-12	0.13013270-12	0.0	-131.795	0.10000E+01
CL2-CL6 (V)	VAPOR	0.16131E-23	0.16500000-23	0.0	-294.001	0.10000E+01
CL-H6 (V)	VAPOR	0.96132E-17	0.98310220-17	0.0	-35.415	0.10000E+01
CL-H (V)	VAPOR	0.0	0.0	0.0	0.0	0.10000E+01
[illegible] (V)	CONDENSED PH	0.10000E+01	0.16500000-23	0.0	-2.605	0.10000E+01
[illegible]2 (S)	CONDENSED PH	0.10000E+01	0.10000000+01	0.0	-131.795	0.10000E+01
[illegible] (S)	CONDENSED PH	0.10000E+01	0.96899695+00	0.0	-3.011	0.10000E+01

0.9735

MOLE FRACTION OF SILICON SPECIES IN VAPOR PHASE = 0.31814E-08

III-V RATIO IN THE VAPOR PHASE = 2.955

TOTAL GRAM-MOLES OF EACH ELEMENT FROM INPUT DATA
AND AS CALCULATED FROM THE EQUILIBRIUM COMPOSITIONS

INPUT DATA	CALCULATED	INPUT DATA	CALCULATED	INPUT DATA	CALCULATED	INPUT DATA	CALCULATED
[illegible]	[illegible]	O 0.30000E+01	0.30000E+01	CL [illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]				

STOICIOMETRIC FORMULATION FOR DETERMINING EQUILIBRIUM COMPOSITIONS

THE GA/AS CHLORIDE SYSTEM SOURCE ZONE. A TEST OF MCMPEC.STOIC.

TEMPERATURE = 923.2 K PRESSURE = 0.10133E+06 PA

A SET OF INDEPENDENT REACTION EQUATIONS FOR THIS SYSTEM IS AS FOLLOWS:

(1.00 AS2 (V)) <= (0.500E+00 AS4 (V))

(1.00 AS3 (V)) <= (0.750E+00 AS4 (V))

(1.00 H-CL (V)) <= (0.500E+00 H2 (V)) + (-0.101E+01 GAX-AS(1-X)) + (0.100E+01 GA-CL (V)) + (0.163E-02 AS4 (V))

(1.00 GA-CL2 (V)) <= (-0.101E+01 GAX-AS(1-X)) + (0.200E+01 GA-CL (V)) - (0.163E-02 AS4 (V))

(1.00 AS-H3 (V)) <= (0.150E+01 H2 (V)) + (0.250E+00 AS4 (V))

(1.00 GA-CL3 (V)) <= (-0.201E+01 GAX-AS(1-X)) + (0.300E+01 GA-CL (V)) + (0.326E-02 AS4 (V))

(1.00 GA (V)) <= (0.101E+01 GAX-AS(1-X)) + (-0.163E-02 AS4 (V))

(1.00 AS-H (V)) <= (0.500E+00 H2 (V)) + (0.250E+00 AS4 (V))

(1.00 SI-H4 (V)) <= (0.100E+01 SI-02 (S)) + (0.400E+01 H2 (V)) + (-0.200E+01 H2-0 (V))

(1.00 H (V)) <= (0.500E+00 H2 (V))

(1.00 SI-H3-CL) <= (0.100E+01 SI-02 (S)) + (0.350E+01 H2 (V)) + (-0.101E+01 GAX-AS(1-X)) + (0.100E+01 GA-CL (V))
+ (0.163E-02 AS4 (V)) + (-0.200E+01 H2-0 (V))

(1.00 AS (V)) <= (0.250E+00 AS4 (V))

(1.00 SI-H2-CL2) <= (0.100E+01 SI-02 (S)) + (0.300E+01 H2 (V)) + (0.201E+01 GAX-AS(1-X)) + (0.200E+01 GA-CL (V))
+ (0.326E-02 AS4 (V)) + (-0.200E+01 H2-0 (V))

(1.00 AS-CL (V)) = (-0.101E+01 GAX-AS(1-X)) + (0.100E+01 GA-CL (V)) + (0.250E+00 AS4 (V))

(1.00 SI-H-CL3) <= (0.100E+01 SI-02 (S)) + (0.250E+01 H2 (V)) + (-1.301E+01 GAX-AS(1-X)) + (0.300E+01 GA-CL (V))
+ (0.489E-02 AS4 (V)) + (3.200E+01 H2-0 (V))

(1.00 SI-CL2 (V)) <= (0.100E+01 SI-02 (S)) + (0.200E+01 H2 (V)) + (-0.201E+01 GAX-AS(1-X)) + (0.200E+01 GA-CL (V))
+ (0.326E-02 AS4 (V)) + (-0.200E+01 H2-0 (V))

(1.00 SI-0 (V)) <= (0.100E+01 SI-02 (S)) + (0.100E+01 H2 (V)) + (-0.100E+01 H2-0 (V))

(1.00 SI-CL3 (V)) <= (0.100E+01 SI-02 (S)) + (0.300E+01 H2 (V)) + (-0.302E+01 GAX-AS(1-X)) + (0.300E+01 GA-CL (V))
+ (0.489E-02 AS4 (V)) + (-0.200E+01 H2-0 (V))

(1.00 SI-CL4 (V)) <= (0.100E+01 SI-02 (S)) + (0.200E+01 H2 (V)) + (-0.403E+01 GAX-AS(1-X)) + (0.400E+01 GA-CL (V))
+ (0.652E-02 AS4 (V)) + (-0.200E+01 H2-0 (V))

(1.00 CL (V)) = (-0.101E+01 GAX-AS(1-X)) + (0.100E+01 GA-CL (V)) + (0.163E-02 AS4 (V))

(1.00 GA2-CL6 (V)) <= (-0.403E+01 GAX-AS(1-X)) + (0.600E+01 GA-CL (V)) + (0.651E-02 AS4 (V))

(1.00 SI-H (V)) <= (0.100E+01 SI-02 (S)) + (0.250E+01 H2 (V)) + (-0.200E+01 H2-0 (V))

(1.00 SI-H2 (V)) <= (0.100E+01 SI-02 (S)) + (0.300E+01 H2 (V)) + (-0.400E+01 H2-0 (V))

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1.00 AS-CL3 (V)  ) = (-0.402E+01 GAX-AS(1-X)) + ( 0.400E+01 GA-CL (V)  ) + ( 0.255E+00 AS4 (V)    )

1.00 SI (V)      ) = ( 0.100E+01 SI-02 (S)  ) + ( 0.200E+01 H2 (V)     ) + (-0.200E+01 H2-O (V)   )

1.00 CL2 (V)     ) = (-0.201E+01 GAX-AS(1-X)) + ( 0.200E+01 GA-CL (V)  ) + ( 0.326E-02 AS4 (V)    )

1.00 O-H (V)     ) = (-0.500E+00 H2 (V)     ) + ( 0.100E+01 H2-O (V)   )

1.00 GA CL2 (V)  ) = (-0.201E+01 GAX-AS(1-X)) + ( 0.200E+01 GA-CL (V)  ) + ( 0.253E+00 AS4 (V)    )

1.00 SI-02 (V)   ) = ( 0.100E+01 SI-02 (S)  )

1.00 SI (S)      ) = ( 0.100E+01 SI-02 (S)  ) + ( 0.200E+01 H2 (V)     ) + (-0.200E+01 H2-O (V)   )

1.00 SI2-CL6 (V)) = ( 0.200E+01 SI-02 (S)  ) + ( 0.400E+01 H2 (V)     ) + (-0.604E+01 GAX-AS(1-X)) + ( 0.600E+01 GA-CL (V)  )
                  + ( 0.226E-02 AS4 (V)    ) + (-0.400E+01 H2-O (V)   )

1.00 O (V)       )<= (-0.100E+01 H2 (V)     ) + ( 0.100E+01 H2-O (V)   )

1.00 O2 (V)      )<= (-0.200E+01 H2 (V)     ) + ( 0.200E+01 H2-O (V)   )
```

EQUILIBRIUM CONSTANTS FOR THE INDEPENDENT REACTIONS

REACTION PRODUCT	GIBBS FREE ENERGY CHANGE (KCAL/G-MOLE)	EQUILIBRIUM CONSTANT FROM GIBBS FREE ENERGY	EQUILIBRIUM CONSTANT FROM PREDICTED COMPOSITION	
AS (V)	32.???	0.32852E-09	0.32852E-09	
AS2 (V)	9.711	0.65973E-02	0.65973E-02	
AS3 (V)	8.978	0.96358E-02	0.96358E-02	
AS4 (V)	0.0	0.10000E+01	0.10000E+01	
AS-CL (V)	35.504	0.10644E-07	0.10644E-07	
AS-CL2 (V)	78.902	0.19115E-17	0.17115E-17	(NOT BINDING)
AS2-CL3 (V)	57.749	0.10754E-12	0.10754E-12	
AS-H (V)	33.751	0.26343E-07	0.26343E-07	
AS H3 (V)	21.239	0.16997E-04	0.16997E-04	
CL (V)	52.506	0.16135E-11	0.16135E-11	
CL2 (V)	73.011	0.40207E-16	0.40207E-16	
GA (V)	35.207	0.12403E-07	0.12403E-07	
GA-CL (V)	-0.000	0.10000E+01	0.10000E+01	
GA-CL2 (V)	5.706	0.52322E-01	0.52322E-01	
GA-CL3 (V)	11.846	0.21870E-02	0.21870E-02	
GA2-CL6 (V)	32.433	0.52084E-07	0.52083E-07	
H (V)	39.928	0.10802E-08	0.10802E-08	
H2 (V)	0.0	0.10000E+01	0.10000E+01	
H CL (V)	12.463	0.15?96E-02	0.15896E-02	
H2-O (V)	0.0	0.10000E+01	0.99979E+00	
O (V)	91.673	0.25912E-20	0.24594E-15	(NOT BINDING)
O2 (V)	92.778	0.14636E-20	0.37488E-07	(NOT BINDING)
O-H (V)	52.251	0.13460E-11	0.18460E-11	
SI (V)	156.375	0.?a?02E-35	0.?a?02E-35	
SI CL (V)	142.221	0.11248E-31	0.11?48E-31	
SI-CL2 (V)	106.746	0.1?58?E-23	0.19a85E-23	
SI-CL3 (V)	107.142	0.87058E-24	0.87058E-24	
SI-CL4 (V)	101.202	0.18780E-22	0.18780E-22	
SI-H (V)	147.224	0.96834E-33	0.96834E-33	
SI H4 (V)	111.451	0.93793E-25	0.93793E-25	
SI H CL3	92.896	0.10432E-21	0.10432E-21	
SI-H2-CL2	101.?59	0.14075E-22	0.14075E-22	
SI H2 CL	106.493	0.12240E-23	0.12240E-23	
SI-O (V)	35.037	0.30042E-19	0.30042E-19	
SI-O2 (V)	101.995	0.12725E-22	0.12725E-22	(NOT BINDING)
SI2-CL6 (V)	214.171	0.50?96E-48	0.51154E-47	(NOT BINDING)
SI2-H6 (V)	221.549	0.12529E-49	0.19?25E-49	
SI (S)	82.893	0.24 02E-18	0.41035E-16	(NOT BINDING)
SI-O2 (S)	0.0	0.10000E+01	0.10000E+01	
GAX-AS(1-X)	-0.000	0.10000E+01	0.10000E+01	
X=0.9935				

Figure B29. The Wrap-up File

```
TEMPERATURE =    973.2 K
PRESSURE =  0.10133E+06 PA
              INITIAL COMPOSITIONS
SPECIE        MOLE FRACTION     GRAM MOLES
 AS (V)         0.10000E-19    0.10000D-19
 AS2 (V)        0.10000E-19    0.10000D-19
 AS3 (V)        0.10000E-19    0.10000D-19
 AS4 (V)        0.10000E-19    0.10000D-19
 AS-CL (V)      0.10000E-19    0.10000D-19
 AS-CL2 (V)     0.10000E-19    0.10000D-19
 AS-CL3 (V)     0.10000E-01    0.10000D-01
 AS-H (V)       0.10000E-19    0.10000D-19
 AS-H3 (V)      0.10000E-19    0.10000D-19
 CL (V)         0.10000E-19    0.10000D-19
 CL2 (V)        0.10000E-19    0.10000D-19
 GA (V)         0.10000E-19    0.10000D-19
 GA-CL (V)      0.10000E-19    0.10000D-19
 GA-CL2 (V)     0.10000E-19    0.10000D-19
 GA-CL3 (V)     0.10000E-19    0.10000D-19
 GA2-CL6 (V)    0.10000E-19    0.10000D-19
 H (V)          0.10000E-19    0.10000D-19
 H2 (V)         0.99000E+00    0.99000D+00
 H-CL (V)       0.10000E-19    0.10000D-19
 H2-O (V)       0.10000E-19    0.10000D-19
 O (V)          0.10000E-19    0.10000D-19
 O2 (V)         0.10000E-19    0.10000D-19
 O-H (V)        0.10000E-19    0.10000D-19
 SI (V)         0.10000E-19    0.10000D-19
 SI-CL (V)      0.10000E-19    0.10000D-19
 SI-CL2 (V)     0.10000E-19    0.10000D-19
 SI-CL3 (V)     0.10000E-19    0.10000D-19
 SI-CL4 (V)     0.10000E-19    0.10000D-19
 SI-H (V)       0.10000E-19    0.10000D-19
 SI-H4 (V)      0.10000E-19    0.10000D-19
 SI-H-CL3       0.10000E-19    0.10000D-19
 SI-H2-CL2      0.10000E-19    0.10000D-19
 SI-H3-CL       0.10000E-19    0.10000D-19
 SI-O (V)       0.10000E-19    0.10000D-19
 SI-O2 (V)      0.10000E-19    0.10000D-19
 SI2-CL6 (V)    0.10000E-19    0.10000D-19
 SI2-H6 (V)     0.10000E-19    0.10000D-19
 INERT (V)      0.0            0.0
VAPOR III/V                 0.0000
SI IN VAPOR    0.14000E-18    0.14000E-18
  I (S)        0.10000E+01    0.10000D+01
 SI-O2 (S)     0.10000E+01    0.10000D+01
 MAX-AS(1-X)   0.10000E+01    0.10000D+01
   X=0.9935

TEMPERATURE =    973.2 K
PRESSURE =  0.10133E+06 PA
              LIQUID EQUILIBRIUM COMPOSITIONS
 AS (V)         0.[illegible]E-09    0.[illegible]D-09
 AS2 (V)        0.31[illegible]E-04    0.32[illegible]D-03
 AS3 (V)        0.99[illegible]E-01    0.10[illegible]D 01
 AS4 (V)        0.22[illegible]E-02    0.[illegible]D-02
 AS-CL (V)      0.42[illegible]E-10    0.[illegible]D-10
 AS-CL2 (V)     0.34[illegible]E-21    0.[illegible]D-21
 AS-CL3 (V)     0.[illegible]E-18    0.[illegible]D-18
 AS-H (V)       0.56[illegible]E-08    0.[illegible]D-08
 AS-H3 (V)      0.[illegible]E-05    0.[illegible]D-05
 CL (V)         0.15[illegible]E-11    0.[illegible]D-11
 CL2 (V)        0.33612E-19    0.[illegible]D-19
 GA (V)         0.12[illegible]E-02    0.[illegible]D-01
 GA-CL (V)      0.22[illegible]E-01    0.[illegible]D-01
 GA-CL2 (V)     0.44[illegible]E-04    0.[illegible]D-03
 GA-CL3 (V)     0.[illegible]E-02    0.[illegible]D-02
 GA2-CL6 (V)    0.31041E-16    0.[illegible]D-15
 H (V)          0.10622E-08    0.10[illegible]D-08
 H2 (V)         0.98803E+00    0.98[illegible]D+00
 H-CL (V)       0.45221E-04    0.44246D-04
 H2-O (V)       0.63506E-08    0.61[illegible]D-08
 O (V)          0.16[illegible]E-23    0.16[illegible]D-23
 O2 (V)         0.16134E-23    0.16[illegible]D-23
 O-H (V)        0.11915E-19    0.11[illegible]D-19
 SI (V)         0.17775E-18    0.18[illegible]D-18
 SI-CL (V)      0.75562E-17    0.[illegible]D-17
 SI-CL2 (V)     0.20754E-10    0.21[illegible]D-10
 SI-CL3 (V)     0.48934E-12    0.50[illegible]D-12
 SI-CL4 (V)     0.30495E-12    0.31[illegible]D-12
 SI-H (V)       0.19851E-16    0.[illegible]D-16
 SI-H4 (V)      0.2[illegible]E-03    0.2[illegible]D-03
 SI-H-CL3       0.57841E-10    0.[illegible]D-10
 SI-H2-CL2      0.36466E-07    0.[illegible]D-07
 SI-H3-CL       0.78[illegible]E-09    0.[illegible]D-09
 SI-O (V)       0.12[illegible]E-10    0.[illegible]D-10
 SI-O2 (V)      0.12[illegible]E-22    0.[illegible]D-22
 SI2-CL6 (V)    0.16134E-23    0.[illegible]D-23
 SI2-H6 (V)     0.96.32E-17    0.[illegible]D-17
 INERT (V)      0.0            0.0
VAPOR III/V                 2.9337
SI IN VAPOR    0.31814E-08    0.32[illegible]D-08
  I (S)        0.10000E+01    0.10[illegible]D+01
 SI-O2 (S)     0.10[illegible]E+01    0.[illegible]D+01
 MAX-AS(1-X)   0.10[illegible]E+01    0.76920D+00
   X=0.9935
```

Figure B30. The Data File

```
THE SARAS CHLORIDE SYSTEM SOURCE ZONE.  A TEST OF ATMOSPHERIC.
     3  32   0   1    971.20 101325.00    971.20 101325.00
  H  O CL SI SA AS
 AS (V)       0.68700E+02 0.33081E-01
 0.49280E-02 0.0          0.0          0.0          0
0.0   0.0   0.0   0.0   0.0   1.000
 AS2 (V)      0.15950E+02 0.43485E-01
 0.76300E-02-0.16700E-06-0.37080E+02 0.21120E-03 0
0.0   0.0   0.0   0.0   0.0   2.000
 AS3 (V)      0.52210E+02 0.48541E-01
 0.13836E-01-0.13650E-06-0.5887?0E+02 0.17200E-03 0
0.0   0.0   0.0   0.0   0.0   3.000
 AS4 (V)      0.37500E+02 0.44110E-01
 0.18513E-01-0.17?5?E-06-0.111?0E+01 0.21900E-03 0
0.0   0.0   0.0   0.0   0.0   4.000
 AS-CL (V)    0.27700E+02 0.31365E-01
 0.28780E-02 0.45306E-07-0.38150E+02 0.0          0
0.0   0.0   1.000 0.0   0.0   1.000
 AS-CL2 (V)   0.14500E+02 0.1?220E-01
 0.13790E-01 0.85560E-07 0.3?100E+02 0.0          0
0.0   0.0   2.000 0.0   0.0   1.000
 AS CL3 (V)  -0.62700E+01-0.10195E-01
 0.19740E-01 0.72600E-07-0.15766E+03 0.0          0
0.0   0.0   3.000 0.0   0.0   1.000
 AS-H (V)     0.53000E+02 0.2?80?E-01
 0.54000E-02 0.14370E-05 0.10300E+02 0.0          0
1.000 0.0   0.0   0.0   0.0   1.000
 AS-H3 (V)    0.15200E+02-0.21?5?E-02
 0.10070E-01 0.54200E-05-0.12000E+03 0.0          0
3.000 0.0   0.0   0.0   0.0   1.000
 CL (V)       0.28?7?E+02 0.12809E-01
 0.  ?90E-02-0.40  0?E-06-0.3052?E+02 0.0          0
0.0   0.0   1.000 0.0   0.0   0.0
 CL2 (V)      0.0          0.0
 0.98000E-02 0.20800E-06-0.67000E+02 0.0          0
0.0   0.0   2.000 0.0   0.0   0.0
 SA (V)       0.65?0?E+02 0.3061?E-01
 0.30173E-01 0.23? 0?E-05-0.2?620E+03-0.38120E-02 0
0.0   0.0   0.0   0.0   1.000 0.0
 SA-CL (V)   -0.1?90?E+02 0.2?05?E-01
 0.  ?50E-02 0.10?1?E-07 0.?7?90E+02 0.0          0
0.0   0.0   1.000 0.0   1.000 0.0
 SA-CL2 (V)   0.?7?0?E+02 0.?04?E-02
 0.11310E-01 0.?1?0?E-?6 0.?344?E+03 0.0          0
0.0   0.0   2.000 0.0   1.000 0.0
 SA-CL3 (V)  -0.1?30?E+?2-0.?7?0?E-02
 0.19740E-01 0.?710?E-07-0.?6?00E+02 0.0          0
0.0   0.0   3.000 0.0   2.000 0.0
 SA2-CL6 (V)  0.?05?0E+?2-0.?14?0E-01
 0.13050E-01 0.?7?0?E-06-0.?7?20E+03 0.0          0
0.0   0.0   6.000 0.0   2.000 0.0
 H (V)        0.?  ?0?E+?2 0.11?0?E-01
 0.49?60E-02 0.?          0.0          0.0          0
1.000 0.0   0.0   0.?   0.0   0.0
 H2 (V)       0.0          0.0
 0.15256E-01 0.21200E-05-0.5?9?0E+02-0.11620E-02 0
2.000 0.0   0.0   0.0   0.0   0.0
 H-CL (V)    -0.220?0E+02 0.2?70?E-02
 0.62240E-02 0.12?0?E-?5-0.?5?10E+02 0.?          0
1.000 0.0   1.000 0.0   0.0   0.0
 H2 O (V)    -0.?7?0?E+02-0.10?04E-01
 0.11?90E-02 0.?44?0?-?? 0.?7?00E-?? 0.?60?0?-?? 0
0.000 1.000 0.0   0.?   0.0   0.0

 (V)          0.?4?0?-01 0.?????0?-??
 0.11931E-01 0.13890E-05 0.?5?0?E+01 0.?????0E-??
1.000 1.000 0.0   0.?   0.?   0.?
 SI (V)       0.10800E+03 0.3563?-01
 0.48200E-02 0.13030E-06 0.?4?0?E+02 0.0          0
0.0   0.0   0.0   1.000 0.0   0.?
 SI-CL (V)    0.47400E+02 0.2563?E-01
 0.88700E-02 0.11070E-06-0.?2?00E+02 0.0          0
0.0   0.0   1.000 1.000 0.?   0.?
 SI-CL2 (V)  -0.30300E+02 0.?5840E-01
 0.11263E-01-0.?4?00E-06-0.11?50E+?2 0.49610E-?? 0
0.0   0.0   2.000 1.000 0.0   0.0
 SI-CL3 (V)  -0.?5300E+02-0.82510E-01
 0.12797E-01-0.76?00E-06-0.?7?07E+02 0.11120E-02 0
0.0   0.0   3.000 1.000 0.0   0.?
 SI-CL4 (V)  -0.15840E+03-0.?19?6E-01
 0.14511E-01-0.12100E-05-0.?4?60E+03 0.12?30E-?? 0
0.0   0.0   4.000 1.000 0.0   0.0
 SI-H (V)     0.?0?0?0E+02 0.?2217E-01
 0.66300E-02 0.14230E-05-0.?9?10E+01 0.0          0
1.000 0.0   0.0   1.000 0.0   0.0
 SI-H4 (V)    0.?2?00E+01-0.19013E-01
-0.74824E-01-0.61?0?  ?? 0.?5?20E+03 0.14597E-01 0
4.000 0.0   0.0   1.000 0.0   0.0
 SI-H-CL3    -0.11?50E+03-0.?5?30E-01
-0.79100E-02-0.?4?00E-05-0.1?  ?E+03 0.49830E-02 0
1.000 0.0   3.000 1.000 0.0   0.0
 SI-H2-CL2   -0.?5?00E+02-0.?0?52E-01
-0.31537E-01-0.?9?00E-05-0.?4?40E+03 0.?1077E-?? 0
2.000 0.0   2.000 1.000 0.0   0.0
 SI-H-CL     -0.?2?0?E+02-0.1?01?E-01
-0.?5?26E-01-0.?04?0?E-05 0.1?3?0E+03 0.11554E-01 0
3.000 0.0   1.000 1.000 0.0   0.?
 SI O (V)    -0.?4?0?E+02 0.?155?E-01
-0.54710E-02-0.1?7?0?  ?? 0.?45?0E+02 0.23610E-?? 0
0.0   1.000 0.0   1.000 0.0   0.0
 SI-O2 (V)   -0.?7?0?E+02 0.12?0?E-?2
-0.14368E-01-0.?7?0?E-05 0.?5?0?E+01 0.14?81E-02 0
0.0   2.000 0.0   1.000 0.0   0.?
 SI2-CL6 (V) -0.?3?0?E+03-0.?7?4?E-01
 0.42150E-01 0.1?7?0?E-05-0.?46?0E+?4 0.?          0
0.0   0.0   6.000 2.000 0.0   0.0
 SI2-H6 (V)   0.1 ?0?E+02 0.?5?7?E-??
 0.?24 0E-02 0.?82?11 04 0.?1?4?E-?? 0.0          1
2.000 0.0   0.0   2.000 0.0   0.?
 INERT (V)    0.0          0.0
 0.?          0.0          0.0          0
0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.?   0.?   0.?
 SI (S)       0.0          0.0
 0.57300E-02 0.681105-06-0.10560E+03 0.0          0
0.0   0.0   0.0   1.000 0.0   0.?
 SI-O2 (S)   -0.?1?20E+03 0.44501E-01
 0.21583E-01 0.1111?C?? 0.?3?0?E+?1 0.37010E-02 0
0.0   2.000 0.0   1.000 0.0   0.?
 SAX-ARG1 X) 0.0          0.0
 0.0          0.0          0.0          0.0          0
0.0   0.0   0.0   0.0   0.0   0.0
    0    0    1    1 1000    0  0.0001       0.0          0.0          0.?
 0.10000E+01
 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19
 0.01000E+00 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19
 0.?????0E-19 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19 0.?????E-??
 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19 0.10000E-19 0.?????E-??
 0.?????E-19 0.?
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