A COMPARATIVE THERMODYNAMIC ANALYSIS OF IMPURITY INCORPORATION IN VAPOR P. (U) FLORIDA UNIV GAINESVILLE DEPT OF CHEMICAL ENGINEERING T J ANDERSON ET AL.

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

Timothy J. Anderson and Doug Meyer

Department of Chemical Engineering
University of Florida
Gainesville, Florida 32611

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A Comparative Thermodynamic Analysis of Impurity Incorporation in Vapor Phase Epitaxial InP and GaAs.

Timothy J. Anderson and Doug Meyer

Department of Chemical Engineering
University of Florida
Gainesville, FL 32611

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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 condensed phases of the group III source material and quartz reactor wall. The work performed included incorporation of a novel pseudo-steady state...
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 H₂O, HCl or VCl₃ to the mixing zone, and replacing the H₂ 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 point 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 $In_xGa_{1-x}As_yP_{1-y}$. 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 $In_xGa_{1-x}As_yP_{1-y}$ 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 $\approx 1.11$ 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

<table>
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<tr>
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<th>Bandgap Type</th>
<th>Energy (eV)</th>
<th>Electron Mobility (cm²/V·s)</th>
<th>Lattice Constant (Å)</th>
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<tr>
<td>Si</td>
<td>indirect</td>
<td>1.12</td>
<td>1500</td>
<td>5.43</td>
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<tr>
<td>InSb</td>
<td>direct</td>
<td>0.17</td>
<td>65000</td>
<td>6.48</td>
</tr>
<tr>
<td>InAs</td>
<td>direct</td>
<td>0.36</td>
<td>23000</td>
<td>6.06</td>
</tr>
<tr>
<td>GaSb</td>
<td>direct</td>
<td>0.72</td>
<td>5500</td>
<td>6.10</td>
</tr>
<tr>
<td>InP</td>
<td>direct</td>
<td>1.35</td>
<td>4000</td>
<td>5.87</td>
</tr>
<tr>
<td>GaAs</td>
<td>direct</td>
<td>1.42</td>
<td>9300</td>
<td>5.65</td>
</tr>
<tr>
<td>GaP</td>
<td>indirect</td>
<td>2.26</td>
<td>300</td>
<td>5.45</td>
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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 μm/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
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 at the mixing and deposition zones.
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 flow rates through these reactors are generally small (Re \( \sim 10 \)) 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 $\text{AsCl}_3$ 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 $\text{Ga}_2\text{O}_3$ 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 \( \sim 40 \text{ kcal mol}^{-1} \), 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 PCl₃ 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 epitaxial 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 PCl₃ liquid source. Using mass spectrometric analysis Easton found Si, S and Zn present in the PCl₃ 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 H₂O in the system.

Fairhurst et al. [46] studied the InP halide system using both PCl₃ and PBr₃. 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 (meas-
ured 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 epitax-
ial 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
\( PA_3 \) used in the chloride system.

Investigations of the dependence of impurity incorporation on \( PA_3 \) inlet composi-
tion, 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 \( PA_3 \) 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 con-
centrations 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 impuri-
ties (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 H₂ 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 AsCl₃ 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 \( \text{In}_x \text{Ga}_{1-x} \text{As} \) \( x=0.53 \) 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 \( \text{In}_x \text{Ga}_{1-x} \text{As} \) 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, \( \text{H}_2 \) 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 \( \text{PH}_3 \) 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 \( \text{P}_4 \) 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 \( \text{In}_x \text{Ga}_{1-x} \text{P} \). 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 PH₃ than was measured. Due to the known slow decomposition kinetics of PH₃ 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, PH₃, P₂, P₄ and H₂.

Usui and Watanabe [57] investigated the effects of temperature and oxygen additions on the unintentional doping of hydride grown InP. Additions of O₂ 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 (~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 species 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 species, 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 ($\sim 95\%$ 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 species 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 species. 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

\[ |\delta n_i| < \sum_{j=1}^{N} \left| \frac{\partial n_i}{\partial \mu_j} \right| \delta \mu_j \]  

(3.1)

Here, \( n_i \) is the number of moles of specie \( i \) present, \( \mu_j \) 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 \( n_i(\mu_j) \) for all values of \( i \). If problems seem apparent for some species this function can be numerically evaluated. The work of Sirtl and Hunt [5] and similar calculations performed here (Section 5) showed by means of a calculated example the effects of changes in the enthalpy of formation of \( S1HC_3 \) on the predicted equilibrium ratio of \( S1A_4/S1HC_3 \). 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$_3$, VC$_1$$_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 (III-V(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 VC$_1$$_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:

$$\frac{d}{dt} \left[ \frac{1}{2} n^c (M_{III} + M_V) + n^i (z M_{III} + (1-z)M_V) \right] = n^V (y M_{III} + (1-y)M_V) = \text{constant} \quad (4.1.1)$$

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

$$\frac{d}{dt} \left[ \frac{1}{2} n^c M_{III} + n^i z M_{III} \right] = n^V y M_{III} \quad (4.1.2)$$
In these expressions: \( n^s \) 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 \( n^V \) 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 \( n^V = \frac{dn^l}{dt} \) 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

\[
\begin{align*}
n^V &= \text{constant} = \frac{(2x-1) \ dn^c}{2(x-y) \ dt} = \frac{(2x-1) \ dn^l}{2y-1 \ dt} \\
\end{align*}
\]  

(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 $\frac{dx}{dt}$ and $\frac{dy}{dt}$ are constant. If $\frac{dn^1}{dt}$ is dependent upon the crust thickness, $n^5$, (i.e. a diffusion limited process) then it is impossible for $\frac{dn^1}{dt}$ to be constant for a finite value of $\frac{dn^5}{dt}$, 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 $\text{SnO}_2(c)$ and $\text{III}_x\text{V}_{1-x}(l)$. The gas input stream contained $\text{VCl}_3$ and carrier gas ($H_2$ or inert). The development of a thermodynamic data set for the hypothetical species $\text{III}_x\text{V}_{1-x}(l)$ 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 $\text{SnO}_2(c)$. The input gas reactants were the hydride ($\text{VH}_3$) 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 $\text{SnO}_2(c)$ and an ideal vapor phase ($\text{HCl}$ 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 $\text{SnO}_2(c)$ 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. $\text{HCl, H}_2\text{O, VCl}_3, \text{VH}_3$) 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 $\text{SiO}_2(c)$ 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)
- $\rho$ = 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% H₂ composition to the Group V source zone. Assuming that all of the HCl reacts to form III-Cl results in 3.7 µ-moles/s of Group III atoms transported. The molar flowrate of Group V atoms would also be 3.7 µ-moles/s. Choosing as typical deposition parameters a 2.54 cm diameter circular substrate, a linear growth rate of 1 µm/min and the molar density of GaAs as 0.0367 moles/cm³ [8] the resulting molar growth rate is 0.31 µ-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 SiO₂ 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 H₂O. 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

<table>
<thead>
<tr>
<th>System</th>
<th>Group III Source Material</th>
<th>% VCl$_3$ in Feed</th>
<th>Total Flowrate (SCCM)</th>
<th>Zone Temperatures (K)</th>
<th>Pressure (kPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>0.1-0.7</td>
<td>250-800</td>
<td>1123</td>
<td>983-1043</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>solid</td>
<td>0.05-10.0</td>
<td>80</td>
<td>1100</td>
<td>850-1050</td>
<td>0.5-100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>0.06-0.6</td>
<td>180-800</td>
<td>1123</td>
<td>1000-1100</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>0.6-1.2</td>
<td>&gt; 100</td>
<td>1073</td>
<td>1023</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>solid</td>
<td>0.6-1.2</td>
<td>&gt; 100</td>
<td>1073</td>
<td>1023</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>0.15-1.0</td>
<td>600</td>
<td>1123</td>
<td>1023</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>0.1-0.8</td>
<td>130</td>
<td>1123</td>
<td>1023</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>0.05-0.9</td>
<td>650</td>
<td>1073</td>
<td>973</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>0.08-0.35</td>
<td>600</td>
<td>1073</td>
<td>943-993</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>?</td>
<td>50</td>
<td>1073</td>
<td>1023</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>liquid</td>
<td>?</td>
<td>50</td>
<td>1073</td>
<td>1023</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>0.23-0.75</td>
<td>100-800</td>
<td>1023</td>
<td>873-1023</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>solid</td>
<td>0.23-0.75</td>
<td>100-800</td>
<td>1023</td>
<td>873-1023</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>?</td>
<td>?</td>
<td>973-1123</td>
<td>873-1023</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>0.2-2.0</td>
<td>?</td>
<td>973-1123</td>
<td>873-1023</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>0.2-4.0</td>
<td>150-250</td>
<td>1023</td>
<td>923</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>0.1-2.9</td>
<td>250</td>
<td>1023</td>
<td>923</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>1.2</td>
<td>100</td>
<td>973</td>
<td>873</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>solid</td>
<td>?</td>
<td>?</td>
<td>973</td>
<td>873</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>0.9-4.6</td>
<td>56</td>
<td>873-1100</td>
<td>848-973</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>solid</td>
<td>4.6</td>
<td>66</td>
<td>1012-1113</td>
<td>887-991</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>2.0-10.0</td>
<td>200</td>
<td>923-1023</td>
<td>823-993</td>
<td>100</td>
</tr>
<tr>
<td>InP</td>
<td>liquid</td>
<td>0.9-4.5</td>
<td>100-200</td>
<td>1023</td>
<td>933-953</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 4.2
Some Typical Operating Parameters for the GaAs and InP Hydride Systems

<table>
<thead>
<tr>
<th>System</th>
<th>% HCl in Feed</th>
<th>% VH₃ in Feed</th>
<th>Total Flowrate (SCCM)</th>
<th>Zone Temperatures (K)</th>
<th>Pressure (kPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Source</td>
<td>Mixing</td>
<td>Deposition</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.2-1.0</td>
<td>0.3-1.4</td>
<td>560-2475</td>
<td>1048</td>
<td>1138</td>
<td>973</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.3-3.0</td>
<td>0.3-6.0</td>
<td>30</td>
<td>1023</td>
<td>1073</td>
<td>1023</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.0-25</td>
<td>0.2-1.6</td>
<td>1410-2650</td>
<td>1123</td>
<td>1123</td>
<td>1023</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.3-2.4</td>
<td>0.7-1.4</td>
<td>420-980</td>
<td>?</td>
<td>?</td>
<td>973-1023</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.2-2.0</td>
<td>0.05-2.0</td>
<td>?</td>
<td>1023</td>
<td>1023</td>
<td>1023</td>
</tr>
<tr>
<td>InP</td>
<td>2.0-2.6</td>
<td>2.0-2.6</td>
<td>177-1510</td>
<td>?</td>
<td>?</td>
<td>923</td>
</tr>
<tr>
<td>InP</td>
<td>0.65</td>
<td>1.2</td>
<td>500-900</td>
<td>1053-1123</td>
<td>1053-1123</td>
<td>923</td>
</tr>
<tr>
<td>InP</td>
<td>?</td>
<td>?</td>
<td>400-2400</td>
<td>?</td>
<td>973-1223</td>
<td>?</td>
</tr>
<tr>
<td>InP</td>
<td>0.11</td>
<td>0.11</td>
<td>5200</td>
<td>1043-1193</td>
<td>1043-1193</td>
<td>943</td>
</tr>
<tr>
<td>InP</td>
<td>0.3-0.9</td>
<td>0.3-1.9</td>
<td>1690-2400</td>
<td>1173</td>
<td>943-1250</td>
<td>923</td>
</tr>
</tbody>
</table>
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:

\[
\begin{align*}
\text{As}_{\text{As}} + V_i &= \text{As}_{\text{I}} + V_{\text{As}} \\
O &= e^- + h^+ \\
\text{As}_{\text{I}} &= \text{As}_{\text{I}}^+ + e^- \\
V_{\text{As}} &= V_{\text{As}}^+ + e^- \\
\frac{1}{2} \text{As}_2(g) + V_i &= \text{As}_{\text{I}} \\
V_{\text{Ga}} &= V_{\text{Ga}}^+ + h^+ \\
O &= V_{\text{Ga}} + V_{\text{As}}
\end{align*}
\]  

(4.3.1)  
(4.3.2)  
(4.3.3)  
(4.3.4)  
(4.3.5)  
(4.3.6)  
(4.3.7)

Reaction 4.3.1 represents Frenkel disorder on the As sub-lattice with As on a normal lattice site, \( \text{As}_{\text{As}} \), moving to a vacant interstitial site, \( V_i \), to produce an arsenic intersti-
tial, $As_1$, 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 $As_1$, $V_{As}$ 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:

$$Si(g) + V_{Ga} = Si_{Ga}^+ + e^- \quad (4.3.8)$$
$$Si(g) + V_{As} = Si_{As}^- + h^+ \quad (4.3.9)$$
$$Si_{Ga}^+ + V_{Ga} = Si_{Ga} V_{Ga}^- + h^+ \quad (4.3.10)$$
$$Si_{As}^- + V_{As} = Si_{Ga} V_{As}^- \quad (4.3.11)$$

The amphoteric nature of Si in GaAs is illustrated in reactions 4.3.5 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 $O$ are constant and normalized to unity, the following equilibrium relations can be written:

$$K_1 = [As_i][V_{As}] \quad (4.3.12)$$
$$K_2 = n_p \quad (4.3.13)$$
$$K_3 = [As_i^+]n / [As_i] \quad (4.3.14)$$
$$K_4 = [V_{As}^+]n / [V_{As}] \quad (4.3.15)$$
$$K_5 = [As_i] / P_{As} \quad (4.3.16)$$
$$K_6 = [V_{Ga}]p / [V_{As}] \quad (4.3.17)$$
$$K_7 = [V_{Ga}]^p / [V_{As}] \quad (4.3.18)$$
$$K_8 = [Si_{Ga}][V_{Ga}]d_{Si} \quad (4.3.19)$$
$$K_9 = [Si_{As}]^p / [V_{As}]d_{As} \quad (4.3.20)$$
$$K_{10} = [Si_{Ga} V_{Ga}]p / [V_{As}]^p S_{Si} \quad (4.3.21)$$
$$K_{11} = [Si_{Ga} S_{Si}] / [Si_{As}]^p S_{As} \quad (4.3.22)$$

In addition the condition of charge neutrality requires that:

$$p + [Si_{Ga}] + [As_i^+] + [V_{As}^+] = n + [V_{Ga}] + [Si_{As}] - [Si_{Ga} V_{Ga}] \quad (4.3.23)$$
In these equations $K_1$ through $K_{11}$ are equilibrium constants and are 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.

$$[As_1] = K_3 P_{As_2}^n$$  \hspace{1cm} (4.3.24)

$$[V_{As}] = (K_1 / K_2) P_{As_2}^n$$  \hspace{1cm} (4.3.25)

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

$$[As_{1*}] = K_3 K_5 P_{As_2}^n$$  \hspace{1cm} (4.3.27)

$$[V_{As}] = (K_1 K_4 / K_5) P_{As_2}^n$$  \hspace{1cm} (4.3.28)

$$[V_{Ga}] = (K_2 K_6 K_7 / K_1 K_2) P_{As_2}^n$$  \hspace{1cm} (4.3.29)

$$P = K_2 n^{-1}$$  \hspace{1cm} (4.3.30)

$$[Si_{Ga}] = (K_2 K_7 K_6 / K_1) P_{As_2}^n$$  \hspace{1cm} (4.3.31)

$$[Si_{As}] = (K_1 K_9 / K_2 K_5) P_{As_2}^n$$  \hspace{1cm} (4.3.32)

$$[Si_{Ga} V_{Ga}] = (K_2^2 K_6 K_7 K_8 K_{10} / K_1 K_2^2) P_{As_2}^n$$  \hspace{1cm} (4.3.33)

$$[Si_{Ga} Si_{As}] = (K_7 K_8 K_11 / K_2) a_{Si}^n$$  \hspace{1cm} (4.3.34)

and the concentration of electrons by

$$n = \frac{K_2 + K_3 K_5 P_{As_2}^n + (K_1 K_4 / K_2) P_{As_2}^n + (K_2 K_7 K_6 / K_1) P_{As_2}^n a_{Si}}{1 + (K_2 K_7 K_6 / K_1 K_2) P_{As_2}^n + (K_1 K_9 / K_2 K_5) P_{As_2}^n a_{Si} + (K_2 K_6 K_7 K_8 K_{10} / K_1 K_2^2) P_{As_2}^n a_{Si}}$$  \hspace{1cm} (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 Furle suggests that for GaAs the two un-ionized native defects under VPE conditions are $e$ and $V'_{as}$. Under these assumptions the electroneutrality conditions reduces to:

$$n \geq [V'_{as}]$$

(4.3.36)

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

$$n = (K_1 K_4 / K_2) [V'_{as}]$$

(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

$$\sum [Si] = [Si_{Ga}] + [Si_{As}] + [Si_{Ga} V'_{Ga}] + 2[Si_{Ga} \cdot \cdot] = (a \cdot P_{As}^2 + b \cdot P_{As}^2) a_{Si} + c \cdot a_{Si}$$

(4.3.38)

where:

$$a = (K_1 / K_2)^{3/2} (K_6 / K_2) K_4^2$$

$$b = (K_5 / K_4)^{3/2} K_4^2 K_7 K_6 [1 + (K_4 K_6 K_7 K_10 / K_4^2)]$$

$$c = K_7 K_6 K_9 K_1 / K_2$$

At room temperature the intrinsic defects become negligible when compared to typical unintentional doping levels examined here ($\sim 10^{14} / \text{cm}^3$). The room temperature compensation ratio then becomes

$$\frac{N_D}{N_A} = \frac{[Si_{Ga}]}{[Si_{Ga} V_{Ga}]} = \frac{P_{As}^2}{g + h \cdot P_{As}^2}$$

(4.3.39)

where

$$g = (K_1 / K_2)^{3} K_4 K_6 / (K_2 K_1 K_8)$$

$$h = K_4 K_6 K_7 K_{10} / K_2$$

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

$$\sum [Si] = [Si_{Ga}] + [Si_{Ga} V_{Ga}] = b \ P_{As_2}^{1/4} a_{As} \tag{4.3.40}$$

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 $a_{As}$) 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

$$P_{Ga}^* = K_{41} P_{As_2}^{1/4} \tag{4.3.42}$$

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 species \( i \) is assumed to be given by

\[
J_i = K(P_i^0 - P_i^s) \tag{4.3.43}
\]

where \( P_i^0 \) and \( P_i^s \) is the partial pressure of species \( i \) 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 species \( i \) and \( \delta \) is the diffusion boundary layer thickness). With this assumption the following relations hold

\[
\sum P_i^{2a} \text{ species} - \sum P_i^{2s} \text{ species} = \sum P_i^{3a} \text{ species} + \sum P_i^{3s} \text{ species} \tag{4.3.44}
\]

\[
\sum P_i^{2a} \text{ species} = \sum P_i^{2s} \text{ species} \tag{4.3.45}
\]

\[
\sum P_i^{2a} \text{ species} = \sum P_i^{2s} \text{ species} \tag{4.3.46}
\]

\[
\sum P_i^{3a} \text{ species} = \sum P_i^{3s} \text{ species} \tag{4.3.47}
\]

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 all 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

\[
\left[ \sum P_i^{3a} \text{ species} - \sum P_i^{3s} \text{ species} \right] \sum S_i = \sum P_i^{3a} \text{ species} - \sum P_i^{3s} \text{ species} \tag{4.3.48}
\]

Given \( T, P, K_{eq}(T) \) and all \( P_i^0 \), 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 $a^S_{\text{Si}}$ should not be much different than the bulk $a^S_{\text{Si}}$. Since the solid represents a "sink" for equal amounts of Ga and As atoms the $P^S_{\text{As}_2}$ will necessarily decrease at the substrate surface. The amount by which $P^S_{\text{As}_2}$ will differ from the bulk value, $P^B_{\text{As}_2}$, 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 $a_{\text{Si}}$ 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

<table>
<thead>
<tr>
<th>Specie</th>
<th>( \Delta H_f^{298K} ) kcal mol(^{-1} )</th>
<th>Ref.</th>
<th>( S_f^{298} ) cal mol(^{-1} K^{-1} )</th>
<th>Ref.</th>
<th>( Q_f^2 ) cal mol(^{-1} K^{-1} )</th>
<th>Ref.</th>
<th>Form*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(c)</td>
<td>0</td>
<td>--</td>
<td>8.53±0.1</td>
<td>1</td>
<td>6.736</td>
<td>1.50</td>
<td>-0.1967</td>
<td>1</td>
</tr>
<tr>
<td>As(g)</td>
<td>68.7±1.0</td>
<td>1</td>
<td>41.61±0.1</td>
<td>1</td>
<td>4.968</td>
<td>--</td>
<td>--</td>
<td>1</td>
</tr>
<tr>
<td>As(_2)</td>
<td>45.95±10.0</td>
<td>**</td>
<td>75.54±0.1</td>
<td>1</td>
<td>7.530</td>
<td>-0.159</td>
<td>-0.3708</td>
<td>0.212</td>
</tr>
<tr>
<td>As(_3)</td>
<td>52.2±1.0</td>
<td>1</td>
<td>74.12±0.1</td>
<td>1</td>
<td>13.836</td>
<td>-0.1365</td>
<td>-0.5589</td>
<td>0.172</td>
</tr>
<tr>
<td>As(_4)</td>
<td>37.5±0.6</td>
<td>**</td>
<td>78.32±0.1</td>
<td>1</td>
<td>14.516</td>
<td>-0.176</td>
<td>-1.1128</td>
<td>0.216</td>
</tr>
<tr>
<td>As(C)(_2)</td>
<td>27±3</td>
<td>48</td>
<td>66.24±2.0</td>
<td>48</td>
<td>6.578</td>
<td>0.0453</td>
<td>-0.3395</td>
<td>--</td>
</tr>
<tr>
<td>AsCl(_2)</td>
<td>14.5±4</td>
<td>48</td>
<td>72.04±2.0</td>
<td>48</td>
<td>13.79</td>
<td>0.0566</td>
<td>-0.3524</td>
<td>--</td>
</tr>
<tr>
<td>AsCl(_3)</td>
<td>-62.7±4.0</td>
<td>**</td>
<td>77.97±2.0</td>
<td>48</td>
<td>18.75</td>
<td>0.0726</td>
<td>-1.1568</td>
<td>--</td>
</tr>
<tr>
<td>AsH(_2)</td>
<td>58±12</td>
<td>**</td>
<td>51±3</td>
<td>6</td>
<td>6.4</td>
<td>1.432</td>
<td>0.108</td>
<td>--</td>
</tr>
<tr>
<td>AsH(_3)</td>
<td>16±2</td>
<td>14-16</td>
<td>53.22±0.8</td>
<td>83</td>
<td>10.07</td>
<td>5.42</td>
<td>-2.20</td>
<td>--</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>28.992±0.002</td>
<td>82</td>
<td>39.454±0.005</td>
<td>82</td>
<td>5.779</td>
<td>-0.4083</td>
<td>-0.387</td>
<td>--</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>0</td>
<td>--</td>
<td>53.29±0.01</td>
<td>82</td>
<td>8.8</td>
<td>0.208</td>
<td>-0.67</td>
<td>--</td>
</tr>
<tr>
<td>Ga(c)</td>
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* Form 1: $C_p(T/K) = a + bT + cT^2 + dT^3$

** 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)

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<td>PH₂(g)</td>
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<td>12.041</td>
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<td>PH₃(g)</td>
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<tr>
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<td>-27.644</td>
<td>-30.526</td>
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<td>Temperature (K)</td>
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<tr>
<td></td>
<td>273.2</td>
<td>873.2</td>
<td>973.2</td>
<td>1173.2</td>
<td>1273.2</td>
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<td>Si(g)</td>
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<td>75.012</td>
<td>70.872</td>
<td>65.679</td>
<td>62.440</td>
<td>58.157</td>
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<td>SiCl(g)</td>
<td>0.373</td>
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<td>SiCl&lt;sub&gt;2&lt;/sub&gt;(g)</td>
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<td>SiCl&lt;sub&gt;3&lt;/sub&gt;(g)</td>
<td>-91.064</td>
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<td>-93.970</td>
<td>-95.442</td>
<td>-97.377</td>
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<td>SiCl&lt;sub&gt;4&lt;/sub&gt;(g)</td>
<td>-149.682</td>
<td>-138.946</td>
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<td>-138.207</td>
<td>-138.125</td>
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<tr>
<td>SiH&lt;sub&gt;2&lt;/sub&gt;(g)</td>
<td>82.557</td>
<td>63.612</td>
<td>60.659</td>
<td>56.812</td>
<td>53.718</td>
<td>48.924</td>
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<td>SiH&lt;sub&gt;2&lt;/sub&gt;(g)</td>
<td>13.109</td>
<td>19.151</td>
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<td>19.234</td>
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<td>SiHCl&lt;sub&gt;3&lt;/sub&gt;(g)</td>
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<tr>
<td>SiHCl&lt;sub&gt;3&lt;/sub&gt;(g)</td>
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<td>-64.060</td>
<td>-64.142</td>
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<td>-63.955</td>
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<tr>
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<td>-27.784</td>
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<td>-22.519</td>
<td>-22.815</td>
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<td>SiHCl&lt;sub&gt;3&lt;/sub&gt;(g)</td>
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<td>SiO(g)</td>
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<td>-79.331</td>
<td>-79.840</td>
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<td>-190.437</td>
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<td>-2.324</td>
<td>-3.047</td>
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<td>-4.655</td>
<td>-5.588</td>
</tr>
<tr>
<td>In(c)</td>
<td>-0.007</td>
<td>-2.665</td>
<td>-3.561</td>
<td>-4.565</td>
<td>-5.622</td>
<td>-6.878</td>
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<tr>
<td>InP(c)</td>
<td>-11.455</td>
<td>-10.140</td>
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<td>-10.950</td>
<td>-11.552</td>
<td>-12.317</td>
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<td>P(c)</td>
<td>-0.006</td>
<td>-2.070</td>
<td>-2.714</td>
<td>-3.416</td>
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<td>-4.977</td>
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<tr>
<td>Si(c)</td>
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<td>-1.399</td>
<td>-2.605</td>
<td>-3.307</td>
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<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;(c)</td>
<td>-203.905</td>
<td>-184.503</td>
<td>-181.795</td>
<td>-178.288</td>
<td>-175.973</td>
<td>-174.944</td>
</tr>
</tbody>
</table>

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:

\[
(1-x)A(c) = (1-x)A(l)
\]

\[
xB(c) = xB(l)
\]

\[
(1-x)A(l) +xB(l) = A_{1-x}B_x(l)
\]

all occurring at the same temperature, \( T \). Since \( A \) and \( B \) are 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 $T_m$, 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, $C_p$, is constant, the Gibbs energy change for reactions (5.2.1) and (5.2.2) are:

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

(5.2.4)

and

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

(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

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

(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

$$(1-x)A(c) + x B(c) = A_1 x B_2(t)$$

(5.2.7)

while the corresponding Gibbs energy of formation of $A_1 x B_2(t)$ is the sum of $\Delta G(1)$ to $\Delta G(3)$. Given the source temperature, T, the procedure is to first calculate the liquidus composition, x, from the implicit equation:

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

(5.2.8)
where $\Delta H_m^{AB}$ 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 $A_{1-x}B_x$ 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 Clarion et al. (102), Hall (103), Koster and Thoma (101), Muszynski and Ribeev (104) and Usman et al. (105) using a maximum likelihood algorithm.

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

<table>
<thead>
<tr>
<th>Property</th>
<th>GaAs Reference</th>
<th>InP Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m^{AB}(K)$</td>
<td>1511</td>
<td>1332</td>
</tr>
<tr>
<td>$\Delta H_m^{AB}(\text{kcal mol}^{-1})$</td>
<td>25.14</td>
<td>14.4</td>
</tr>
<tr>
<td>$a(\text{cal mol}^{-1})$</td>
<td>see text</td>
<td>5.055</td>
</tr>
<tr>
<td>$b(\text{cal mol}^{-1}.K^{-1})$</td>
<td>-8.74</td>
<td>-5.0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Ga Ref.</th>
<th>In Ref.</th>
<th>As Ref.</th>
<th>P Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m(K)$</td>
<td>302.9</td>
<td>429.76</td>
<td>1090</td>
<td>313.3</td>
</tr>
<tr>
<td>$\Delta H_m(\text{kcal mol}^{-1})$</td>
<td>1.336</td>
<td>0.78</td>
<td>5.123</td>
<td>0.157</td>
</tr>
<tr>
<td>$\Delta C_p(\text{cal mol}^{-1}.K^{-1})$</td>
<td>0.27</td>
<td>-0.2</td>
<td>1.0</td>
<td>0.472</td>
</tr>
</tbody>
</table>

### 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 39.54 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 Koster et al. (2) by a static method produced a value of 39.14 kcal mol$^{-1}$. In addition, Rana (17) has measured the total vapor pressure over solid and liquid arsenic from 250° to 450° C with a Bourdon
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 $Ga_2As_3$, $Mo_2As_3$, GaAs, InAs, and InAs + InSb sources with improved Knudsen-cell mass-spectrometer designs (19,19,21) and reduction of PVT measurements (17) have indicated a much lower value for the dissociation enthalpy ($54.21 \pm 1.5$, $54.26 \pm 1.1$, $54.2 \pm 1.4$ and $54.8 \pm 1.0$ kcal mol$^{-1}$, respectively). The value selected here is the average of these four measurements, $54.4 \pm 1.5$ kcal mol$^{-1}$. Using the selected values from the standard enthalpies, $\Delta H_f^\circ (GaAs,g,298K) = 19.52$ kcal mol$^{-1}$, $\Delta H_f^\circ (As_4,g,298K) = 37.5$ kcal mol$^{-1}$ and the above dissociation enthalpy yields $\Delta H^\circ (GaAs,s) = Ga(s) + \frac{1}{2} As_2(g), 298K) = 42.5$ 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 $\Delta H_f^\circ (GaAs,s,298K)$ is $19.52$ kcal mol$^{-1}$ as determined by Martosovski 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 (19,19,20,25,27,35-41) and flow equilibrium investigations with reactive gases (23,41) 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), GaC\(_3\)(g), Ga\(_2\)Is\(_3\)(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\(^0\)(GaAs,c,298K) was taken from the low temperature heat capacity measurements of Piesbergen (12) 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 (39) 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 \(\Delta H^\circ_{f}(AsCl_3(g),298K) = -62.7\) 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 \(\Delta H^\circ_{f}(AsH_3(g),298K) = 16.0\pm1.5\) 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 \(\Delta H^\circ_{f}(GaCl_3,c,298K) = -125.0\) kcal mol\(^{-1}\) (53) and the enthalpy of sublimation taken from the vapor pressure measurements of Kanyta et al. (54). \(\Delta H^\circ_{f}(GaCl_3(c) = GaCl_3(g),298K) = 17.7\) kcal mol\(^{-1}\), producing \(\Delta H^\circ_{f}(GaCl_3(g),298K) = -107.3\pm3\) kcal mol\(^{-1}\). The enthalpy of formation of gallium trichloride is the reported value \(\Delta H^\circ_{f}(GaCl_3(g),298K) = -19.5\) kcal mol\(^{-1}\) and is taken from the dissociation energy of Barrow (55) and \(\Delta H^\circ_{f}(GaCl_3(g),298K) = \Delta(SG/Cl_3)/2\) and values selected. However, a value of \(\Delta H^\circ_{f}(GaCl_3(g),298K) = -12.0\) kcal mol\(^{-1}\) as obtained using \(\Delta H^\circ_{f}(GaAs(c) + HCl(g) = GaH_2(g) + \frac{1}{2}\) H\(_2\) + \(\frac{1}{2}\) Cl\(_2\)\) -175.2 kcal mol\(^{-1}\) determined by
Battat et al. (11) and the 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 reported a second law $\Delta H^\circ(\text{GaCl}_3(g) = \text{GaCl}_4(g) + \text{Cl}_2(g), 1083K) = 45.912$ kcal mol $^{-1}$. The value selected was $\Delta H^\circ\text{(GaCl}_4, g, 298K) = -17.0 \pm 5$ kcal mol $^{-1}$ is based on the first two reports, weighting the value of Barlow (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. (11). The enthalpy of formation for gallium dichloride was taken from the measurements of Battat et al. (11) 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, $\Delta H^\circ(2\text{GaCl}_3(g) = \text{Ga}_2\text{Cl}_6(g), 298K) = -22.6$ to $-29.9$ kcal mol $^{-1}$ and $\Delta S^\circ(2\text{GaCl}_3(g) = \text{Ga}_2\text{Cl}_6(g), 298K) = -31.6$ to $-36.0$ cal mol $^{-1}$ K$^{-1}$. Accepting the enthalpy and entropy of dimerization as $-21.0$ kcal mol $^{-1}$ and $-34.0$ cal mol $^{-1}$ K$^{-1}$, respectively, and combining with the selected thermochemical data for $\text{GaCl}_3$ produces $\Delta H^\circ(\text{Ga}_2\text{Cl}_6, g, 298K) = -235.6 \pm 10$ kcal mol $^{-1}$ and $\Delta S^\circ(\text{Ga}_2\text{Cl}_6, g, 298K) = 127 \pm 6.0$ cal mol $^{-1}$ K$^{-1}$. The standard entropy and heat capacity for $\text{GaCl}_3, \text{GaCl}_2$ and $\text{GaCl}_3$ were taken from Shaulov and Mosin (56) while the heat capacity of $\text{Ga}_2\text{Cl}_6$ was taken as the same for $\text{M}_2\text{Cl}_6$ (29). In addition other species are expected to exist (i.e. $\text{Ga}_2\text{Cl}_4, \text{Ga}_3\text{Cl}_2$) (61, 62) but no thermochemical data is 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 56.1 kcal mol $^{-1}$ for $\Delta H^\circ(\text{In}, g, 298K)$. More recent mass spectrometry results of Lamish and Arthur (63) and Farrow (61) suggest the values 46.9 and 58.9 kcal mol $^{-1}$, respectively, with the average value expected to lie between the two values. The thermochemical
properties of phosphorus selected by Bulger (11) 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) reported a value of \( \Delta H^\circ(298K) = 57.9 \pm 1 \text{ kcal mol}^{-1} \) while Panish and Arthur (63) reported \( \Delta H^\circ(298K) = 54.6 \pm 0.9 \text{ kcal mol}^{-1} \) from third law calculations of their mass spectrometric results. The third law reduction of the mass spectrometric results of Foxon (64) produced a value of \( \Delta H^\circ(298K) = 58.04 \pm 0.3 \text{ kcal mol}^{-1} \), while the JANAF tables (29) list \( \Delta H^\circ(298K) = 54.6 \pm 1.1 \text{ kcal mol}^{-1} \). An average value was selected of \( \Delta H^\circ(298K) = 56.1 \pm 2.0 \text{ kcal mol}^{-1} \).

A rather wide range in the reported values for the standard enthalpy of formation of solid InP exists (−13.5 to −22.3 \text{ 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 (53) used \( C_p \) for AlSb which produces a decrease in \( \Delta H^\circ(\text{InP,}c,298K) \) of 0.5 \text{ kcal mol}^{-1} \) when compared to \( C_p(\text{InP,}o,T) \) of Pankratz (69)). 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 (69) 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 (59) and the suggested value of Maslov and Maslov (45).
Table 5.4 The reported standard enthalpy of formation of InP(c). $\Delta H^\circ_{298}$ InP(c,298K)

<table>
<thead>
<tr>
<th>$\Delta H^\circ_{298}$ [InP(c)]</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-18.03±0.7(a)</td>
<td>flow equilibration</td>
<td>61</td>
</tr>
<tr>
<td>-18.58±0.7(b)</td>
<td>mass spectrometry</td>
<td>64</td>
</tr>
<tr>
<td>-23.3±1.5</td>
<td>mass spectrometry</td>
<td>25</td>
</tr>
<tr>
<td>-19.13±0.5(c)</td>
<td>vapor pressure</td>
<td>29,65</td>
</tr>
<tr>
<td>-17.93±1.4(d)</td>
<td>calculated</td>
<td>28</td>
</tr>
<tr>
<td>-21.2</td>
<td>calculated</td>
<td>66</td>
</tr>
<tr>
<td>-20.33(e)</td>
<td>mass spectrometry</td>
<td>64</td>
</tr>
<tr>
<td>-13.52±0.26</td>
<td>solution calorimetry</td>
<td>32</td>
</tr>
<tr>
<td>-21.0±2</td>
<td>bomb calorimetry</td>
<td>67</td>
</tr>
<tr>
<td>-21.5±1.5</td>
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<td>68,70</td>
</tr>
<tr>
<td>-14.5±0.44</td>
<td>solution calorimetry</td>
<td>referenced in 32</td>
</tr>
</tbody>
</table>

(a) $lnP(c) = ln(c) + \frac{1}{2} P_2(g)$, $\Delta H^\circ_{298} = 360$ kcal mol$^{-1}$
(\[\Delta H^\circ_{298} [P_2(g)]\text{ taken as 34.34 kcal mol}^{-1}\])

(b) $lnP(c) = ln(c) + \frac{3}{4} P_4(g)$, $\Delta H^\circ_{298} = 22.1$ kcal mol$^{-1}$
(\[\Delta H^\circ_{298} [P_4(g)]\text{ taken as 14.08 kcal mol}^{-1}\])

(c) $lnP(c) = ln(c) + \frac{1}{2} P_2(g)$, $\Delta H^\circ_{298} = 36.5$ kcal mol$^{-1}$
(\[\Delta H^\circ_{298} [P_2(g)]\text{ taken as 34.34 kcal mol}^{-1}\])

(d) $lnP(c) = ln(c) + \frac{1}{2} P_4(g)$, $\Delta H^\circ_{298} = 35.0$ kcal mol$^{-1}$
(\[\Delta H^\circ_{298} [P_4(g)]\text{ taken as 34.34 kcal mol}^{-1}\])

(e) $lnP(c) = ln(c) + \frac{1}{2} P_2(g)$, $\Delta H^\circ_{298} = 37.50±0.1$ kcal mol$^{-1}$
(\[\Delta H^\circ_{298} [P_2(g)]\text{ taken as 34.34 kcal mol}^{-1}\])

Barrow (55) reports the dissociation energy of InCl to be 102.5 kcal mol$^{-1}$ and combining this with the value of the enthalpy of formation of In(g) and Cl(g) gives $\Delta H^\circ_{298}(lnCl,g,298K) = -16.21$ kcal mol$^{-1}$. However the atomic fluorescence value for the dissociation energy also reported by Barrow (55) ($D_0 = 104.6$ kcal mol$^{-1}$) yields $\Delta H^\circ_{298}(lnCl,g,298K) = -19.31$ kcal mol$^{-1}$. Klemm and Brautigan (76) reported $\Delta H^\circ_{298}(lnCl,c,273K) = -44.8$ kcal mol$^{-1}$ (77) and when combined with the enthalpy of sublimation, $\Delta H^\circ_{298}(lnCl,c,298K) = 27.8$ kcal mol$^{-1}$, gives $\Delta H^\circ_{298}(lnCl,g,298K) = -16.8$ kcal mol$^{-1}$ and is the value adopted here. The standard entropy of InCl was taken from the calculations of Manakova and Faschkin (78) while the heat capacity is that recommended by Kele (79). The standard enthalpy of formation and entropy of lnCl$^2$...
was taken from the estimate of Glasson (11) and the heat capacity is the same as listed for \( \text{GaAl}_2 \). The standard enthalpy of formation and entropy of \( \text{GaAl}_2 \) was taken to be the values suggested by Muller and Burke (14) and the zero pressure heat capacity estimated by Shaw (15). The thermochemical properties of the dimer, \( \text{In}_2\text{Cl}_6 \), were taken from the values suggested by Schafer and Binnemans (16).

The standard enthalpy of formation of phosphine, \( \text{PH}_3 \), was taken from the decomposition studies of Gunn and Green (31) and the remaining properties from the JANAF tables (29,30). The JANAF tables were also used for the other phosphorus 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 Huggeren 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, \( \Delta_{f}H^\circ(\text{Si},298K) = 86.75 \) to \( 109.06 \text{ kcal mol}^{-1} \). The value selected was in between the Knudsen studies of Davis et al. (84) and Grieveon 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 Hunt and Sirtl (37). The posture taken here is to assume that \( \text{SiCl}_4 \) has the most reliable thermodynamic data with these values being fixed by the JANAF tables (29).

The reaction

\[
\text{Si}(g) + \text{SiCl}_4(g) = 2 \text{SiCl}_2(g)
\]  
(5.5.1)

has been investigated extensively (89-93). Employing the thermochemical data for the three species in reaction (5.1) from the JANAF tables (29), third law values of \( \Delta_{f}H^\circ(\text{SiCl}_2,298K) \) were calculated from the experimental data. The diffusion-mass spectrometric determination of Poon and Sirtl (91) is used at temperature
range of 1593K to 1792K produced the value $\Delta H^\circ_r(SiCl_2(g), 298K) = -40.39 \pm 0.3 \text{ kcal mol}^{-1}$ and showed no temperature dependence. This result is in good agreement with flow equilibration data of Schafer et al. (88) (1273K to 1743K) 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 $-40.52$, $-40.54$, and $-40.44 \text{ kcal mol}^{-1}$, respectively. The flow equilibration values of Antopin and Sergeev (90) (1273K to 1673K) and the static values of Ishim et al. (91) (1443K to 1573K) were more negative and exhibited a marked temperature dependence. On the basis of these calculations the value, $\Delta H^\circ_r(SiCl_2(g), 298K) = -40.4 \text{ kcal mol}^{-1}$ 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 $47.4 \pm 0.6$ and $-93.3 \pm 0.5 \text{ kcal mol}^{-1}$, 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 $\Delta H^\circ_r(SiHCl_3(g), 298K)$. 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

$$SiCl_4(g) + HCl(g) = SiHCl_3(g) + HCl(g)$$

(5.5.2)
over the temperature range 1155K to 1500K. By plugging the thermodynamic data listed in Table 5.1 and these results, a relatively temperature insensitive third law value for $\Delta H_f^\circ(SiHCl_3,g,298K) = -119.30 \pm 1.0$ is obtained. Using both static and dynamic methods, Wolf and Teichmann (98) investigated reaction (5.5.2) and the reaction

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

Third law values of $\Delta H_f^\circ(SiHCl_3,g,298K)$ were calculated from the original results and the thermodynamic data of Table 5.1. The value obtained for reaction (5.5.3) is $-119.47 \pm 0.40 \text{ kcal mol}^{-1}$ and for the three data sets with reaction (5.5.2) are $-119.33 \pm 0.90$, $-119.58 \pm 0.2$ and $-119.50 \pm 0.60 \text{ kcal mol}^{-1}$ and the results are seen to be in good agreement with the measurements of Farber and Srivastava (97). Since these values are nearly $3 \text{ kcal mol}^{-1}$ more negative than that developed by Hunt and Sirtl (86), values of $\Delta H_f^\circ(SiHCl_3,g,298K)$ 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. $SiCl_4/H_2$, $H_2/HC1$, $SiHCl_3/H_2$) which were contacted with Si(c) at different temperatures during a deposition/etching process. The results of these calculations for 14 data sets suggest $\Delta H_f^\circ(SiHCl_3,g,298K) = -119.16 \pm 1.70 \text{ kcal mol}^{-1}$. Based on these results and the new experimental determinations, the value adopted is $\Delta H_f^\circ(SiHCl_3,g,298K) = -119.5 \pm 1.5 \text{ kcal mol}^{-1}$.

The standard enthalpy of formation of the d- 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 $\Delta H_f^\circ(SiH_2Cl_2,g,298K) = -75.5 \pm 2 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(SiH_3Cl,g,298K) = -32.7 \pm 2.5 \text{ kcal mol}^{-1}$.

No additional experimental information on the thermochemistry of $SiH_4$ and $SiH$ exists and thus the JANAF tables recommend the following. The standard
enthalpy of formation of disilane was taken from the calculations of Patzinger et al. (99). \( \Delta H_f^\circ(Si_2H_6, g, 298K) = 17.1 \pm 3 \text{ kcal mol}^{-1} \) and is compared with the calculations of O'Neal and Ring (100). \( \Delta H_f^\circ(Si_2H_6, g, 298K) = 19.1 \text{ kcal mol}^{-1} \) at the value of 16.0 kcal mol\(^{-1}\) obtained from the estimated enthalpy of formation for \( SiH_3 (35 \text{ kcal mol}^{-1}) \) and Si-Si (−54 kcal mol\(^{-1}\)). The standard entropy and heat capacity of \( Si_2H_6 \) were obtained by comparison with \( C_2H_6 \).
References: Thermochemical Properties


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 1:1 AsCl$_3$ to H$_2$) is shown in Figures 6.1 and 6.2. Figures 6.1 and 6.2 apply to the systems which used a 1:1 Group III source.
Effect of temperature in the GaAs chloride system source zone (liquid source)

Figure v.1
Effect of temperature in the GaAs chloride system source zone (liquid source)

Figure 1.3
Effect of temperature in the GaAs chloride system source zone (solid source)
Effect of temperature in the GaAs chloride system source zone
Ga₄As₁₂, and Figures 6.3 and 6.4 represent the system which employed GaAs(c) as the Group III source material. At low temperatures GaCl₄ and GaCl₂ 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 species over the entire temperature range examined (873K ≤ T ≤ 1173K). In both systems As₄ was the dominant arsenic specie at low temperature while As₂ became important at high temperatures. In contrast to previous studies [30,31], the trimer As₃ 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.

\[ SiO₂(c) + nHCl + (4-n)H₂ = 2H₂O + SiH₄-nClₙ \quad n=0,1,2,3,4 \quad (6.2.1) \]

\[ kSiO₂(s) + kₘHCl + k(2-m/2)H₂ = 2kH₂O + SiₘClₖm \quad k=1,2 \quad m=0,1,2,3 \quad (6.2.2) \]

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:
\[ K_{1,n} = \frac{y_{A,n}^{b_n} y_{A,A}^{a_n} P_T}{y_{A}^{b_n} y_{A}^{a_n} P_T} \quad (6.2.3) \]

and

\[ K_{2,k,n} = \frac{y_{A,n}^{b_k} y_{A,A}^{a_k} P_T^{1/k_m/2}}{y_{A}^{b_k} y_{A}^{a_k} P_T} \quad (6.2.4) \]

where

\[ y_i = \text{vapor phase mole fraction of specie } i \]

\[ P_T = \text{system total pressure ratio (total pressure/reference state pressure)} \]

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.

\[ \text{Si}(c) + 2H_2 = \text{SiH}_4, \quad a_{Si} = \frac{y_{\text{SiH}_4} y_{H_2}^{a_{H_2}} P_T}{K_5 y_{H_2}^{b_{H_2}}} \quad (6.2.5) \]

\[ \text{Si}(c) + 4\text{HCl} = \text{SiCl}_4 + 2H_2, \quad a_{Si} = \frac{y_{\text{SiCl}_4} y_{H_2}^{b_{H_2}}}{K_6 y_{H_2}^{a_{H_2}} P_T} \quad (6.2.6) \]

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 \( \text{SiH}_4 \) or \( \text{SiCl}_4 \) 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 \( \text{SiH}_4 \) 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 considered. 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 \( \text{SiH}_4 \) 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 \( \text{HCl} \) was formed due to the decomposition of \( \text{AsCl}_3 \) 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% \( \text{AsCl}_3 \) in \( \text{H}_2 \), 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 and 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 metal-silicon bonds and therefore stable species. Since equilibrium represents the lowest 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 would result in a higher total silicon concentration in the vapor phase that is due to the stability of these
Effect of temperature on the GaAs chloride system presource zone

Figure 6.1
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

<table>
<thead>
<tr>
<th>Vapor Specie</th>
<th>$\Delta H^{298K}_{f}$ (kcal/mol$^{-1}$)</th>
<th>$\Delta G^{298K}_{f}$ (kcal/mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SiCl_4$</td>
<td>-158.4</td>
<td>51.4</td>
</tr>
<tr>
<td>$SiHCl_3$</td>
<td>-119.5</td>
<td>60.5</td>
</tr>
<tr>
<td>$SiCl_3$</td>
<td>-93.3</td>
<td>69.8</td>
</tr>
<tr>
<td>$SiH_2Cl_2$</td>
<td>-75.5</td>
<td>76.9</td>
</tr>
<tr>
<td>$SiHCl_2$</td>
<td>-40.3</td>
<td>81.9</td>
</tr>
<tr>
<td>$SiCl_2$</td>
<td>-32.7</td>
<td>94.0</td>
</tr>
<tr>
<td>$SiH_4$</td>
<td>8.2</td>
<td>111.5</td>
</tr>
<tr>
<td>$SiCl$</td>
<td>47.4</td>
<td>129.9</td>
</tr>
<tr>
<td>$Si_2Cl_6$</td>
<td>-236.0</td>
<td>139.5</td>
</tr>
</tbody>
</table>

*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 same 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% AsCl₃ in H₂ inlet to the reactor, has shown GaCl and As₄ to be the dominant Group III and V species. A measure of the supersaturation of the vapor was defined based on the reaction

\[ \text{GaAs}(c) = \text{Ga} + \text{As} \]  \hspace{1cm} (6.2.7)

using the equilibrium relationship

\[ R_{\text{sat}} = \frac{P_{\text{Ga}} P_{\text{As}}}{K_{\text{sat}}} \]  \hspace{1cm} (6.2.8)

where:

\[ K_{\text{sat}} = \exp(-\Delta G_{\text{ren}}^\circ / RT) \]

This saturation ratio was observed to decrease from \(4 \times 10^5\) at 773K to 700 at 973K which shows the vapor phase to be highly supersaturated. When \(\text{SiO}_2(c)\) was not included in the deposition zone the condensed phase silicon activity changed only slightly from \(9 \times 10^{-9}\) at 773K to \(6 \times 10^{-3}\) at 973K. Including \(\text{SiO}_2(c)\) 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 \(9 \times 10^{-5}\).
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 $\text{As}_4$, but GaCl, $\text{GaCl}_2$ and $\text{GaCl}_3$ were all important contributors to the Group III vapor species. The condensed phase silicon activity was found to increase with temperature from $9 \times 10^{-6}$ at 773K to $7 \times 10^{-7}$ at 973K for the case where $\text{SiO}_2(c)$ was not included in the deposition zone. When $\text{SiO}_2(c)$ was included the silicon activity at 773K fell to $2 \times 10^{-9}$.

The effect of pressure was investigated over the range of 1 to 1000 kPa (temperature 973K; inlet composition: 1% $\text{AsCl}_3$ in $\text{H}_2$) 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 $\text{GaCl}_2$ and $\text{GaCl}_3$ at the higher pressures. The dominant Group V vapor specie was $\text{As}_4$ at pressures above 10 kPa with $\text{As}_2$ 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 $\text{SiH}_4$ mole fraction rising faster than $P_2$ in the 1 to 10 kPa range. Applying equation 6.2.3 to the specie $\text{SiH}_4 (n=0)$ and referring to Figure 6.6 shows that the $\text{SiH}_4$ 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)
due to the $H_2O$ mole fraction changes in this range ($y_{H_2O} \approx 1$). The change in $H_2O$ mole fraction is due to changes in the total amount of $SiO_2(c)$ which are 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 species present at the low end of the pressure range is $SiO$ which is formed via the reaction

$$2SiO_2(c) + H_2 = 2SiO + H_2O$$  \hspace{1cm} (6.2.9)

with the corresponding equilibrium relationship

$$K_3 = \frac{y_{SiO}^2 y_{H_2O}}{y_{H_2}}$$  \hspace{1cm} (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 $Si(1\text{-l})$ mole fraction being offset by an order of magnitude increase in $HCl$ mole fraction ($a_{Si} \times y_{HCl}$) and the $P^2$ 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 $Ga_2As_3$ 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 6.3 and 6.9, exhibited a saturation ratio of approximately $2 \times 10^3$ at a pressure of 1 kPa rising to approximately $2 \times 10^4$ 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 $7 \times 10^{-3}$ at 0.1% $AsCl_3$ to $5 \times 10^{-3}$ at 1% $AsCl_3$ and finally to $7 \times 10^{-4}$ at 10% $AsCl_3$. These results agree qualitatively with previous calculations [23,27] and observations [23,21,22,26].

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 FCl 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 $9 \times 10^{-5}$ at 0.1% $AsCl_3$ to $1 \times 10^{-5}$ 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.

- **74 -**
Effect of pressure on the GaAs chloride system deposition zone
Effect of pressure on the GaAs chloride system deposition zor
\[ GaAs(c) + HCl = GaCl + \frac{1}{4} \text{Si} + \frac{1}{2} H_2 \]  \hspace{1cm} (6.2.11)

\[ Ga(l) + HCl = GaCl + \frac{1}{2} H_2 \]  \hspace{1cm} (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\(_5\)) 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\times10^{-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(c). This effect is demonstrated in Figure 6.11 for small additions of H2O to the mixing zone (basis: 1 mole of vapor in the mixing zone) where the mole fraction of H2O prior to the additions was 5.5x10^-9. This effect was predicted by Rai-Choudhury [27] and observed by Pelm [23].

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(c) as shown in Figure 6.12. Reduction of silicon incorporation using an inert to replace H2 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 H2 and SiH4 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, H2O, 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$_2$O on the GaAs chloride system deposition zone

Initial H$_2$O before additions

Mole Fraction

Silicon Activity

Moles of H$_2$O Added To Mixing Zone
Effect of replacing He with inerts on the GaAs chloride system deposition zone.
V source zones of the... 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\(_2\)(s). The saturation ratio, as defined by equation 6.1.8, was found to decrease from \(2 \times 10^4\) 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.
Effect of temperature on the Group III source zone of the GaAs hydride system

Figure 9.14
Effect of temperature on the Group III pre-source zone of the GaAs hydride system

Figure 6.15
Effect of temperature on the mixing zone of the GaAs hydride system.
silicon activity varied only slightly, increasing from $2 \times 10^{-3}$ at 773K to $5 \times 10^{-3}$ at 973K, which is consistent with the effects observed in the chloride system using a liquid Ga$_2$As$_{1.2}$ 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 PCI 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 $3 \times 10^{-2}$ to $4 \times 10^{-4}$ 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-
Therefore, the silane mole fraction was not significantly affected. In contrast, Pogge and Kemlage [35] found that increased \( \text{AsH}_3 \) 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 \( \text{AsH}_3 \) 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 \( \text{AsH}_3 \) 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 \( \text{H}_2\text{O} \) to the mixing zone. This preserves the same III/V ratio from the hydride system source zones and shifts reactions 6.2.1 and 6.2.2 in favor of \( \text{SiO}_2(\mathrm{c}) \). 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 \( \text{AsH}_3 \). Figure 6.19 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 \( 4 \times 10^{-5} \). 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 \( \text{H}_2\text{O} \) to the mixing zone appears to be the most promising method of attain-
Effect of adding HCl on the GaAs hydride system deposition zone

![Graph showing mole fraction and silicon activity as functions of percent HCl and AsH₃](image-url)
A COMPARATIVE THERMODYNAMIC ANALYSIS OF IMPURITY INCORPORATION IN VAPOR P. (U) FLORIDA UNIV GAINESVILLE DEPT OF CHEMICAL ENGINEERING T J ANDERSON ET AL.
Figure 6.13

Effect of replacing Si with others on the GaAs hydride system deposition zone.
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 5.14
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 (−9 kcal/g-mole at 973K) of the following reaction when compared to reaction 6.1.11 (3.2 kcal/g-mole at 973K).

\[ \text{InP}(c) + HCl = \text{InCl} + \frac{1}{4} \text{P}_4 + \frac{1}{2} \text{H}_2 \]  
(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 \( \text{In}_x \text{P}_{1-x} \) 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 \( \text{PCl}_3 \) inlet concentration on the InP system was similar to that of \( \text{AsCl}_3 \) in the GaAs system with the following differences. When liquid \( \text{In}_x \text{P}_{1-x} \) 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 \( \text{InCl}_3 \) being a less important specie in the InP system than \( \text{GaCl}_3 \) was in the GeAs 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 \( \text{InCl} \) 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 \( \text{HCl} \), \( \text{H}_2\text{O} \), and \( \text{PCl}_3 \) 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 \( \text{HCl} \) concentrations (~0.1%) the silicon activities were nearly the same while at large inlet \( \text{HCl} \) 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 \( \text{GaCl} \) (~41.5 kcal/mol at 973K) which caused a greater production of \( \text{GaCl} \) via reaction 6.1.12 than \( \text{InCl} \) in the analogous reaction where \( \text{In} \) is the Group III specie. The differences in the Gibbs energies of formation at 973K for \( \text{Ga}(l) \) and \( \text{In}(l) \) were not significant. Thus, more \( \text{HCl} \) 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, H2O or VCl3 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 99% 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 H2 liberated from the decomposition of HCl and V/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 condensation zone. The influence of inlet composition on silicon activity was not as strong as that of temperature, pressure, replacement of $H_2$ by inert 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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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 development 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,
Main Program Flowsheet for MCMPEC.RAND

Dimension arrays and set limits for the maximum number of species and elements present in the system.

Suppress printing of overflow, underflow, divide by zero and exponential argument error messages.
(Subroutine ERRSET)

Read: 1) Number of elements, species, Temperature and Pressure
2) Thermophysical data for the vapor, solution and pure condensed phase species
5) Maximum number of iterations allowed and computational options.

Read initial compositions in the vapor, solution and pure condensed phases

Write-out the input data if IWRAP<2

Calculate: The Standard State Chemical Potentials
(Subroutine STSTCP)

\[ \text{ISS} > 0 \]

Calculate Source Zone Liquid Composition
(Subroutine STEADY)

Determine a set of linearly independent formation reactions and calculate the equilibrium constant for each reaction from the Gibbs free energy change.
(Subroutine IDPTEQ)
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)

\[ \text{IWRAP} > 0 \]

- **YES**
  - Write out temperature, pressure and initial composition estimate to the wrapup file. (Subroutine WRAPUP)
- **NO**
  - 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 force. (Subroutine CNVFRP)
  - 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).
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.

Write-out results to the wrap-up file. (Subroutine WRAPUP).

Temp. or Press. Loop?

Composition Loop?

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 accommodate.

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 suppress the printing of overflow, underflow, divide by zero and exponential argument error messages. These errors occur commonly in the IMSL matrix routine LEQTIF 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 affect 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 3$V$ 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.
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<th>Comments</th>
<th>Format</th>
</tr>
</thead>
<tbody>
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<td>Title (1),..., TITLE (20)</td>
<td>80 Character Title</td>
<td>20A4</td>
</tr>
<tr>
<td>E, V, S, C, T, P, T0, Po</td>
<td></td>
<td>4I5, 4F10.0</td>
</tr>
<tr>
<td>ELMNT (1), ELMNT (2) .... ELMNT (E)</td>
<td>Element Symbols</td>
<td>13 (1X, A2)</td>
</tr>
<tr>
<td>SPECIE (I,K), DMO(I), DSO(I)</td>
<td></td>
<td>3A4, 2E12.5</td>
</tr>
<tr>
<td>AO(I), Al(I), A2(I), A3(I), ICP(I)</td>
<td>Each vapor phase specie</td>
<td>4E12.5, I2</td>
</tr>
<tr>
<td>A(I,1), A(I,2).... A(I,E)</td>
<td></td>
<td>13(F5.0, 1X)</td>
</tr>
<tr>
<td>Inert(K), DHOZ, DSOZ</td>
<td></td>
<td>3A4, 12E12.5</td>
</tr>
<tr>
<td>IDUMMY</td>
<td></td>
<td>13(F5.0, 1X)</td>
</tr>
<tr>
<td>SPECIE(I, K), DHO(I), DSO(I)</td>
<td></td>
<td>3A4, 12E12.5</td>
</tr>
<tr>
<td>AO(I), Al(I), A2(I), A3(I), ICP(I)</td>
<td>Each solution phase specie</td>
<td>4E12.5, I2</td>
</tr>
<tr>
<td>A(I,1), A(I,2).... A(I,E)</td>
<td></td>
<td>13(F5.0, 1X)</td>
</tr>
<tr>
<td>SPECIE(I,K), A2(I), A3(I), ICP(I)</td>
<td></td>
<td>3A4, 12E12.5</td>
</tr>
<tr>
<td>AO(I), Al(I), A2(I), A3(I), ICP(I)</td>
<td>Each pure condensed phase</td>
<td>4E12.5, I2</td>
</tr>
<tr>
<td>A(I,1), A(I,2).... A(I,E)</td>
<td></td>
<td>13(F5.0, 1X)</td>
</tr>
<tr>
<td>IDEBUG, IOPT, ISSN, IWRAP, MAXIT, NMAX CNVG, TINC, PINC</td>
<td></td>
<td>6I5, 3F10.0</td>
</tr>
<tr>
<td>TOTMV</td>
<td></td>
<td>E12.5</td>
</tr>
<tr>
<td>FRAC(1), FRAC(2).... FRAC(V), FRACZ</td>
<td></td>
<td>6E12.5</td>
</tr>
<tr>
<td>TOTMS</td>
<td></td>
<td>E12.5</td>
</tr>
<tr>
<td>FRAC(V+1), FRAC(V+2)... FRAC(V+S)</td>
<td></td>
<td>6E12.5</td>
</tr>
<tr>
<td>IXSCOR, AXS, BXS</td>
<td></td>
<td>15, 2E12.5</td>
</tr>
<tr>
<td>TOTMC(V+S+1)...TOTMC(V+S+C)</td>
<td></td>
<td>6E12.5</td>
</tr>
</tbody>
</table>
### Table A.2

**Description of Input Variables**

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

#### Heat Capacity Correlations

<table>
<thead>
<tr>
<th>ICP (I)</th>
<th>A2 (I)</th>
<th>A3 (I)</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>kcal-K/g-mole</td>
<td>kcal/g-mole-K-$\ln$(k)</td>
<td>$AO + A1<em>T + A2/T^2 + A3</em>\ln(T)$</td>
</tr>
<tr>
<td>1</td>
<td>kcal/g-mole-K$^3$</td>
<td>kcal/g-mole-K$^4$</td>
<td>$AO + A1<em>T + A2</em>T^2 + A3*T^3$</td>
</tr>
</tbody>
</table>
INERT (3) 12 character name for inert vapor specie
DHOZ  Inert specie enthalpy of formation
DSOZ  Inert specie entropy of formation
AQZ  
A12  
A2Z  Inert specie heat capacity correlation parameters
A3Z 
ICPZ 

IDEBUG  Debugging output parameter

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

IOPT  Looping option parameter

<table>
<thead>
<tr>
<th>IOPT</th>
<th>FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>One pass through routine</td>
</tr>
<tr>
<td>1</td>
<td>Temperature loop</td>
</tr>
<tr>
<td>2</td>
<td>Pressure loop</td>
</tr>
<tr>
<td>3</td>
<td>Composition loop</td>
</tr>
</tbody>
</table>

ISS  Source zone steady state option parameter

<table>
<thead>
<tr>
<th>ISS</th>
<th>FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Steady state option is inactive</td>
</tr>
<tr>
<td>1</td>
<td>Ga/As liquid composition is at steady state with GaAs solid</td>
</tr>
<tr>
<td>2</td>
<td>In/P liquid composition is at steady state with InP solid.</td>
</tr>
</tbody>
</table>
IWRAP  Data output option parameter

<table>
<thead>
<tr>
<th>IWRAP</th>
<th>FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Write-out input data, execution diagnostics and results to printer</td>
</tr>
<tr>
<td>1</td>
<td>IWRAP=O function plus writes-out a concise wrap-up file.</td>
</tr>
<tr>
<td>2</td>
<td>No printer output just a wrap-up file</td>
</tr>
<tr>
<td>3</td>
<td>Write a wrap-up to the printer</td>
</tr>
</tbody>
</table>

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 each 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

<table>
<thead>
<tr>
<th>IXSCOR</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ideal solution</td>
</tr>
<tr>
<td>1</td>
<td>binary simple solution</td>
</tr>
<tr>
<td>2</td>
<td>Henry's Law</td>
</tr>
</tbody>
</table>

AXS, BXS  activity coefficient correlation coefficients for the solution phase

<table>
<thead>
<tr>
<th>IXSCOR</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ideal solution</td>
</tr>
<tr>
<td>1</td>
<td>$G^E = (AXS + BXS * T) \times X1 \times X2$</td>
</tr>
<tr>
<td>2</td>
<td>$H = AXS \times EXP (BXS/T)$</td>
</tr>
</tbody>
</table>
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 signif-
icant specie concentration is less than CNVG. A significant specie is
one which is present in a concentration of $1\times10^{-50}$ 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 enthalpy 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\times10^{-25} \text{ 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 species 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 species in the vapor or solution phases may attain is set to 10^{-50} \text{ 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} \text{ 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.
A2.6 Listing of The Main Program

1 C MCMPEC.RAND .... MULTICOMPONENT MULTIPHASE EQUILIBRIUM CODE
2 C RAND ALGORITHM
3 C
4 C
5 DOUBLE PRECISION ALEQ(63,63), BLEQ(63), D(13,13), DPRMF(13,13),
6 & DINV(13,13), WKA1(13), WKA(63)
7 DIMENSION A(50,13), A0(50), A1(50), A2(50), A3(50), ACOEF(50), B(13),
8 & BCA(50), CHMPT(50), COEFF(6), DELN(50), DG(50),
9 & DTST(50), DHO(50), DS0(50), FRAC(50), FRACIN(50), GNU(50),
10 & ICP(50), IDXBAS(50), INERT(3), O(50), STDCP(50), TOTMC(50)
11 INTEGER ISPCE(50,3), PHASE(50,3), SPECIE(50,3), STRING(6,4),
12 & TITLE(20), V, S, C, E, VP1, VPS, VPS1, VSC, VSCE, ECP2,
13 & ELMNT(1230/13*0, VAPOR(3)/V994APO'.' R
14 & SOLN(3)/SOL*/' UTI, ' ON, ' CON, ' DEN*, ' SED*/
15 & RPSPS/* RPS*/' RPBL/*, 'SSPS/* + '.*
16 & BLK*/ ' LP/*(''*'
17 REAL N(50), KEQ(50), NV, NS, LAMBD
18 C
19 C A(I,J) : ELEMENTAL ABUNDANCE MATRIX
20 C B(IJ) : TOTAL NUMBER OF GRAM-MOLES OF ELEMENT J
21 C DHO(I) : ENTHALPY OF FORMATION OF SPECIES I
22 C DS0(I) : ENTROPY OF FORMATION OF SPECIES I
23 C STDCP(I) : STANDARD CHEMICAL POTENTIAL OF SPECIES I
24 C
25 C *********** HEAT CAPACITY CORRELATIONS ***********
26 C ICP(I)=0 : CP(I) = A0(I) + A1(I)*T + A2(I)/T**2 + A3(I)*ALOG(T)
27 C ICP(I)=1 : CP(I) = A0(I) + A1(I)*T + A2(I)*T**2 + A3(I)*T**3
28 C
29 C ****************************************************
30 C * DOUBLE PRECISION IS USED IN THE MATRIX ROUTINE LEOTIF *
31 C ****************************************************
32 C
33 IRD=5
34 IWRT=6
35 IFILE=2
36 IDIM1=50
37 IDIM2=13
38 IDIM3=IDIM1+IDIM2
39 C
40 C SUPRESS PRINTING OF OVERFLOW, UNDERFLOW, DIVIDE BY ZERO
41 C AND EXPONENTIAL ARGUMENT ERROR MESSAGES
42 C
43 CALL ERRSET(207,0,-1.0,0.209)
44 CALL ERRSET(252,0,-1.0,0.253)
45 C
46 C READ TITLE
47 C
48 READ(IRD,5) (TITLE(K),K=1,20)
49 C FORMAT(204A)
50 C
51 C NUMBER OF ELEMENTS, VAPOR SPECIES, SOLUTION SPECIES,
52 C CONDENSED PURE PHASES, SYSTEM TEMPERATURE (K) AND PRESSURE (PA)
53 C
54 READ(IRD,10) E, V, S, C, T, P, T0, P0
10 FORMAT(4I5,4F10.0)
11 FORMAT('0*.50(***),/1X,'PROBLE4 CANNOT BE SOLVED USING THE ','&RAND ALGORITHM',/1X,'NUMBER OF VAPOR PHASE SPECIES = ',I2,'&/1X,50(***')
12 IF(V.EQ.0) GO TO 3000
13 VPI=V+1
14 VPS=V+S
15 VPSP1=V+S+1
16 VSC=V+S+C
17 VSCE=V+S+C+E
18 EPCP2=E+C+2
19 IF(S.EQ.0) EPCP2=E+C+1
20 C READ ELEMENTS
21 READ(IRD,15) (ELMNT(J),J=1,E)
22 15 FORMAT(13(IX,A2))
23 C VAPOR SPECIES INFORMATION
24 DO 110 I=1,V
25 READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
26 READ(IRD,21) AO(I),A1(I),A2(I),A3(I),ICP(I)
27 READ(IRD,22) (A(I,J),J=1,E)
28 20 FORMAT(3A4,2E12.5)
29 21 FORMAT(4E12.5,I2)
30 22 FORMAT(13(F5.0,1X))
31 DO 110 J=1,3
32 PHASE(I,J)=VAPOR(J)
33 110 CONTINUE
34 C INERT VAPOR SPECIE DATA
35 READ(IRD,20) (INERT(K),K=1,3),DH0Z,DS0Z
36 READ(IRD,21) AOZ,A1Z,A2Z,A3Z,ICPZ
37 READ(IRD,22) IDUMMY
38 C SOLUTION SPECIES INFORMATION
39 IF(S.EQ.0) GO TO 125
40 DO 120 I=VPI,VPS
41 READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
42 READ(IRD,21) AO(I),A1(I),A2(I),A3(I),ICP(I)
43 READ(IRD,22) (A(I,J),J=1,E)
44 120 CONTINUE
45 125 CONTINUE
46 C CONDENSED PHASE DATA
47 IF(C.EQ.0) GO TO 135
48 DO 130 I=VPSP1,VSC
109 READ(IRO,20) (SPECIE(I,K),K=1,3),DMO(I),DSO(I)
110 READ(IRO,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
111 READ(IRO,22) (A(I,J),J=1,E)
112 DO 130 J=1,3
113 PHASE(I,J)=COND(J)
114 130 CONTINUE
115 135 CONTINUE
116 C MAXIMUM NUMBER OF ITERATIONS, CONVERGENCE CRITERION AND OPTIONS
118 C
119 READ(IRO,136) IDEBUG,IOPT,ISS,WRAP,MAXIT,NMAX,CNVG,TINC,PINC
120 136 FORMAT(6I5,3F10.0)
121 IF(WRAP.EQ.3) IFILE=IWRT
122 C
123 C SET THE LOOP LIMITS FOR THE TEMPERATURE, PRESSURE AND COMPOSITION
124 C LOOPS. THE COMPOSITION LOOP STARTS HERE
125 C
126 NCMP=1
127 NTP=1
128 IF(IOPT.EQ.1.OR.IOPT.EQ.2) NTP=NMAX
129 IF(IOPT.EQ.3) NCMP=NMAX
130 DO 2000 ICMP=1,NCMP
131 C
132 C TOTAL NUMBER OF MOLES OF VAPOR AND MOLE FRACTIONS
133 C
134 READ(IRO,137) TOTMV
135 READ(IRO,137) (FRACIN(I),I=1,V),FRACIN
136 137 FORMAT(6E12.5)
137 C
138 C TOTAL NUMBER OF MOLES OF SOLUTION SPECIES, MOLE FRACTIONS
139 C AND EXCESS FREE ENERGY CORRELATION PARAMETERS
140 C
141 IF(S.EQ.0) GO TO 139
142 READ(IRO,137) TOTMS
143 READ(IRO,137) (FRACIN(I),I=VP1,VPS)
144 READ(IRO,138) IXSCOR,A1S,BXS
145 138 FORMAT(15,2E12.5)
146 139 CONTINUE
147 C
148 C TOTAL NUMBER OF MOLES IN PURE CONDENSED PHASES
149 C
150 IF(C.EQ.0) GO TO 140
151 READ(IRO,137) (TOTMC(I),I=VPSPI,VSC)
152 140 CONTINUE
153 C
154 C SAVE THE ORIGINAL SPECIE ORDER SO THAT THE PROBLEM CAN BE PLACED
155 C IN THIS ORDER IF ANY PURE CONDENSED PHASES ARE REMOVED OR SHIFTED
156 C
157 DO 165 I=1,VSC
158 DO 165 K=1,3
159 ISPCE(I,K)=SPECIE(I,K)
160 165 CONTINUE
161 IF(ICMP.GT.1.OR.WRAP.EQ.3) GO TO 187
162 C
C WRITE-OUT SOME OF THE INPUT DATA

IPAGE=1
WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
WRITE(IWRT,410) TP
IF(IWRAP*GT1) GO TO 187
WRITE(IWRT,170)
170 FORMAT(*0/,1X,T55,'HEAT CAPACITY CORRELATION COEFFICIENTS',
      6/,1X,T16,'ENTHALPY OF',T33,'ENTROPY OF',T58,'ICP=O: CP = A0',
      6* A1*T + A2/T**2 + A3*LN(T)'/.1X,T17,'FORMATION',T33,'FORMAT',
      6'ION',T58,'ICP=1: CP = A0 + A1*T + A2*T**2 + A3*T**3'/.1X,T4,
      6'SPECIE',T20,'DHO',T37,'DSO0',T45,'A0',T93,'A1',T93,'A2',T113,
      6'A3',T122,'ICP'/.1X,T4,'SYMBOL',T15,'(KCAL/G-MOLE)',T30,
      6'(KCAL/G-MOLE-K)',T47,'(KCAL/G-MOLE-K**2)',T76,
      6'T86,'(**************)',T106,'(**************)',T122,'(-)',
      6'/**',12'(-_'),T15,13('(''),T30,15('(''),T47,15('(''),
      6'T65,18('(''),T86,15('(''),T106,15('(''),T122,'(')
      DO 180 I=1,VSC
      WRITE(IWRT,175) (SPECIE(I,K),K=1,3),DHO(I),DSO(I),A0(I),A1(I),
      A2(I),A3(I),ICP(I)
      175 FORMAT(1X,3A4,T7F9.3,T33F9.6,T50,F9.6)
      IF(I*EQ.V) WRITE(IWRT,175) (INERT(K),K=1,3),DHOZ,DSOZ,A0Z,A1Z,
      A2Z,A3Z,ICPZ
      180 CONTINUE
      WRITE(IWRT,184) TO,P0,MAXIT,CNVG,IDEBUG
      184 FORMAT(*0/,1X,T10,'THE ENTHALPY AND ENTROPY OF FORMATION',
      5X,'REFERENCE TEMPERATURE AND PRESSURE ARE:*5X,'T0 = *F6.1,' K',
      5X,'P0 = *F9.1,' PA',5X,'0',T35,'MAXIMUM NUMBER OF ITERATIONS',
      5X,'ALLOWED = *5X,' O',T50,'CONVERGENCE CRITERION = *E12.4',
      6*0',T48,'OUTPUT PARAMETER IDEBUG = *I2',
      IF(S*GT.I) WRITE(IWRT,185) IXSCOR,AXS,IKS
      185 FORMAT(*0/,'EXCESS FREE ENERGY CORRELATION :',2X,'IXSCOR = ',
      6* I5,5X,'AXS = ',E12.5,5X,'BXS = ',E12.5)
      IF(ISS*GT.0) WRITE(IWRT,186) ISS
      186 FORMAT(*0/,'THE III-V LIQUID SOLUTION IS AT:',
      6' EQUILIBRIUM WITH THE III-V STOICHIOMETRIC STO',ID*)
      200 187 CONTINUE
      CALCULATE THE STANDARD STATE CHEMICAL POTENTIALS
      AND AN INITIAL ESTIMATE OF THE EQUILIBRIUM COMPOSITION
      DO 2000 ITP=1,NTP
      IF(OPT*EQ.0) GO TO 207
      IF(OPT*EQ.2) GO TO 208
      CALL STSTCP(A0,A1,A2,A3,A07,A1Z,A2Z,A3Z,DHO,DSO,DHOZ,DSOZ,
      STDCP,STDCPZ,ICPZ,TP,T,IDIM1,V,S,C)
      IF(ITP*GT.1) GO TO 195
      CONTINUE
      FRACZ=FRACZ
      CALL ESTMTE(TOTMV,TOTMS,TOTMC,FRACN,FRACZ,V,
      IDIM1,V,S,C)
195 CONTINUE
196 C
197 C SOURCE ZONE STEADY-STATE LIQUID COMPOSITION MODEL
198 C
199 IF(ISSH.GT.0) CALL STEADY(SPECIEA,STDC,P,ELMNT,XIII,T,TO,V,S,C,
200 & IDIM1,IDIM2,ISS,IWR)
201 C
202 CALCULATE THE TOTAL GRAM-MOLES OF EACH ELEMENT
203 BASED ON THE INITIAL COMPOSITION ESTIMATES IN THE PHASES
204 C
205 DO 200 J=1,E
206 BCALC(J)=0.
207 DO 200 I=1,VSC
208 BCALC(J)=B(I,J)*N(I)+BCALC(J)
209 B(J)=BCALC(J)
210 CONTINUE
211 C
212 DETERMINE A SET OF INDEPENDENT REACTION EQUATIONS,
213 THE GIBBS FREE ENERGY CHANGE FOR THESE REACTIONS,
214 AND THE REACTION EQUILIBRIUM CONSTANTS
215 C
216 RT=0.0019872*T
217 CALL IDPOEQ(TA,D,OPRME,DINV,STDC,P,GNU,IOXBS,KEQ,WKA1,DG,
218 & RT,IDIM1,IDIM2,V,S,C,E,IWR)
219 IF(IWRAP.GT.1) GO TO 476
220 IF(IITP.GT.1) GO TO 472
221 C
222 WRITE-OUT THE INITIAL COMPOSITION ESTIMATES, STANDARD STATE
223 CHEMICAL POTENTIALS AND THE ELEMENTAL ABUNDANCE MATRIX
224 C
225 IPAGE=IPAGE+1
226 C
227 WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
228 400 FORMAT('I',/,'0',T38,'RAND ALGORITHM FOR DETERMINING ',
229 & 'EQUILIBRIUM COMPOSITIONS',/,'0',T30,20A4,T120,
230 & 'PAGE ',I2)
231 WRITE(IWRT,410) T,P
232 410 FORMAT('I',/,'0',T43,'TEMPERATURE=',T6.1,' K',T5X,'PRESSURE=',T12.5,
233 & ' PA')
234 WRITE(IWRT,420) (ELMNT(K),K=1,13)
235 420 FORMAT('I',/,'0',T48,'INPUT DATA AND INITIAL COMPOSITION ESTIMATES',,
236 & '/,'0',T29,'INITIAL',T43,'STANDARD',/,'1X,T27,COMPOSITION',,
237 & T43,'CHEMICAL',/,'1X,T4,'SPECIE',T29,'ESTIMATE',T42,'Potential',,
238 & T72,'ELEMENTAL ABUNDANCE MATRIX',/,'1X,T4,'SYMBOL',T17,'PHASE',,
239 & T28,'G-MOLES',T40,'(KCAL/G-MOLE)',T55,13(A2,4X),/,'1',
240 & T12(' ',_'),T15.9(' '),T25.14(' '),T40.13(' '),T55.78(' '))
241 DO 440 I=1,VSC
242 WRITE(IWRT,430) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),N(I),
243 & STOCPI(I),(A(I,J),J=1,E)
244 430 FORMAT(1X,3A4,T15,3A3,T25,E14.7,T42,F9.3,T55,13(F5.3,1X))
245 IF(I.EQ.V) WRITE(IWRT,440) (INERT(K),K=1,3),
246 & (PHASE(I,K),K=1,3),ZV,STOCPR
247 CONTINUE
248 C
249 IF(ISSH.GT.0) WRITE(IWRT,445) XIII
250 445 FORMAT(4X*X=0F6.4)
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',/1X,T40,44,4X,'(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+N
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
400 WRITE(IWRT,410) T,P
410 WRITE(IWRT,475)
475 FORMAT(*0',TS8,*EXECUTION DIAGNOSTICS',/1X,T58.9(' '),1X,
& 11(' '),/0'))
476 CONTINUE

DIVIDE THE STANDARD STATE CHEMICAL POTENTIALS BY RT
DO 480 I=1,VSC
STDCP(I)=STDCP(I)/RT
480 CONTINUE
STDCPZ=STDCPZ/RT

CALCULATE THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR
AND WRITE-OUT THE INITIAL RESULTS TO THE WRAPUP FILE
IF(ITP.GT.1) GO TO 485
CALL TOTS(A,ELMNT,FRAC,N,SITOT,SMF,IDI1,IDI2,V,E)
CALL RATIO(A,ELMNT,FRAC,IIIIV,IDI1,IDI2,V,E)
IF(IIAP.GT.0) CALL WRAPUP(TITLE,SPECIE,INERT,N,FRAC,ZV,FRACZ,
& SITOT,SMF,IIIIV,CNVG,CNVG,ISS,XIII,
& T,P,DATA,IDI1,FILE,V,VSC)
485 CONTINUE

ITERATIVE SOLUTION FOR THE EQUILIBRIUM COMPOSITIONS
RELMAX=1000
IACFF=0
DO 600 I=1,MAXIT
ITER=I
600
REMOVE OR ADD PURE CONDENSED PHASES INTO THE CALCULATION
BASED ON THEIR INCREMENTAL GIBBS FREE ENERGIES
CALL ADDRMOV(A,N,DGTST,STDCP,BLEO,SPECIE,DELN,VPSPI,VSC,F,C,
A26

CALL ACTCOF(N,ACOEF,ZACT,IDI1,IXSCOR,AXS,PSX,T,VS,C,IAEFF, &
   RELMAX)

CALL RAND(A,BCALC,DELN,STDCP,ALEQ,BELEQ,WA,ACOEF, &
   ZACT,VS,C,E,VSC,EPCP2,IDI1,IDI2,IDI3,ITER,P0,P,ZV, &
   ISTOP,IWRT,DEBUG,WRAP)

C CALCULATE THE CONVERGENCE FORCES AND THE NEW ESTIMATE TO THE EQUILIBRIUM COMPOSITION
C
IALG=1
CALL CNVFRC(STDCP,N,DELN,ACOEF,V,SC,IDI1,IALG,ZV, &
P,P,PRT,LAMBDA,ITER,IWRT)

DO 510 II=1,VSC
   N(II)=N(II)*LAMBOA*DELN(II)
   IF(II.LT.CVPS.AND.N(II).LE.1.0E-50) N(II)=1.0E-50
510 CONTINUE

C RESTORE THE CONSTANTS AND ARRAYS TO THE ORIGINAL PROBLEM FORMULATION
C (THIS UNDOES THE SHIFTING DONE IN SUBROUTINE ADDRMV)
CALL RESTOR(A,SPECIE,ISPCE,STDCP,N,DELN,IDI1,IDI2,VSC, &
   EPCP2,C,VSPEC,STDCP,IDI1,IDI2,SC)

IF(DEBUG.GE.1) CALL GIBBS(N,STDCP,STDCPZ,ACOEF,ZACT,ZV,T,P0, &
   IDI1,VS,C,GFE)
IF(DEBUG.GE.1) CALL DEBJG(N,OELN,STDCP,STDCPZ,ACOEF,ZACT,ZV,T,P0, &
   IDI1,VS,C,GFE)

C CHECK FOR CONVERGENCE OF THE EQUILIBRIUM COMPOSITIONS
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(WRAP.LT.3) WRITE(IWRT,605) MAXIT
605 FORMAT('** ****** AFTER *** ITERATIONS THE EQUILIBRIUM **
   COMPOSITION DID NOT CONVERGE**')
610 CONTINUE
CALL GIBBS(N,STDCP,STDCPZ,ACOEF,ZACT,ZV,T,P0,IDI1,VS,C,GFE)

C CALCULATE NV, NS, MOLE FRACTIONS, AND THE CHEMICAL POTENTIALS
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
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))
CONTINUE
IF(S.EQ.0) GO TO 835
DO 830 I=VPI,VPS
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))
CONTINUE
IF(C.EQ.0) GO TO 845
DO 840 I=VPS1,VSC
FRAC(I)=1.
IF(N(I).LT.1.0E-50) FRAC(I)=0.
CNMPT(I)=STOCP(I)*RT
CONTINUE
840 CONTINUE
CONTINUE
845 CONTINUE
FRACZ=ZV/NV
DZV=0.
CHMPTZ=0.
IF(FRACZ.LE.0.0) GO TO 850
CHMPTZ=(STDCPZ+ALOG(ZACT*FRACZ))RT
CONTINUE
850 CONTINUE
C CALCULATE THE EQUILIBRIUM CONSTANTS FROM COMPOSITION
CALL CALCQ(GNU,N,ACOEF,FRAC,IDXNAS,0.
P,PO,V,S,C,E,IDIM1,IDIM2)
CALL THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR
CALL TOTS1(A,ELMNT,FRAC,N,SITOT,SIMF,IDIM1,IDIM2,V,E)
CALL RATIO(A,ELMNT,FRAC,III(V,IDIM1,IDIM2,V,E)
IF(IWRAP.GT.1) GO TO 971
WRITE-OUT THE RESULTS
IPAGE=IPAGE+1
WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
WRITE(IWRT,410) T,P
WRITE(IWRT,420) ITER,GFE,RELMAX,CNVG,LAMBDA
900 FORMAT('EQUILIBRIUM COMPOSITIONS AFTER ',IS, 
* ITERATIONS*/.0**,T45,*SYSTEM GIBBS FREE ENERGY = ',.E14.7, 
* (KCAL),', 
**RELATIVE ERROR = ',.E12.5,5X,CONVERGENCE CRITERION = ', 
* E12.5,5X,*RELAXATION PARAMETER AT LAST ITERATION = ',.F12.5, 

& '/0.TS7.'ESTIMATED',/1X.T25.'EQUILIBRIUM',T39.'EQUILIBRIUM'.
& T55.'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)'.
& T59.'(G-MOLES)',T90.'(KCAL/G-MOLE)',T107.'COEFFICIENT'.
& '/4'.T15.'T25.'T37.'T48.'T54.
& '14(''-').T89.14(''-').T109.12(''-').T54.
& DO 920 I=1,VSC
WRITE(IWRT,910) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),FRAC(I),
& N(I),DELT(I),CHMPT(I),ACOE(I)
& T109,E12.5)
& IF(I.EQ.V) WRITE(IWRT,910) (INERT(K),K=1,3),(PHASE(I,K),K=1,3),
& FRACZ,VZ,ZZV,CHMPTZ,ZACT
20 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',/4*.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),BIJ,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,FRACTZ,VE,VSC)
& SSITOT,SMF,RIIV,RELMAX,CONV,ISS,III,T,P,IOATA,IOIM1,IFILE,
& VE,VSC)
& IF(ITP.GT.1.OR.ICMP.GT.1.OR.IWRAP.GT.1) GO TO 1000
& 1000 WRITE-Out THE INDEPENDENT EQUATIONS
& 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
DETERMINE THE NUMBER OF BASIS SPECIES IN EACH FORMATION REACTION

NSPEC=0

DO 990 K=1,E

IF(I.EQ.IDXBAS(K)) GO TO 1100

IF(ABS(SIGNU(I,K)).LT.1.0E-6) GO TO 990

NSPEC=NSPEC+1

990 CONTINUE

FILL THE CHARACTER ARRAY "STRING" WITH THE FORMATION REACTION SPECIES

NLOOP=1

IF(NSPEC.GT.4) NLOOP=FLOAT(NSPEC)/4.0+0.9

DO 1000 K=1,.3

STRING(I,K)=SPECIE(I,K)

1000 CONTINUE

STRING(I,4)=RPAS

COEFF(I)=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(SIGNU(I,IBASE)).LT.1.0E-6) GO TO 1015

IDX=IDX+1

DO 1010 K=1,3

STRING(IDX*K)=SPECIE(IDXB,K)

1010 CONTINUE

COEFF(IBASE)=SIGNU(I,IBASE)

STRING(IDX,4)=RPSPS

GO TO 1018

1018 CONTINUE

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(1X,6A1,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

WRITE-OUT A COMPARISON BETWEEN THE EQUILIBRIUM CONSTANTS

AS CALCULATED BY THE GIBBS FREE ENERGY CHANGE AND BY COMPOSITION

IPAGE=IPAGE+1

WRITE(IWRT,400) (TITLE(K),K=1,20), IPAGE

WRITE(IWRT,410) TP

WRITE(IWRT,1110)
1110 FORMAT(*0.+,1X,T40,*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*),T46,*FROM GIBBS FREE*,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
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*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
*ENERGY*,T70,*FROM PREDICTED COMPOSITION*,/1X.*16(*_*)*),T20,
Variables which are used in the IMSL subroutines LINVF, LEQTF, LUDATF and LUELMF are not included in this list. FORTRAN default typing applies unless otherwise specified.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (I,J)</td>
<td>elemental abundance matrix</td>
<td>atoms of element j molecule of specie i</td>
</tr>
<tr>
<td>ACOEF (I)</td>
<td>activity coefficient of specie i</td>
<td>-</td>
</tr>
<tr>
<td>ALEQ (I, J)</td>
<td>matrix containing coefficients in the RAND algorithm</td>
<td>variable</td>
</tr>
<tr>
<td>AMAX</td>
<td>maximum value the convergence forcer may attain</td>
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</tr>
<tr>
<td>AMIN</td>
<td>minimum value the convergence forcer may attain</td>
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</tr>
<tr>
<td>AXS</td>
<td>activity coefficient correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>A0 (I)</td>
<td>heat capacity correlation parameter</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>A1 (I)</td>
<td>heat capacity correlation parameter</td>
<td>kcal/g-mole-K^2</td>
</tr>
<tr>
<td>A2 (I)</td>
<td>heat capacity correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>A3 (I)</td>
<td>heat capacity correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>AOZ</td>
<td>inert specie heat capacity correlation parameter</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>A1Z</td>
<td>inert specie heat capacity correlation parameter</td>
<td>kcal/g-mole-K^2</td>
</tr>
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</tr>
<tr>
<td>A3Z</td>
<td>inert specie heat capacity correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>B (J)</td>
<td>moles of element J specified in the system</td>
<td>g-moles</td>
</tr>
<tr>
<td>BCALC (J)</td>
<td>moles of element J as calculated by algorithm</td>
<td>g-moles</td>
</tr>
<tr>
<td>BK (J)</td>
<td>same as BCALC (J)</td>
<td>g-moles</td>
</tr>
<tr>
<td>BLEQ (I)</td>
<td>vector containing the right-hand-side of the RAND algorithm</td>
<td>variable</td>
</tr>
<tr>
<td>BXS</td>
<td>activity coefficient correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>C</td>
<td>number of pure condensed phases</td>
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</tr>
<tr>
<td>CHMPT (I)</td>
<td>chemical potential of specie i</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>CHMPTZ</td>
<td>chemical potential of the inert</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>CNVG</td>
<td>composition convergence criterion</td>
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<tr>
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<td>vector containing the character string 'CONDENSED'</td>
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<tr>
<td>D (I, J)</td>
<td>matrix of basis species</td>
<td>atoms of j mole of i</td>
</tr>
<tr>
<td>DELH</td>
<td>total enthalpy change</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>DELN (I)</td>
<td>change in moles of specie i</td>
<td>g-mole</td>
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<tr>
<td>DELS</td>
<td>total entropy change</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>DG (I)</td>
<td>Gibbs Free Energy change of reaction i</td>
<td>kcal/g-mole</td>
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<tr>
<td>DGDL</td>
<td>change in system Gibbs Free Energy with respect to the convergence forcer</td>
<td>kcal/g-mole</td>
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<tr>
<td>Variable</td>
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<td>Units</td>
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<td>----------</td>
<td>-------------</td>
<td>-------</td>
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<tr>
<td>DGTST (I)</td>
<td>incremental change in Gibbs free energy for specie i</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>DHO (I)</td>
<td>enthalpy of formation of specie i</td>
<td>kcal/g-mole</td>
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<tr>
<td>DHOZ</td>
<td>enthalpy of formation of the inert specie</td>
<td>kcal/g-mole</td>
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<tr>
<td>DINV (I, J)</td>
<td>inverse of matrix D</td>
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<tr>
<td>DPRME (I, J)</td>
<td>Gram-Schmidt orthogonalization of matrix D</td>
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</tr>
<tr>
<td>DSO (I)</td>
<td>entropy of formation of specie i</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>DSOZ</td>
<td>entropy of formation of the inert specie</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>E</td>
<td>number of elements in the system (integer)</td>
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</tr>
<tr>
<td>ELIII (K)</td>
<td>vector containing character string of group III elements</td>
<td>-</td>
</tr>
<tr>
<td>ELMNT (J)</td>
<td>vector containing character strings of the elements present in the system</td>
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</tr>
<tr>
<td>ELV (K)</td>
<td>vector containing character strings of group V element</td>
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</tr>
<tr>
<td>EPCP2</td>
<td>E + C + 2 (integer)</td>
<td>-</td>
</tr>
<tr>
<td>EP3</td>
<td>E + 3 (integer)</td>
<td>-</td>
</tr>
<tr>
<td>EP3PC</td>
<td>E + 3 + C (integer)</td>
<td>-</td>
</tr>
<tr>
<td>FRAC (I)</td>
<td>mole fraction of specie i in its phase</td>
<td>-</td>
</tr>
<tr>
<td>FRACZ</td>
<td>mole fraction of inert in the vapor</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>GNU (I, J)</td>
<td>formation reaction coefficient matrix g-mole</td>
<td></td>
</tr>
<tr>
<td>GFE</td>
<td>Gibbs Free Energy of the system</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>GSTAR</td>
<td>GFE divided by RT</td>
<td>-</td>
</tr>
<tr>
<td>IACFF</td>
<td>activity coefficient switch</td>
<td>-</td>
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<tr>
<td>IALG</td>
<td>convergence forcer algorithm switch</td>
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<tr>
<td>ICMP</td>
<td>index for the composition loop</td>
<td>-</td>
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<tr>
<td>ICP (I)</td>
<td>heat capacity correlation parameter</td>
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<tr>
<td>IDATA</td>
<td>switch used with the wrap-up file</td>
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<tr>
<td>IDGT</td>
<td>number of significant figures in each matrix element</td>
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<tr>
<td>IDIM1</td>
<td>maximum number of species allowed in system</td>
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</tr>
<tr>
<td>IDIM2</td>
<td>maximum number of elements allowed in system</td>
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</tr>
<tr>
<td>IDIM3</td>
<td>IDIM1 + IDIM2</td>
<td>-</td>
</tr>
<tr>
<td>IDEBUG</td>
<td>option to aid in trouble-shooting</td>
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<tr>
<td>IDXBAS (J)</td>
<td>vector containing the index of each basis specie</td>
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<td>IFILE</td>
<td>logical unit designator of the wrap-up file</td>
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<td>INERT (3)</td>
<td>vector containing the inert specie name</td>
<td>-</td>
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<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>-------</td>
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<tr>
<td>IOPT</td>
<td>parameter to allow various computational options</td>
<td>-</td>
</tr>
<tr>
<td>IOUT</td>
<td>number of pure condensed phases removed by subroutine ADDRMV</td>
<td>-</td>
</tr>
<tr>
<td>IROD</td>
<td>logical unit designator for data input</td>
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<tr>
<td>ISPCE (I, J)</td>
<td>array containing the original specie order</td>
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<td>ISS</td>
<td>steady state option parameter</td>
<td>-</td>
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<tr>
<td>ISTOP</td>
<td>switch which halts the computation if problems develop</td>
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<tr>
<td>ITER</td>
<td>current iteration number in the equilibrium calculation</td>
<td>-</td>
</tr>
<tr>
<td>ITP</td>
<td>index for the temperature and pressure loop</td>
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<tr>
<td>ITST</td>
<td>parameter which indicates linear dependence in the basis specie matrix</td>
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<tr>
<td>IWRAP</td>
<td>switch used with the wrap-up file</td>
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</tr>
<tr>
<td>IWRT</td>
<td>logical unit designator for data output</td>
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</tr>
<tr>
<td>IXSCOR</td>
<td>parameter which chooses the solution phase activity coefficient model</td>
<td>-</td>
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<tr>
<td>KEQ (I)</td>
<td>equilibrium constant for formation reaction i as calculated from the Gibbs Free Energy change (real)</td>
<td>-</td>
</tr>
<tr>
<td>LAMBDA</td>
<td>convergence forcer (real)</td>
<td>-</td>
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<tr>
<td>MAXIT</td>
<td>maximum number of iterations to be used</td>
<td>-</td>
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<tr>
<td>N (I)</td>
<td>moles of specie i (real) g-moles</td>
<td>-</td>
</tr>
<tr>
<td>NMAX</td>
<td>total number of loops to be made in the composition or temperature and pressure loops</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NS</td>
<td>total moles in solution (real)</td>
<td>g-moles</td>
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<tr>
<td>NSPEC</td>
<td>number of species in the formation reaction</td>
<td>-</td>
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<tr>
<td>NV</td>
<td>total moles in the vapor (real)</td>
<td>g-moles</td>
</tr>
<tr>
<td>P</td>
<td>system pressure</td>
<td>Pa</td>
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<tr>
<td>PHASE (I, 3)</td>
<td>matrix containing a character string to denote the phase of each specie</td>
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<tr>
<td>PINC</td>
<td>pressure increment for each loop</td>
<td>Pa</td>
</tr>
<tr>
<td>PO</td>
<td>formation data reference pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>Q (I)</td>
<td>equilibrium constant for formation reaction i as calculated from composition</td>
<td>-</td>
</tr>
<tr>
<td>RELERR</td>
<td>fractional change in composition resulting from one iteration</td>
<td>-</td>
</tr>
<tr>
<td>RELMAX</td>
<td>maximum fractional change in composition of all species resulting from one iteration</td>
<td>-</td>
</tr>
<tr>
<td>RIIIIV</td>
<td>vapor phase III/V atomic ratio</td>
<td>-</td>
</tr>
<tr>
<td>RT</td>
<td>product of the ideal gas constant and the temperature</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>S</td>
<td>total number of species in the solution phase</td>
<td>-</td>
</tr>
<tr>
<td>SIMF</td>
<td>mole fraction of silicon species in the vapor</td>
<td>-</td>
</tr>
<tr>
<td>SITOT</td>
<td>moles of silicon species in the vapor</td>
<td>g-moles</td>
</tr>
<tr>
<td>SOLN (3)</td>
<td>vector containing the character string 'SOLUTION'</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SPECIE (I, 3)</td>
<td>matrix of character strings containing the names of each specie</td>
<td>-</td>
</tr>
<tr>
<td>STDCP (I)</td>
<td>standard chemical potential of specie i</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>STDCPZ</td>
<td>standard chemical potential of the inert</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>SUMIII</td>
<td>total moles of group III atoms in the vapor</td>
<td>g-mole</td>
</tr>
<tr>
<td>SUMV</td>
<td>total moles of group V atoms in the vapor</td>
<td>g-mole</td>
</tr>
<tr>
<td>T</td>
<td>system temperature</td>
<td>K</td>
</tr>
<tr>
<td>TITLE (K)</td>
<td>vector containing an 80 character title</td>
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</tr>
<tr>
<td>TINC</td>
<td>temperature increment for each loop</td>
<td>K</td>
</tr>
<tr>
<td>TOTMC (I)</td>
<td>total moles of pure condensed phase  i as input</td>
<td>g-moles</td>
</tr>
<tr>
<td>TOTMOL</td>
<td>total moles in a single phase</td>
<td>g-moles</td>
</tr>
<tr>
<td>TOTMS</td>
<td>total moles in the solution phase</td>
<td>g-moles</td>
</tr>
<tr>
<td>TOTMV</td>
<td>total moles in the vapor phase</td>
<td>g-moles</td>
</tr>
<tr>
<td>TO</td>
<td>formation data reference temperature</td>
<td>K</td>
</tr>
<tr>
<td>US</td>
<td>coefficient for the solution species</td>
<td>-</td>
</tr>
<tr>
<td>UV</td>
<td>coefficient for the vapor species</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>total number of species in the vapor (integer)</td>
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</tr>
<tr>
<td>VAPOR (3)</td>
<td>vector containing the character string 'VAPOR'</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------------------------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>WKA</td>
<td>work area for LEQT1F</td>
<td></td>
</tr>
<tr>
<td>WKA1</td>
<td>work area for LINV1F</td>
<td></td>
</tr>
<tr>
<td>XIII</td>
<td>group III specie fraction in the steady state liquid &quot;pure&quot; condensed phase</td>
<td></td>
</tr>
<tr>
<td>ZV</td>
<td>moles of inert in the system</td>
<td>g-moles</td>
</tr>
<tr>
<td>ZACT</td>
<td>activity coefficient of the inert</td>
<td></td>
</tr>
</tbody>
</table>
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 LINVIF and LEQTIF. 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 $P_0$, 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 $T_0$ and pressure $P_0$ is:

$$ u_i^0 (T_0, P_0) = \frac{\Delta H_f}{T_0} - T_0 \frac{\Delta S_f}{T_0} $$

(1)

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

$$ u_i^0 (T, P_0) = \Delta H_f (T_0) + \left[ \int_{T_0}^{T} C_p^i \, dT - T \left[ \Delta S_f (T_0) \right] \right] + \left[ \int_{T_0}^{T} \frac{C_p^i}{T} \, dT \right] $$

(2)

Two heat capacity correlations are available and are chosen by the


Figure A2

Subprogram Structure of MCMPEC.RAND

MAIN PROGRAM

ERRSET
Suppresses printing of arithmetic overflow error messages.

STSTCP
Calculates standard chemical potentials.

ESTMTE
Calculates an initial estimate to the equilibrium compositions.

STEADY
Inserts a steady state composition liquid phase if ISS > 0.

IDPTEQ
Determines a linearly independent set of formation reaction equations.

TESTD
Tests for linear dependencies among the basis species.

LINVIF
Inverts the matrix of basis species.

TOTSI
Determines the total moles of silicon species in the vapor phase.
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 matrices ALEQ and BLEQ when IDEBUG=2

LEQTIF
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 ADDRMOV.

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.

TOTS1

RATIO

WRAPUP
(executed if IWRA1 > 0).

End
SUBROUTINE STSTCP(A0,A1,A2,A3,A4Z,A1Z,A2Z,A3Z,DO0,DS0,DOZ,DSZ, 
& STDCP,STDCPZ,ICP,ICPZ,T0,T,IDIM1,V,S,C) 
C THIS SUBROUTINE CALCULATES THE STANDARD STATE CHEMICAL POTENTIALS 
& AT TEMPERATURE T. 
DIMENSION A0(IDIM1),A1(IDIM1),A2(IDIM1),A3(IDIM1),DO0(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 
DLNT3=T*ALOG(T)-T0*ALOG(T0) 
CHEMICAL POTENTIALS FOR THE VAPOR, SOLUTION AND CONDENSED PHASES 
DO 100 I=1,VSC 
DELM=A0(I)*DT+A1(I)*DT2/2.-A2(I)*DTM1+A3(I)*(DLNT-DT) 
DELS=A0(I)*DLNT+A1(I)*DT-A2(I)*DTM2/2+A3(I)*DLNT2/2. 
IF(IP(I).EQ.1) DELM=A0(I)*DT+A1(I)*DT2/2.*A2(I)*DT3/3. 
& +A3(I)*DT4/4. 
IF(IPZ.EQ.1) DELS=A0Z*DLNT+A1Z*DT-A2Z*DT2/2.*A3Z*DLNT2/2. 
& +A3Z*DLNT3/3. 
STDCP(I)=DH0(I)+DELM-T*(DS0(I)+DELS) 
100 CONTINUE 
CHEMICAL POTENTIAL FOR THE INERT COMPONENT IN THE VAPOR PHASE 
DELM=A0Z*DT+A1Z*DT2/2.-A2Z*DTM1+A3Z*(DLNT-DT) 
IF(IPZ.EQ.1) DELM=A0Z*DT+A1Z*DT2/2.*A2Z*DT3/3. 
IF(IP(EQ.1) DELS=A0Z*DLNT+A1Z*DT-A2Z*DT2/2.*A3Z*DLNT3/3. 
& +A3Z*DT3/3. 
STDCPZ=DH0Z+DELM-T*(DS0Z+DELS) 
RETURN 
END
parameter ICP. These correlations are:

<table>
<thead>
<tr>
<th>ICP</th>
<th>Heat Capacity Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( C_p(T) = a_0 + a_1 T + a_2 T^{-2} + a_3 \ln(T) ) (3)</td>
</tr>
<tr>
<td>1</td>
<td>( C_p(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 ) (4)</td>
</tr>
</tbody>
</table>

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 THIS SUBROUTINE CALCULATES AN INITIAL ESTIMATE
C TO THE SYSTEM EQUILIBRIUM COMPOSITIONS

DIMENSION TOTMC(IDIM1),FRAC(IDIM1)
INTEGER V,S,C,VS,VSI,VSC
REAL N(IDIM1)
VS=V+S
VSI=VS+I
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=VSI,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.

\[
\begin{align*}
(1-x)\text{III}(s) & \equiv (1-x)\text{III}(\ell) \\
x\text{V}(s) & = x\text{V}(\ell) \\
(1-x)\text{III}(\ell) + x\text{V}(\ell) & = \text{III}_{1-x}\text{V}_x(\ell) \\
(1-x)\text{III}(s) + x\text{V}(s) & = \text{III}_{1-x}\text{V}_x(\ell)
\end{align*}
\]

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

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.

\[
\begin{align*}
\Delta G_1 &= (1-x) \left[ \Delta S_{\text{III}}^{\text{m}} (T_m - T) + \Delta C_p^{\text{III}} (T-T_m) \ln \frac{T_m}{T} \right] \\
\Delta G_2 &= x \left[ \Delta S_{\text{V}}^{\text{m}} (T_m - T) + \Delta C_p^{\text{V}} (T-T_m) \ln \frac{T_m}{T} \right]
\end{align*}
\]

where it has been assumed that \(\Delta C_p\), 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]:
\[ \Delta G_3 = RT \left[ x \ln x + (1-x) \ln (1-x) \right] + (A_{xs} + B_{xs} T) x (1-x) \] (7)

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

\[ \Delta G_4 = \Delta G_1 + \Delta G_2 + \Delta G_3 \] (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.

\[ T = \frac{T_{III IV}^{IIII} \Delta S_{III IV}^{IIII} - A_{xs} (2x - 2x^2 - 0.5)}{\Delta S_{III IV}^{IIII} - R \ln 4x(1-x) + B_{xs} (2x-2x^2-0.5)} \] (9)

The thermodynamic constants necessary for the evaluation 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>
<thead>
<tr>
<th></th>
<th>( \Delta S_m ) (cal/g-mole-k)</th>
<th>( T_m ) (K)</th>
<th>( \Delta C_p ) (cal/g-mole-K)</th>
<th>( A_{xs} ) (cal/g-mole)</th>
<th>( B_{xs} ) (cal/g-mole-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>4.411</td>
<td>302.9</td>
<td>-0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>4.7</td>
<td>1090</td>
<td>1.0</td>
<td>4666</td>
<td>-8.741</td>
</tr>
<tr>
<td>GaAs</td>
<td>16.64</td>
<td>1511</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>1.815</td>
<td>429.8</td>
<td>-0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.5011</td>
<td>313.3</td>
<td>0.47</td>
<td>32750</td>
<td>-23.95</td>
</tr>
<tr>
<td>InP</td>
<td>10.81</td>
<td>1332.2</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure A5
The Si/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

$$GNU = A D^{-1}$$  \hspace{1cm} (1)
SUBROUTINE STEADY(SPECIE,A,STDCP,ELMNT,XIII,T,T0,V,S,C,IDIM1,
IDIM2,ISS,IVRT)

SUBROUTINE TO CALCULATE THE SOLID- LIQUID EQUILIBRIUM COMPOSITIONS
FOR USE IN THE STEADY-STATE APPROXIMATION IN THE SOURCE ZONE

DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1)
INTEGER SPECIE(IDIM1,3),ELMNT(IDIM2),III,I(I12),V,L(2),V.S,C,VSC,
DATA III(1)/"GA"/III(2)/"AS"/III(3)/"SL"/III(V)/"IN"/III(P)/
&THETA2(XV)=(TMIIIIV*DSIIIIV-AXS*(0.5-XV**2-(1.-XV)**2))/
&VSC=V+S+C
SPECIE(VSC,1)=III(1)
SPECIE(VSC,2)=III(2)
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

GA-AS SYSTEM
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

IN- P SYSTEM

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
60 CONTINUE

C BINARY ROOT FINDING ROUTINE FOR THE GROUP III AND V COMPOSITIONS

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.0.00001) GO TO 200
SWITCH=(THET2-THTOLD)/(XV-XOLD)
THTOLD=THET2
XOLD=XV
IF(SWTCH.GT.0.AND.THET2.LT.THETA1) GO TO 80
IF(SWTCH.LT.0.AND.THET2.GT.THETA1) GO TO 80
XMAX=XV
XV=0.5*(XMIN+XV)
GO TO 100
XMIN=XV
XV=0.5*(XMAX+XV)
100 CONTINUE
WRITE(120)
FORMAT(*',***** SUBROUTINE STEADY: ITERATION FOR SOURCE ',
& 'COMPOSITION DID NOT CONVERGE')
200 CONTINUE

C CALCULATE THE STANDARD CHEMICAL POTENTIAL OF THE SOURCE SOLUTION

DGA=(1.0-XV)*(DSIII*(TMIII-T)+DCIII*(T-TMIII-T)*ALOG(T/TMIII))
DBG=XV*(DSV*(TMOV-T)+DCV*(T-TMV-T)*ALOG(T/TMOV))
DGC=(AXS+BXS*T)*XV*(1.-XV)+R*T*(XV*ALOG(XV)+(1.-XV)*ALOG(1.-XV))
STDCP(VSC)=DGA+DBG+DGC

C LOCATE THE GROUP III AND V ELEMENTS IN THE ELEMENTAL ABUNDANCE ARRAY
C AND INSERT THE CALCULATED ABUNDANCES INTO THIS ARRAY

IDX3=0
IDX5=0
DO 300 I=1,IDIM2
IF(ISS.EQ.2) GO TO 250
IF(ELMN(T(I),EQ.GA) IDX3=I
IF(ELMN(T(I),EQ.AS) IDX5=I
GO TO 300
250 IF(ELMN(T(I),EQ.IN) IDX3=I
IF(ELMN(T(I),EQ.P) IDX5=I
300 CONTINUE
A(VSC,IDX3)=1.0-XV
A(VSC,IDX5)=XV
XIII=1.0-XV
RETURN
END
Figure A8

Flowsheet for Subroutine IDPTEQ

Transfer the first row of the elemental abundance matrix A into the orthogonal matrix DPRME. Let MA = 0, MD = 0.

Increment MD by 1

Increment MA by 1

Transfer row MA of elemental abundance matrix A into row MD of basis matrix D.

YES

MA = 1 ?

Test the rows in matrix D for linear dependence (Subroutine TESTD)

YES

Linearly Dependent ?

NO

All elements accounted for

YES

Invert the matrix of basis species and calculate the matrix of formation reaction coefficients GNU. (Subroutine LINV1F)

Calculate the equilibrium constants for each of the formation reactions from the Gibbs Free Energy change of each reaction.

RETURN
SUBROUTINE IDPTEQ(A,D,DPRME,DINV,STDCP,GNU,IDXAS,KEQ,WKA,DO,RT,IDI1,IDI2,V,S,C,F,IWRT)

C THIS SUBROUTINE DETERMINES A SET OF LINEARLY INDEPENDENT REACTION EQUATIONS AND CALCULATES THE EQUILIBRIUM CONSTANTS FOR THESE REACTIONS FROM THE GIBBS FREE ENERGY CHANGE OF EACH REACTION.

DOUBLE PRECISION D,DPRME,DINV,WKA
DIMENSION D(IDIM2,IDIM2),DPRME(IDIM2,IDIM2),DINV(IDIM2,IDIM2),A(IDIM2),IDXAS(IDIM2),STDCP(IOII),GNU(IDIM1,IDIM2)
REAL KEQ(IDIM2)
INTEGER V,S,C,E,VSC
VSC=V+S+C

BUILD THE D MATRIX WHICH WILL CONTAIN THE LINEARLY INDEPENDENT BASIS SPECIES

DO 100 J=1,E
DPRME(I,J)=A(I,J)
100 CONTINUE
MA=0
DO 200 MD=1,E
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.O) GO TO 200
CALL TESTO(D,DPRME,MD,E,IDI1,ITST)
IF(ITST.EQ.1) GO TO 140
200 CONTINUE
WRITE(IWRT,260)
260 FORMAT('0000**** A COMPLETE SET OF BASIS SPECIES COULD NOT BE FOUND IN SUBROUTINE IDPTEQ')
280 CONTINUE

INVERT MATRIX D USING IMSL SUBROUTINE LINV1F

AND CALCULATE THE REACTION COEFFICIENT MATRIX GNU

IDGT=4
CALL LINV1F(D,E,IDI1,DINV,IDGT,WKA,IER)
IF(IER.EQ.12) WRITE(IWRT,310) IDGT
310 FORMAT('0000**** ACCURACY TEST FAILED DURING MATRIX INVERSION**** IN SUBROUTINE IDPTEQ.... IDGT=',I2)
320 FORMAT('0000**** MATRIX D IS SINGULAR IN SUBROUTINE IDPTEQ')
DO 400 J=1,E
TEMP=0.0
DO 350 JJ=1,E
TEMP=TEMP+A(I,JJ)*DINV(JJ,J)
350 CONTINUE
GNU(I,J)=TEMP
400 CONTINUE
C
CALCULATE THE EQUILIBRIUM CONSTANTS FOR THE FORMATION REACTIONS
C
DO 500 I=1,VSC
ARG=(-1.0)*STDCP(I)
DO 450 K=1,E
IDX8=IDX8AS(K)
ARG=ARG+GNU(I,K)*STDCP(IDX8)
450 CONTINUE
DG(I)=(-1.0)*ARG
ARG=ARG/RT
KEQ(I)=EXP(ARG)
500 CONTINUE
RETURN
END
The equilibrium constants for each reaction are then calculated in lines 58 through 70 by

\[ K_{eqi} = \exp \left( \frac{\left( \sum_{j=1}^{E} \gamma_{ij} \mu_{ij}^o - \mu_i^o \right)}{RT} \right) \]  

(2)

Where \( \mu_{ij}^o \) is the standard chemical potential of basis specie \( j \) and \( \gamma_{ij} \) 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]:

\[
\begin{align*}
    d_{ij}' &= d_{ij} - \sum_{k=1}^{E} d_{ik} \frac{\sum_{k=1}^{E} d_{jk} d_{lk}'}{\sum_{k=1}^{E} (d_{lk}')^2} \\
    d_{ij} &= d_{ij} - \sum_{k=1}^{E} d_{ik} \frac{\sum_{k=1}^{E} d_{jk} d_{lk}'}{\sum_{k=1}^{E} (d_{lk}')^2}
\end{align*}
\]  

(1)

(2)

Where: \( i=2,3,\ldots,m_d \) = row index

\( j = 1, 2, \ldots, E \) = 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 occurrence 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, DGST(I), is given by [8].

\[
DGST_I = \mu_I^0 - \sum_{j=1}^{E} a_{ij} \pi_j 
\]

(1)

Where \( \pi_j \) 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.
SUBROUTINE TESTO (D, DPRME, MD, E, IDIM2, ITST)

C THIS SUBROUTINE TESTS THE D MATRIX FOR LINEAR DEPENDENCE
C USING A GRAM-SCHMIDT ORTHOGONALIZATION ALGORITHM

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

DO 500 J=1, E
IF (DABS(DPRME(MD, J)) .GT. 1.0E-5) ITST=ITST+1
500 CONTINUE

RETURN
END
SUBROUTINE ADDRMV(A,N,DGTST,STDCP,BLEO,SPECIE,DELN,VPSP1,VSC,EC,EP2C,P1,U,I dimension A(IDIM1,IDIM2),DELN(IDIM1),DGTST(IDIM1),STDCP(IDIM1)
REAL N(IDIM1)
INTEGER SPECIE(IDIM1,3),VPSP1,VSC,EC,EP2C,C
IDENT 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)*BLEO(J)
100 CONTINUE
IF(DGTST(I).LT.0.0) INDEX=I
200 CONTINUE
IF(INDEX*EQ.O) GO TO 400
C
C FIND THE ZERO COMPOSITION PURE CONDENSED PHASE WITH THE SMALLEST NEG
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
SUBROUTINE TO ADD OR REMOVE PURE CONDENSED PHASES
IN THE EQUILIBRIUM CALCULATION BASED ON THE INCREMENTAL
GIBBS FREE ENERGY OF THESE PHASES

DOUBLE PRECISION BLEO(IDIM3)
DIMENSION A(IDIM1,IDIM2),DELN(IDIM1),DGTST(IDIM1),STDCP(IDIM1)
REAL N(IDIM1)
INTEGER SPECIE(IDIM1,3),VPSP1,VSC,EC,EP2C,C
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

Figure A11. Subroutine ADDRMV
DO 500 I=VPSP1,VSC
55 IF(N(I)*GT.1.65E-24) GO TO 500
56 IPI=I+1
57 IF(IPI*GT.VSC) IPI=VSC
58 DO 450 IJ=IPI*VSC
59 IF(N(IJ)*LT.1.65E-24) GO TO 450
60 TMPVAR=N(I)
61 N(I)=N(IJ)
62 N(IJ)=TMPVAR
63 TMPVAR=STDCP(I)
64 STDCP(I)=STDCP(IJ)
65 STDCP(IJ)=TMPVAR
66 TMPVAR=DELN(I)
67 DELN(I)=DELN(IJ)
68 DELN(IJ)=TMPVAR
69 DO 420 J=1,E
70 TMPVAR=A(I,J)
71 A(I,J)=A(IJ,J)
72 A(IJ,J)=TMPVAR
73 420 CONTINUE
74 DO 430 K=1,J
75 ITMPV=SPECIE(I,K)
76 SPECIE(I,K)=SPECIE(IJ,K)
77 SPECIE(IJ,K)=ITMPV
78 430 CONTINUE
79 DO 500 K=1,E
80 GO TO 500
81 450 CONTINUE
82 C=C-1OUT
83 VSC=VSC-1OUT
84 EPCP2=EPCP2-1OUT
85 RETURN
86 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:

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

The third option (IXSCOR = 2) allows the first specie in the solution phase to have an activity coefficient described by Henry's constant, \( H \).
SUBROUTINE ACTCOF(N,ACOEF,ZACT,IDIM1,IXSCOR,AXS,BXS,T,V,S,C, IACFF,RELMAX)

SUBROUTINE TO CALCULATE ACTIVITY COEFFICIENTS FOR EACH COMPONENT

IXSCOR ALGORITHM

1 BINARY SIMPLE SOLUTION THEORY GE=(AXS+BXS*T)*X1*X2
2 HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE H=AXS*EXP(BXS/T)

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+1
150 CONTINUE
IF(IXSCOR.EQ.2) GO TO 200

X1=N(VP1)/NS
X2=1.0-X1
ARG1=(AXS+BXS*T)*X2*X2/RT
ARG2=(AXS+BXS*T)*X1*X1/RT
ACOEF(VP1)=EXP(ARG1)
ACOEF(VPS)=EXP(ARG2)
GO TO 900

HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE

200 ACOEF(VP1)=AXS*EXP(BXS/T)

900 RETURN
END
\[ \gamma_{v+1} = H = A_{xs} \exp \left[ \frac{B_{xs}}{T} \right] \] (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

\[ \text{ALEQ} \cdot \text{X} = \text{BLEQ} \] (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 \( \hat{e}_{ni} \) values from the solution vector and assign them to their appropriate position in the DELN vector.
SUBROUTINE RAND(A,B,BK,N,DELN,STDCP,ALEQ,BLEQ,WKA,ACOEF,
ZACT,V,S,C,E,VSC,EPCP2,IDIM1,IDIM2,IDIM3,IT,F,P0,
PZV,ISTOP,IWRIT,DEBUG,WRAP)

RAND ALGORITHM TO MINIMIZE THE GIBBS ENERGY OF A
MULTIPHASE, MULTICOMPONENT SYSTEM CONTAINING A VAPOR PHASE INERT

DOUBLE PRECISION ALEQ(IDIM3,IDIM3),BLEQ(IDIM3),WKA(IDIM3),
DIMENSION A(IDIM1,IDIM2),B(IDIM2),BK(IDIM2),DEL4(IDIM1),
INTEGER V,S,C,E,VSC,EPCP2,VPS,VP1,EP3,EP3PC,
REAL N(IDIMI),NV,NS
ISTOP=0
VPS=V+S
VPS1=V+S+1
VP1=V+1
EP3=E+3
EP3PC=E+3+C
50 CONTINUE

ZERO MATRIX ALEQ BEFORE ASSIGNING VALUES
DO 100 I=1,EPCP2
DO 100 J=1,EPCP2
ALEQ(I,J)=0.
100 CONTINUE

FILL THE UPPER E ROWS OF MATRIX ALEQ FROM EQUATION 21
THE FIRST E COLUMNS ARE THE LAGRANGE MULTIPLIER COEFFICIENTS
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

COLUMNS E+1 AND E+2 IN MATRIX ALEQ ARE THE
COEFFICIENTS FOR VARIABLES UV AND US RESPECTIVELY
IEP1=E+1
IEP2=E+2
TMPVAR=0.
DO 150 K=1,V
TMPVAR=TMPVAR+A(K,I)*N(K)
150 CONTINUE
55 ALEQ(I,IEP1)=TMPVAR
56 IF(S*EQ.0) GO TO 165
57 TMPVAR=0.
58 DO 160 K=VPI,VPS
59 TMPVAR=TMPVAR+A(K,I)*N(K)
60 160 CONTINUE
61 ALEQ(I,IEP2)=TMPVAR
62 165 CONTINUE
63 C
64 C THE FINAL C COLUMNS OF ALEQ ARE FOR THE DELTA-N
65 C COEFFICIENTS RELATING TO THE PURE CONDENSED PHASES
66 C
67 IADD=2
68 IF(S*EQ.0) IADD=1
69 IF(C*EQ.0) GO TO 180
70 DO 170 K=VPSPI,VSC
71 INDEX=K-VPS+E+IADD
72 ALEQ(I,INDEX)=A(K,I)
73 170 CONTINUE
74 180 CONTINUE
75 C
76 C FILL THE NEXT TWO ROWS (ROWS E+1 AND E+2) OF MATRIX ALEQ
77 C BASED ON EQUATIONS 22 AND 23
78 C
79 DO 250 J=1,E
80 TMPVAR=0.
81 DO 230 K=1,V
82 TMPVAR=TMPVAR+A(K,J)*N(K)
83 230 CONTINUE
84 ALEQ(IEP1,J)=TMPVAR
85 IF(S*EQ.0) GO TO 250
86 TMPVAR=0.
87 DO 240 K=VPI,VPS
88 TMPVAR=TMPVAR+A(K,J)*N(K)
89 240 CONTINUE
90 ALEQ(IEP2,J)=TMPVAR
91 250 CONTINUE
92 ALEQ(IEP1,IEP1)=(-1.0)*ZV
93 C
94 C THESE FINAL C ROWS IN MATRIX ALEQ ARE FILLED BY EQUATION 17
95 C
96 EP3=E+1+IADD
97 EP3PC=EP3+C
98 IF(C*EQ.0) GO TO 300
99 INDEX=VPS
100 DO 290 I=EP3,EP3PC
101 INDEX=INDEX+1
102 DO 290 J=1,E
103 ALEQ(I,J)=A(INDEX,J)
104 290 CONTINUE
105 300 CONTINUE
106 C
107 C CALCULATE BK, NV AND NS VALUES FROM THE PREVIOUS ESTIMATE OF N
108 C
A65

109  DO 360 J=1,E
110  TMPVAR=0.,
111  DO 350 I=1,VSC
112  TMPVAR=A(I,J)*N(I)+TMPVAR
113  350 CONTINUE
114  BK(J)=TMPVAR
115  360 CONTINUE
116  NV=ZV
117  DO 365 I=1,V
118  NV=NV+N(I)
119  365 CONTINUE
120  NS=0.,
121  IF(S.EQ.0) GO TO 375
122  DO 370 I=VPI,VPS
123  NS=NS+N(I)
124  370 CONTINUE
125  375 CONTINUE
126  C
127  C NOW ASSIGN VALUES TO VECTOR BLEQ
128  C THE FIRST E VALUES ARE FROM EQUATION 21
129  C
130  DO 400 J=1,E
131  TMPVAR=B(J)-BK(J)
132  DO 380 I=1,V
133  ARG=ACOEF(I)*N(I)*P/P0/NV
134  IF(ARG.LE.1.0E-50) ARG=1.0E-50
135  TMPVAR=TMPVAR+A(I,J)*N(I)*STDCP(I)+ALOG(ARG))
136  380 CONTINUE
137  IF(S.EQ.0) GO TO 395
138  DO 390 I=VPI,VPS
139  ARG=ACOEF(I)*N(I)/NS
140  IF(ARG.LE.1.0E-50) ARG=1.0E-50
141  TMPVAR=TMPVAR+A(I,J)*N(I)*STDCP(I)+ALOG(ARG))
142  390 CONTINUE
143  395 CONTINUE
144  BLEQ(J)=TMPVAR
145  400 CONTINUE
146  C
147  C THE NEXT 2 POSITIONS IN VECTOR BLEQ (POSITIONS E+1 AND E+2)
148  C ARE FROM EQUATIONS 22 AND 23
149  C
150  TMPVAR=0.,
151  DO 410 I=1,V
152  ARG=ACOEF(I)*N(I)*P/P0/NV
153  IF(ARG.LE.1.0E-50) ARG=1.0E-50
154  TMPVAR=TMPVAR+N(I)*STDCP(I)+ALOG(ARG))
155  410 CONTINUE
156  BLEQ(I-1)=TMPVAR
157  TMPVAR=0.,
158  IF(S.EQ.0) GO TO 425
159  DO 420 I=VPI,VPS
160  ARG=ACOEF(I)*N(I)/NS
161  IF(ARG.LE.1.0E-50) ARG=1.0E-50
162  TMPVAR=TMPVAR+N(I)*STDCP(I)+ALOG(ARG))
THE FINAL C POSITIONS OF VECTOR BLEQ ARE FROM EQUATION 17

IF(C.EQ.0) GO TO 435

INDEX=VPS
DO 430 I=EP3,EP3PC
INDEX=INDEX+1
BLEQ(I)=STDCP(INDEX)
CONTINUE
430 CONTINUE
CONTINUE
435 CONTINUE
IF(IDEBUG.EQ.2) CALL PRNTAB(ALEQ,BLEQ,EP3PC,IDIM3,IWRT)

SOLVE THE MATRIX PROBLEM USING SUBROUTINE LEQTIF

M=1
IDGT=3
CALL LEQTIF(ALEQ,M,EP3PC,IDIM3,BLEQ,IDGT,WK,A,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 *.IS,* ******')
IF(IER.EQ.34 .AND. IWRT.LT.2) WRITE(IWRT,440) IER,IDGT
440 FORMAT('0','****** ACCURACY TEST IN SUBROUTINE LEQTIF*')

IF(IER.EQ.1) ITER=1
IF(IER.EQ.129) ISTOP=1
IF(IER.EQ.129) IDEBUG=2
IF(IDBG.LT.2 .AND. IER.EQ.129) GO TO 50
490 CONTINUE
IF(IDERUG.EQ.2) WRITE(IWRT,495) (BLEQ(K),K=1,EP3PC)
495 FORMAT('0','THE TRANSPOSED X VECTOR IS:*'./ix,10(D11.4,2x))

FILL THE DELN VECTOR FROM BLEQ USING EQUATIONS 19 AND 20
THE FIRST E VALUES IN BLEQ ARE NOW THE LAGRANGE MULTIPLIERS;
THE NEXT 2 VALUES ARE UV AND US RESPECTIVELY;
THE LAST C VALUES ARE THE DELN VALUES FOR THE PURE CONDENSED PHASES

UV=BLEQ(IEP1)
DO 510 I=1,V
ARG=ACOF(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 THE FINAL C DELN VALUES ARE THE LAST C VALUES OF BLEQ
C
IF(C.EQ.0) GO TO 550
INDEX=E+IA0
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)

<table>
<thead>
<tr>
<th>Row#</th>
<th>Variable</th>
<th>Row#</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\pi_1$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\pi_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\vdots$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pi_E$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$U_v$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$U_s$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta n_{v+s+1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta n_{v+s+2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta n_{v+s+c}$</td>
<td></td>
</tr>
</tbody>
</table>

(Note: RHS = Right Hand Side)
Figure A15

Detailed MATRIX FORMULATION of Linear Equations

SOLVE: \[ \text{ALEQ}.X = \text{BLEQ} \] for \( X \)

\[
X = \begin{bmatrix}
\mu_1 \\
\mu_2 \\
\vdots \\
\mu_E \\
\nu_v \\
\nu_s \\
\delta n_v + s + 1 \\
\delta n_v + s + 2 \\
\vdots \\
\delta n_v + s + c
\end{bmatrix}
\]

\[
\begin{align*}
b_1 &= b_1^k + \sum_{i=1}^{v} a_{ii} n_i \left[ \mu_i^o + \ln \left( \frac{n_i}{n_{v0}} \right) \right] + \sum_{i=v+1}^{v+s} a_{ii} n_i \left[ \mu_i^o + \ln \left( \frac{n_i}{n_{s}} \right) \right] \\
b_E &= b_E^k + \sum_{i=1}^{v} a_{iE} n_i \left[ \mu_i^o + \ln \left( \frac{n_i}{n_{v0}} \right) \right] + \sum_{i=v+1}^{v+s} a_{iE} n_i \left[ \mu_i^o + \ln \left( \frac{n_i}{n_{s}} \right) \right] \\
\sum_{i=1}^{v} n_i \left[ \mu_i^o + \ln \left( \frac{n_i}{n_{v0}} \right) \right] \\
\sum_{i=v+1}^{v+s} n_i \left[ \mu_i^o + \ln \left( \frac{n_i}{n_{s}} \right) \right] \\
\mu_v + s + 1 \\
\mu_v + s + 2 \\
\vdots \\
\mu_v + s + c
\end{align*}
\]
|   | a_{1,1} | a_{1,2} | a_{1,3} | \cdots | a_{1,v} | a_{1,v+1} | a_{1,v+2} | \cdots | a_{v+1,1} | a_{v+1,2} | a_{v+1,3} | \cdots | a_{v+1,v} | a_{v+1,v+1} | a_{v+1,v+2} | \cdots | a_{v+1,v+c} | a_{v+1,v+c+1} | a_{v+1,v+c+2} | \cdots |
| 1 | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots |
| 2 | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots |
| 3 | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots | 0 | 0 | 0 | \cdots |

**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:

\[ n'_i = n_i + \lambda \delta n_i \]  

Where:  
\( n'_i \) = updated estimate to the equilibrium, composition  
\( n_i \) = previous estimate of equilibrium, composition  
\( \delta n_i \) = step change in composition as calculated in subroutine RAND  
\( \lambda \) = 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 \( \frac{dG}{d\lambda} \) at the maximum and minimum allowable values of \( \lambda \) where \( G \) is the system Gibbs Free Energy. An estimate to the optimum value of the convergence forcer is then obtained by

\[ \lambda \approx \frac{(dG)}{d\lambda} \bigg|_{\lambda=0} \]  

\[ (dG)_{\lambda=0} - (dG)_{\lambda=\text{MAX}} \]
SUBROUTINE CNVFRC(STOCP,N,DELN,ACOEF,V,S,C,IDIM1,IALG,ZV,P,PO,RT,LAMDA,ITER,IWRT)

C THIS SUBROUTINE CALCULATES THE CONVERGENCE FORCER FOR THE CURRENT ITERATION

DIMENSION STOCP(IDIM1),ACOEF,IDIM1),DELN(IDIM1)
REAL N(IDIM1),LAMDA
INTEGER V,S,C,VSC

VSC=V+S+C

AMIN=0.

AMAX=1.

C LIMIT THE MAXIMUM VALUE OF THE CONVERGENCE FORCER BY APPLYING THE CONSTRAINT OF NON-NEGATIVE COMPOSITION

DO 50 I=1,VSC
  IF(ABS(DELN(I)) .LT. 1.0E-50) GO TO 50
  LAMBDA=(-1.0)*N(I)/DELN(I)
  IF(LAMBDAGT.0.0 .AND. LAMBDALT.AMAX) AMAX=LAMBD
50 CONTINUE

LAMBD=AMAX

IF(IALG.EQ.0) RETURN

ATEST=AMAX-AMIN

IF(ATESTLT.0.01) RETURN

C ESTIMATE THE OPTIMUM VALUE OF THE CONVERGENCE FORCER

DGDMAX=DGDLAM(N,DELN,STOCP,ACOEF,ZV,P,PO,RT,AMAX,
& IDIM1,V,S,C)

DGDMIN=DGDLAM(N,DELN,STOCP,ACOEF,ZV,P,PO,RT,AMIN,
& IDIM1,V,S,C)

IF(DGDMIN.EQ.DGDMAX) DGDMAX=0.0

LAMBD=DGDMIN/(DGDMIN-DGDMAX)

IF(LAMBDGT.0.05) LAMBD=AMAX

LAMBD=AMIN

RETURN

END

FUNCTION DGDLAM(N,DELN,STOCP,ACOEF,ZV,P,PO,RT,LAMDA,
& IDIM1,V,S,C)

C EVALUATION OF DG/DLAMDA FOR DETERMINING THE CONVERGENCE FORCER

DIMENSION ACOEF(IDIM1),DELN(IDIM1),STOCP(IDIM1)
REAL N(IDIM1),NV,NS
INTEGER V,S,C,VP1,VPS,VSC,VSI
VP1=V+1
VPS=V+S
VSI=VPS+1
VSC=VPS+C
NV=ZV
55 DO 100 I=1,V
56 NV=NV+N(I)
57 100 CONTINUE
58 IF(S.EQ.0) GO TO 210
59 NS=0.0
60 DO 200 I=VPI,VPS
61 NS=NS+N(I)
62 200 CONTINUE
63 210 CONTINUE
64 C CALCULATE DG/DLAMBD
65 C
66 C DGDL=0.0
67 DO 300 I=1,VPS
68 ARG=ACOEF(I)*(N(I)+ALAM*DELN(I))*P/PO/NV
69 IF(I.GT.V) ARG=ACOEF(I)*(N(I)+ALAM*DELN(I))/NS
70 DGDL=DGDL+DELN(I)*(STDCP(I)+ALOG(ARG))
71 300 CONTINUE
72 IF(C.EQ.0) GO TO 410
73 DO 400 I=VS1,VSC
74 DGDL=DGDL+DELN(I)*STDCP(I)
75 400 CONTINUE
76 410 DGDLAM=DGDL*RT
77 RETURN
78 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 $\lambda$. The value of $\lambda$ 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

$$\frac{dG}{d\lambda} = RT \left\{ \sum_{i=1}^{V} \delta n_i [u^o + \ln \left( \frac{n_i^p}{n_i^o} \right)] + \sum_{i=v+1}^{v+s} \delta n_i [u^o + \ln (-i)] \right\}$$

$$+ \sum_{i=v+s+1}^{V+S+C} \delta n_i [u^o]$$

(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, V3C 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).
SUBROUTINE RESTOR(A,SPECIE,ISPCF,STDCP,V,STDCP,N,DELN,IDIM1,IDIM2, 
& VSC,EPCP2,C,VPSP1,E,IOU)
&
C THIS SUBROUTINE RESTORES MATRICES 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

DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1),DELP(IDIM1),ISPCF,IDIM1,3) 
INTEGER SPECIE(IDIM1,3),VSC,F,EPCP2,C,VPSP1,VSCM1
REAL N(IDIM1)

1) IF(IOUT.EQ.0) GO TO 400
2) EPCP2=EPCP2+IOUT
3) C=C+IOUT
4) VSC=VSC+IOUT
5) VSCM1=VSC-1
6) DO A CHARACTER STRING COMPARISON OF SPECIE WITH ISPCF AND PUT
7) THE ARRAYS AND VECTORS INTO THEIR ORIGINAL ORDERS
8) DO 300 I=VPSP1,VSCM1
9) IP1=I+1
10) IF(IP1.GT.VSC) IP1=VSC
11) DO 200 II=IP1,VSC
12) IF(ISPCF(II).EQ.SPECIE(II).AND.
13) & ISPCF(II.2).EQ.SPECIE(II.2).AND.
14) & ISPCF(II.3).EQ.SPECIE(II.3)) GO TO 50
15) GO TO 200
16) TEMP=N(I)
17) N(I)=N(II)
18) N(II)=TEMP
19) TEMP=STDCP(I)
20) STDCP(I)=STDCP(II)
21) STDCP(II)=TEMP
22) TEMP=DELP(I)
23) DELP(I)=DELP(II)
24) DELP(II)=TEMP
25) DO 100 J=1,E
26) TEMP=A(I,J)
27) A(I,J)=TEMP
28) A(I,J)=TEMP
29) 100 CONTINUE
30) DO 120 K=1,3
31) IFM=SPECIE(I,K)
32) SPECIE(I,K)=SPECIE(II,K)
33) SPECIE(II,K)=ITEMP
34) 120 CONTINUE
35) GO TO 300
36) 400 CONTINUE
37) END
SUBROUTINE GIBBS(N,STDCP,STDCPZ,ACOEФ,ZACT,ZV,T,P,PO,IDIM1),
& V,S,C,GFE)
C SUBROUTINE TO CALCULATE THE GIBBS FREE ENERGY OF THE SYSTEM
C USING EQUATION 1 IN THE PROPOSAL
C
DIMENSION STDCP(IDIM1),ACOEФ(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 GAS CONSTANT IS IN UNITS OF: KCAL/G-MOLE-K
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
IF(S.EQ.0) GO TO 170
ARG=ZACT*ZV*P/PO/NV
IF(ARG.EQ.1.0E-50) ARG=1.0E-50
GSTAR=ZV*(STDCPZ+ALOG(ARG))
DO 150 I=1,V
ARG=ACOEФ(I)*N(I)*P/PO/NV
IF(ARG.EQ.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=ACOEФ(I)*N(I)*P/PO/NS
IF(ARG.EQ.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:

\[ Q_i = \gamma_i x_i p_{\text{doi}} / \prod_{k=1}^{E} (\gamma_k x_k p_{p_{0k}}) \]

Where:
\( \gamma_i \) = activity coefficient of specie \( i \)
\( x_i \) = mole fraction of specie \( i \) in its phase
\( \gamma_j \) = stoichiometric reaction coefficient
\( p_{\text{poi}} = \begin{cases} 1 & \text{for solution or pure condensed phase} \\ P/P_0 & \text{for vapor phase} \end{cases} \)

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
SUBROUTINE CALCQ(GNU,N,ACOEF,FRAC,IDXBASE,J,
                   P,P0,V,S,C,F,IDIM1,IDIM2)
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,F,VSC
REAL N(IDIM1)

VSC=V+S+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=IDXBASE(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
SUBROUTINE TOTSI(A,ELMNT,FRAC,N,SITOT,SMF,IDIM1,IDIM2,V,F)
C SUBROUTINE TO CALCULATE THE TOTAL SI IN THE VAPOR PHASE
C
DIMENSION A(IDIM1,IDIM2),FRAC(IDIM1)
INTEGER ELMNT(IDIM2),V,F,SIVPR,SI/
REAL N(IDIM1)
SITOT=0.0
SMF=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)
SMF=SMF+FRAC(I)
140 CONTINUE
150 CONTINUE
RETURN
END
SUBROUTINE RATIO(A,ELMNT,FRAC,RIIV,IDIM1,IDIM2,V,E)
C
THIS SUBROUTINE CALCULATES THE VAPOR III/V RATIO
C
DIMENSION A(IDIM1,IDIM2),FRAC(IDIM1),KIII(K),V
C
INTEGER ELMNT(IDIM2),EIII(5),ELV(5),E
DATA EIII(1)="B",EIII(2)="Al",EIII(3)="Ga",EIII(4)="In",
E ELV(5)="Sb",ELV(5)="Bi"

C DETERMINE WHICH INDECIES CORRESPOND TO COLUMN III AND V ELEMNTS

DO 100 K=1,5
KIII(K)=0
DO 100 J=1,E
IF(ELMNT(J)==EIII(K)) KIII(K)=J
100 CONTINUE

SUM-UP THE GROUP III AND V SPECIES AND CALCULATE THE RATIO

SUMIII=0.0
SUMV=0.0
DO 200 I=1,V
DO 200 K=1,5
IDIII=KIII(K)
IDXV=KV(K)
200 CONTINUE
IF(IDXIII==0) GO TO 120
SUMIII=SUMIII+A(I,IDXIII)*FRAC(I)
120 CONTINUE
IF(IDXV==0) GO TO 200
SUMV=SUMV+A(I,IDXV)*FRAC(I)
200 CONTINUE
RIIV=1.0E10
IF(SUMV>0.0) RIIV=SUMIII/SUMV
RETURN
END
A COMPARATIVE THERMODYNAMIC ANALYSIS OF IMPURITY INCORPORATION IN VAPOR PHASE.

Florida State University
Gainesville

T. J. Anderson et al.

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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 A23.

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.
SUBROUTINE WRAPUP(TITLE,SPECIE,N,FRA,C,ZV,FRA,C,SITOT,SIMF,RIIV, RELMAX,CNVG, ISS,XIII,T,P, IDATA, IDIM1, IFILE)

SUBROUTINE TO WRITE-OUT A SUMMARY OF THE RESULTS TO A FILE

DIMENSION INERT(3), FRA(C,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
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), FRA(C), N(I)
100 FORMAT(3A4,2X,E12.5,2X,E12.5)
IF(IDATA.EQ.0) WRITE(IFILE,105) RIIV
105 FORMAT("VAPOR III/V",10X,F9.4)
IF(IDATA.EQ.0) WRITE(IFILE,110) SIMF,SITOT
110 FORMAT("SI IN VAPOR",2X,E12.5,2X,E12.5)
CONTINUE
200 IF(ISST.GT.0) WRITE(IFILE,205) XIII
205 FORMAT(3X,"X=",F6.4)
WRITE(IFILE,210)
210 FORMAT(" ")
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), FRA(C), N(I)
100 RETURN
END
SUBROUTINE DEBUG(N, DELN, DGTST, VSC, IDIM1, ITER, LAMBDA, GFE, RMX, IWRT)

C ROUTINE TO WRITE-OUT N, DELN, ALMBDA DURING THE ITERATION PROCESS

C

REAL LAMBDA, N(IDIM1), DGTST(IDIM1), DELN(IDIM1)
INTEGER VSC

WRITE(IWRT, 10) ITER, LAMBDA, GFE, RMX

10 FORMAT(*0*, *ITERATION = '*, I5, '*, 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
SUBROUTINE PRNTAB(A,B,N,IDIM3,IWRT)
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 '*12,' THROUGH '*12,' OF MATRIX ALEQ:')
20 FORMAT(*0', 'COLUMNS '*12,' THROUGH '*12,' OF MATRIX ALEQ:')
IF(LINE*GT.80) LINE=0
DO 40 ILIN=1,N
WRITE(IWRT,30) (A(ILIN*JJJIST+IEND), 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
LINVIF, LEQTIF, 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

\[ \mathbf{A} \mathbf{X} = \mathbf{B} \quad (1) \]

for vector \( \mathbf{X} \). The matrix inversion subroutine, LINVIF, is called from line 43 of subroutine IDPTEQ. LINVIF defines \( \mathbf{B} \) to be a matrix instead of a vector and simply puts ones on the diagonal of this matrix and zeros elsewhere. Subroutine LEQTIF is then called upon to solve the matrix problem

\[ \mathbf{A}^{-1} \mathbf{A} = \mathbf{B} \quad (2) \]

to yield the inverted \( \mathbf{A} \) matrix \( \mathbf{A}^{-1} \).

Subroutine LEQTIF is called from line 182 of subroutine RAND to solve the linear algebra problem in equation 1 for the vector \( \mathbf{X} \). The \( \mathbf{X} \) vector solution is then returned as vector \( \mathbf{B} \) 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 \( \mathbf{A} \) is singular IER is returned as 129.
Figure A25

IMSL Subroutine Calling Sequence

LINV1F: Driver program to invert matrix A. This subroutine puts ones on the diagonal of matrix B for LEQT1F.

LEQT1F: Driver program to solve the matrix problem $A\times X = B$ for vector $X$.

LUDATF: Performs an LU decomposition of matrix $A$ with partial Pivoting.

LUELMF: Performs appropriate substitutions to obtain the $X$ vector and writes the $X$ vector into B.
SUBROUTINE LINVIF (AN, IA, AINV, IDGT, WKAREA, IER)

IMSL SUBROUTINE FOR INVERTING REAL MATRICES

DOUBLE PRECISION A(IA,N), AINV(IA,N), WKAREA(1), ZERO, ONE
DATA ZERO/0.000/, ONE/1.000/

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 (AN, N, IA, AINV, IDGT, WKAREA, IER)
IF (IER .EQ. 0) GO TO 9005
9000 CONTINUE
9005 RETURN
END
SUBROUTINE LEOTIF (A,N,IA,B,IDGT,WKAREA,IER)
C
IMSL SUBROUTINE LEQTIF FOR SOLVING THE MATRIX PROBLEM A*X=B
C
DIMENSION A(IA,1),B(IA,1),WKAREA(I)
DOUBLE PRECISION A,B,WKAREA,D1,D2,WA
C
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
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 LUOATF (A, LU, N, IA, IDGT, DI, D2, IPVT, EQUIL, WA, IFP)

THIS SUBROUTINE IS USED WITH SUBROUTINE LEOITIF

DIMENSION A(IA,1), LU(LA,1), IPVT(1), EQUIL(1)

DOUBLE PRECISION A, LU, D1, D2, EQUIL, WA, ZERO, ONE, FOUR, SIXTH, SIXTH

R, WREL, BIQA, BIG, P, SUM, AI, WI, T, TEST, O

DATA ZERO, ONE, FOUR, SIXTH, 0.00, 1.00, 4.00, 16.00, 0.062500/

FIRST EXECUTABLE STATEMENT

INITIALIZATION

IER = 0
RN = N
WREL = ZERO
DI = 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
CONTINUE

IF (BIG .GT. BIGA) BIGA = BIG
IF (BIG .EQ. ZERO) GO TO 110
EOUIL(I) = ONE/BIG
CONTINUE

DO 105 J=1,N
JM1 = J-1
IF (JM1 .LE. 1) GO TO 40
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

WITH ACCURACY TEST

AI = DABS(SUM)
WI = ZERO
IF (IM1 .LT. 1) GO TO 20
DO 15 K=1,IM1
T = LU(I, K) .times. LU(K, J)
SUM = SUM-T
WI = WI + DABS(T)
CONTINUE

15

LU(I, J) = SUM
WI = WI + DABS(SUM)
IF (AI .EQ. ZERO) AI = BIGA
TEST = WI/AL
IF (TEST .GT. WREL) WREL = TEST
GO TO 35

WITHOUT ACCURACY

IF (IM1 .LT. 1) GO TO 25
DO 30 K=1,IM1
   SUM = SUM-LU(I,K)*LU(K,J)
30  CONTINUE
L(U(I,J)) = SUM
CONTINUE
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
   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
   DO 55 K=1,JM1
   SUM = SUM-LU(I,K)*LU(K,J)
55  CONTINUE
   LU(I,J) = SUM
   Q = EQUIL(I)*DABS(SUM)
   IF (P *GE. Q) GO TO 70
   P = 0
   IMAX = I
70  CONTINUE
   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
   DI = -DI
   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)
   IPVT(J) = IMAX
   D1 = DI*LU(J,J)
   IF (DABS(D1) *LE. ONE) GO TO 90
   D1 = D1*SIXTH
   D2 = D2+FOUR
   GO TO 85
   IF (DABS(D1) *GE. SIXTH) GO TO 95
D1 = D1*SIXTN
D2 = D2-FOUR
GO TO 90
CONTINUE
JPI = J+1
IF (JPI .GT. N) GO TO 105
C
P = LU(J,J)
DO 100 I=JPI,N
LU(I,J) = LU(I,J)/P
CONTINUE
100
C
IF (IDGT .EQ. 0) GO TO 9005
P = 3*N+3
WA = P*WREL
IF (WA+10.0D0*(-IDGT) .NE. WA) GO TO 9005
IER = 34
GO TO 9005
C
110 IER = 129
120 D1 = ZERO
130 D2 = ZERO
9005 RETURN
END
SUBROUTINE LUELME (A,B,IPVT,N,IA,X)  

C  THIS SUBROUTINE IS USED WITH SUBROUTINE LELTMF 

C  DIMENSION A(IA,1),B(1),IPVT(1),X(1)  

DOUBLE PRECISION A,9,X,SUM  

FIRST EXECUTABLE STATEMENT  
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. 0.0) IW = I  
20 X(I) = SUM  
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:

\[
G^* (T, P, n_i) / RT = G = \sum_{i=1}^{v+s} n_i \left( \mu_i^0 + \ln \frac{n_i}{n_v} \right) + Z_v \left( \mu_v^0 + \ln \frac{Z_v}{n_v} \right) + \sum_{i=v+1}^{v+s+c} n_i \mu_i^0
\]

(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
- \( \mu_i^0 \) = 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

\[ v+s+c \sum_{i=1}^{k} a_{ji} n_i - b_j = 0, \tag{2} \]

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 \( n^k \) as

\[ G^{k+1} = G^k + \sum_{i=1}^{v+s+c} \frac{\partial G}{\partial n_i} \delta n_i + \frac{1}{2} \sum_{i=1}^{v+s+c} \sum_{j=1}^{v+s+c} \frac{\partial^2 G}{\partial n_i \partial n_j} \delta n_i \delta n_j, \tag{3} \]

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

For \( i = 1, \ldots, v \)

\[ \frac{\partial G}{\partial n_i} = \mu_i + \ln \frac{n_i}{n_v}, \tag{4} \]

\[ \frac{\partial^2 G}{\partial n_i^2} = -\frac{1}{n_v} \tag{5} \]

and

\[ \frac{\partial^2 G}{\partial n_i \partial n_j} = -\frac{1}{n_v} \tag{6} \]

For \( i = v+1, \ldots, v+s \)

\[ \frac{\partial G}{\partial n_i} = \mu_i + \ln \frac{n_i}{n_s}, \tag{7} \]

\[ \frac{\partial^2 G}{\partial n_i^2} = 1/n_i - 1/n_s \tag{8} \]

\[ \frac{\partial^2 G}{\partial n_i \partial n_{j \neq i}} = -1/n_s \tag{9} \]
and

\[
\text{For } i = v+s+1, \ldots, v+s+c
\]

\[
\frac{\partial G^k}{\partial n_i} = \mu_i^o
\]  

(10)

\[
\frac{\partial^2 G^k}{\partial n_i^2} = \frac{\partial^2 G^k}{\partial n_i \cdot \partial n_{i \neq 1}} = 0
\]  

(11)

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

\[
G^{k+1} = G^k + \sum_{i=1}^{v} \delta n_i \left[ \left( \mu_i^o + \xi n \frac{n_i}{n_v} \right) + \frac{1}{2} \sum_{i=1}^{v} \left[ \frac{\delta n_i^2}{n_i} - \frac{\xi n_i \xi n_v}{n_v} \right] \right]
\]

\[
+ \frac{1}{2} \sum_{i=v+1}^{v+s+c} \left[ \delta n_i^2 \frac{n_i}{n_i} - \frac{\xi n_i \xi n_s}{n_s} \right] + \sum_{i=v+s+1}^{v+s+c} \xi n_i \xi \nu_i
\]  

(12)

Since the atom balance must also be satisfied for the new solution estimate, \(n_{k+1}\), 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, \( \phi^{k+1} \), results when using Lagrange multipliers for each atom balance, \( \pi_j (j=1,2,\ldots,E) \).

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

(13)

The problem has now been reduced to minimizing \( \phi^{k+1} \) as:

\[
\frac{\partial \phi}{\partial n_i^{k+1}} = 0
\]

\[
= \mu_i^o + \xi n \frac{n_i}{n_v} + \frac{\xi n_i}{n_i} - \sum_{j=1}^{v+s} \frac{\xi n_j}{n_v} - \sum_{j=v+s+1}^{E} \pi_j a_{ji}
\]  

(15)

\[
= \mu_i^o + \xi n \frac{n_i}{n_s} + \frac{\xi n_i}{n_i} - \sum_{j=v+1}^{v+s} \frac{\xi n_j}{n_s} - \sum_{j=v+s+1}^{E} \pi_j a_{ji}
\]  

(16)

\[
= \mu_i^o - \sum_{j=1}^{E} \pi_j a_{ji}
\]  

for \( v+s+1 < i < v+s+c \)  

(17)
with the addition of Equation 2 rewritten as

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

we now have \(v+s+c+E\) linear equations (Equations 15 - 18) in the same number of unknowns (\(v+s+c\) \(\delta n_i\)'s and \(E\) \(\pi_j\)'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 \(\delta n_i\) yields

\[
\delta n_i = n_i \left[ \sum_{j=1}^{v} \frac{\delta n_j}{n_v} + \sum_{j=1}^{E} \pi_j a_{ji} \mu_i - \frac{n_i p}{n_v} \right] \quad \text{for } 1 < i < v \tag{19}
\]

and

\[
\delta n_i = n_i \left[ \sum_{j=v+1}^{v+s} \frac{\delta n_j}{n_s} + \sum_{j=1}^{E} \pi_j a_{ji} \mu_i - \frac{n_i p}{n_s} \right] \quad \text{for } v+1 < i < v+s \tag{20}
\]

Equations 19 and 20 contain only \(\delta n_i\) on the right hand side in terms of \(\sum_{j=1}^{v} \frac{\delta n_j}{n_v}\) 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 \(\delta n_i\) for \(1 < i < v+s\) can be eliminated in Equation 18 with the result

\[
\sum_{i=1}^{v} \pi_i \sum_{j=1}^{E} a_{ji} \delta n_i + u_v \sum_{i=1}^{v} a_{ji} n_i + u_s \sum_{i=v+1}^{v+s} a_{ji} n_i + \sum_{i=v+1}^{v+s} \sum_{i=1}^{E} a_{ji} \delta n_i =
\]

\[
b_j - b_j^k + \sum_{i=1}^{v} a_{ji} n_i \left( \mu_i + \frac{\pi_i n_i p}{n_v} \right) + \sum_{i=v+1}^{v+s} \left( \mu_i + \frac{\pi_i n_i p}{n_s} \right) a_{ji} n_i \quad \text{for } 1 < j < E
\]

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 \( v+s-2 \) variables were hand eliminated, the remaining two equations must be a linear combination of this set, for example

\[
\sum_{i=1}^{v+s} \delta n_i
\]

and

\[
\sum_{i=v+1}^{i=v+s} \delta n_i \text{ results in}
\]

\[
\sum_{x=1}^{V} \sum_{i=1}^{V} a_{x \xi} n_{i} - z_{x} u_{V} = \sum_{i=1}^{V} n_{i} \left( \frac{\mu_{i} + \gamma n_{i}}{n_{V}} \right)
\]

(22)

and

\[
\sum_{x=1}^{V} \sum_{i=v+1}^{i=v+s} a_{x \xi} n_{i} = \sum_{i=v+1}^{i=v+s} n_{i} \left( \frac{\mu_{i} + \gamma n_{i}}{n_{i}} \right)
\]

(23)

Thus the final set of linear equations to be solved includes Equations 17, 21 - 23 (\( E + c + 2 \) equations) for unknowns \( \pi_{x} \) (1 < \( x \) < \( E \)), \( \delta n_{i} \) (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 \( \pi_{x} \), \( u_{V} \), \( u_{s} \) and the \( C \) \( \delta n_{i} \)'s allows the computation of the remaining \( v+s \) \( \delta n_{i} \)'s with Equations 19 and 20. A new solution estimate can now be obtained as

\[
n_{i}^{k+1} = n_{i}^{k} + \delta n_{i}
\]

(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% \( \text{H}_2 \) 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

**RANALGORITHM FOR DETERMINING EQUILIBRIUM COMPOSITIONS**

**THE Ga/As/H SYSTEM WITH AN INERT PRESENT**  A TEST OF MCMPRC RAN.

**TEMPERATURE = 1273.2 K**
**PRESSURE = 0.1013250 PA**

<table>
<thead>
<tr>
<th>SPECIE SYMBOL</th>
<th>ENTHALPY OF FORMATION (KCAL/MOLE)</th>
<th>ENTROPY OF FORMATION (KCAL/MOLE-K)</th>
<th>IN-HEAT CAPACITY CORRELATION COEFFICIENTS</th>
<th>ICP = 1: CP = A0 + A1<em>P + A2</em>P<strong>2 + A3*P</strong>3</th>
<th>A0</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (V)</td>
<td>45.750</td>
<td>0.0454</td>
<td>-0.16990E-06</td>
<td>0.37080E-02</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0.21120E-03</td>
</tr>
<tr>
<td>A3 (V)</td>
<td>52.100</td>
<td>0.0434</td>
<td>-0.16350E-06</td>
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<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0.21800E-03</td>
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<tr>
<td>A3H (V)</td>
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<td>0.11120E-03</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0.21800E-03</td>
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<tr>
<td>A1+H2 (V)</td>
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<td></td>
<td></td>
<td>0.21800E-03</td>
</tr>
<tr>
<td>H2 (V)</td>
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<td>0.0360</td>
<td>-0.20990E-03</td>
<td>0.90020E-03</td>
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<tr>
<td>Ga-As (S)</td>
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</tr>
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</table>

The enthalpy and entropy of formation reference temperature and pressure are:

**T0 = 298.2 K**  **P0 = 101325.0 PA**

**MAXIMUM NUMBER OF ITERATIONS ALLOWED = 1000**

**CONVERGENCE CRITERION = 0.10000E-03**

**OUTPUT PARAMETER IDESG = 0**
RAND ALGORITHM FOR DETERMINING EQUILIBRIUM COMPOSITIONS
THE GA/AS/H SYSTEM WITH AN INERT PRESENT: A TEST OF MCMPEC RAND
TEMPERATURE = 1273 K
PRESSURE = 0.10133E 06 PA

INPUT DATA AND INITIAL COMPOSITION ESTIMATES

<table>
<thead>
<tr>
<th>SPECIE</th>
<th>INITIAL COMPOSITION</th>
<th>STAND. ABUNDANCE POTENTIAL</th>
<th>ELEMENTAL ABUNDANCE MATRIX</th>
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<tbody>
<tr>
<td></td>
<td>(O-MOLE)</td>
<td>(KCAL/MOLE)</td>
<td>H  O  CA  AC</td>
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<tr>
<td>AS</td>
<td>VAPO</td>
<td>0.000000E-01</td>
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<td>AJL</td>
<td>VAPO</td>
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<td>AJAL</td>
<td>VAPO</td>
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<td>AJH</td>
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<td>0.0  0  0  0</td>
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<tr>
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<tr>
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<td>CONCLUDED</td>
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</table>

TOTAL OROMOLE OF EACH ELEMENT FROM INPUT DATA
AND AS CALCULATED FROM THE INITIAL COMPOSITION ESTIMATES

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<th>INPUT DATA</th>
<th>CALCULATED</th>
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<tr>
<td>O 1000OE 00</td>
<td>0 1000OE 00</td>
</tr>
<tr>
<td>CA 0 1000OE 00</td>
<td>0 1000OE 00</td>
</tr>
<tr>
<td>AS 0 1000OE 00</td>
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</table>
A R AN ALGORITHM FOR DETERMINING EQUILIBRIUM COMPOSITIONS
THE CA/NH SYSTEM WITH AN INERT PRESENT: A TEST OF MCMPEC N AND
TEMPERATURE = 123 K PRESSURE = 0 101325 0 6 PA
EXECUTION DIAGNOSTICS
<table>
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<th>SPECIE</th>
<th>VAPOR</th>
<th>EQUILIBRIUM COMPOSITION</th>
<th>EQUILIBRIUM FRACTION</th>
<th>ESTIMATED COMPOSITION</th>
<th>ESTIMATED UNCERTAINTY</th>
<th>CHEMICAL POTENTIAL</th>
<th>ACTIVITY COEFFICIENT</th>
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<td>0.344</td>
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<td>0.125</td>
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</table>
A SET OF INDEPENDENT REACTION EQUATIONS FOR THIS SYSTEM IS AS FOLLOWS

\[ 1.00 \text{ AS}^{1} (V) \rightarrow 1.0 \times 200 \text{ AS}^{1} (V) \]
\[ 1.00 \text{ AS}^{1} (V) \rightarrow 1.0 \times 300 \text{ AS}^{1} (V) \]
\[ 1.00 \text{ AS}^{1} (V) \rightarrow 1.0 \times 400 \text{ AS}^{1} (V) \]
\[ 1.00 \text{ AS}^{1} (V) \rightarrow 1.0 \times 200 \text{ AS}^{1} (V) + (0.000 \text{ AS}^{1} \text{ AS}^{2} (V)) \]
\[ 1.00 \text{ H}^{1} (V) \rightarrow 1.0 \times 100 \text{ H}^{1} \text{ AS}^{1} (V) \]
\[ 1.00 \text{ H}^{1} (V) \rightarrow 1.0 \times 200 \text{ H}^{1} \text{ AS}^{1} (V) \]
\[ 1.00 \text{ H}^{1} (V) \rightarrow 1.0 \times 100 \text{ H}^{1} \text{ AS}^{1} (V) \]
\[ 1.00 \text{ H}^{1} (V) \rightarrow 1.0 \times 200 \text{ H}^{1} \text{ AS}^{1} (V) \]
\[ 1.00 \text{ GA}^{1} (V) \rightarrow 1.0 \times 100 \text{ GA}^{1} \text{ AS}^{1} (V) \]
\[ 1.00 \text{ H}^{1} (V) \rightarrow 1.0 \times 100 \text{ H}^{1} \text{ GA}^{1} (V) \]
# EQUILIBRIUM CONSTANTS FOR THE INDEPENDENT REACTIONS

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<th>REACTION PRODUCT</th>
<th>ΔG (kJ/mol)</th>
<th>ΔG FROM PREDICTED COMPOSITION</th>
<th>EQUILIBRIUM CONSTANT</th>
<th>EQUILIBRIUM CONSTANT</th>
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<td>0.7942E 10</td>
<td>0.7942E 10</td>
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<td>0.1710E 16</td>
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<td>0.7129E 12</td>
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References

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

B.1 Introduction

B.2 The Main Program

B.2.1 Array Dimensions, Expandability and Initialization
B.2.2 Data Input
B.2.3 Preparation for the Iterative Solution
B.2.4 Iterative Solution for the Equilibrium Composition
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B.4.2 ESTMTE
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B.6 Example Calculation: The Ga/As system source zone
Appendix B


B.1 Introduction

The calculation of chemical equilibria 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

\[ S_i = \sum_{j=1}^{E} \nu_{ij} S_j^b \]  \hspace{1cm} (1)

where:  
- \( S_i \) = specie being formed  
- \( S_j^b \) = basis specie in the system  
- \( \nu_{ij} \) = 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 variables 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.
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 dimensioned 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 accommodate 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 accommodate.

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.STGIC

Dimension arrays and set limits for the maximum number of species and elements present in the system.

Suppress printing of overflow, underflow, divide by zero and exponential argument error messages (subroutine ERRSET).

Read: 1) number of elements, species temperature and pressure
2) thermophysical data for the vapor, solution and pure condensed phase species
5) maximum number of iterations allowed and computational options

Read the initial compositions in the vapor, solution and pure condensed phases.
Write-out the input state if IWRAP>2.

Calculate the standard state chemical potentials (subroutine STSTCP).

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).
Write out the temperature pressure and composition estimate to the wrap-up files (subroutine WRAPUP).

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 species (subroutine ACTCOF).

Calculate the equilibrium constants for the formation reactions from the current composition estimate (subroutine CALCQ).

Has the solution converged?

Yes

No
Make adjustments to the formation reaction extents in order to obtain a better estimate of the equilibrium composition (subroutine ADJEXT).

Calculate the convergence force (subroutine CNVFRC).

Update the molar amounts of each species using the adjusted reaction extents (subroutine CORMOL).

Maximum number of iterations exceeded?

Yes

Write out a message to indicate that the solution did not converge.

No

Calculate the Gibbs Free Energy of the system (subroutine Gibbs).
Calculate the molar 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 TOTS1 and RATIO).

Write out the results if IWRAP<2.

Yes

IWRAP>0

Write out the results to the wrap-up file (subroutine WRAPUP)

No

(A)

Yes

Temp. or Pressure loop?

No

(B)

Yes

composition loop?

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 CALCO 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 species name and the enthalpy and entropy of formation at temperature $T_0$ and pressure $P_0$ for this species. 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 species are on the third record. Records $3V+1$ to $3V+3$ contain this same information for an inert species in the vapor phase. The inert species 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 species in the solution phase and each pure condensed phase.
Table B.1  
Input Data Set for *MC*PEC.STOIC

<table>
<thead>
<tr>
<th>Record</th>
<th>Comments</th>
<th>Format</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title (1), ..., TITLE (20)</td>
<td>80 Character Title</td>
<td>20A4</td>
</tr>
<tr>
<td>E, V, S, C, T, P, T0, Po</td>
<td></td>
<td>4I5, 4F10.0</td>
</tr>
<tr>
<td>ELMNT (1), ELMNT (2) ..., ELMNT (E)</td>
<td>Element Symbols</td>
<td>13 (IX, A2)</td>
</tr>
<tr>
<td>SPECIE (I,K), DMO(I), DSO(I)</td>
<td></td>
<td>3A4, 2E12.5</td>
</tr>
<tr>
<td>AO(I), AI(I), A2(I), A3(I), ICP(I)</td>
<td>Each vapor phase specie</td>
<td>4E12.5, I2</td>
</tr>
<tr>
<td>A(I,1), A(I,2) ..., A(I,E)</td>
<td></td>
<td>13(F5.0, IX)</td>
</tr>
<tr>
<td>Inert(K), DHOZ, DSOZ</td>
<td></td>
<td>3A4, 12E12.5</td>
</tr>
<tr>
<td>AOZ, AIZ, A2Z, A3Z, ICPZ</td>
<td>Inert vapor phase specie</td>
<td>4E12.5, I2</td>
</tr>
<tr>
<td>IDUMMY</td>
<td></td>
<td>13(F5.0, IX)</td>
</tr>
<tr>
<td>SPECIE(I,K), DMO(I), DSO(I)</td>
<td></td>
<td>3A4, 12E12.5</td>
</tr>
<tr>
<td>AO(I), AI(I), A2(I), A3(I), ICP(I)</td>
<td>Each solution phase specie</td>
<td>4E12.5, I2</td>
</tr>
<tr>
<td>A(I,1), A(I,2) ..., A(I,E)</td>
<td></td>
<td>13(F5.0, IX)</td>
</tr>
<tr>
<td>SPECIE(I,K), A2(I), A3(I), ICP(I)</td>
<td></td>
<td>3A4, 12E12.5</td>
</tr>
<tr>
<td>AO(I), AI(I), A2(I), A3(I), ICP(I)</td>
<td>Each pure condensed phase</td>
<td>4E12.5, I2</td>
</tr>
<tr>
<td>A(I,1), A(I,2) ..., A(I,E)</td>
<td></td>
<td>13(F5.0, IX)</td>
</tr>
<tr>
<td>NERUG, IOPT, ISS, IWRAP, MAXIT, MMAX, CNVG, TINC, PINC, RLXMIN</td>
<td></td>
<td>6I5, 4F10.0</td>
</tr>
<tr>
<td>TOTMV</td>
<td></td>
<td>E12.5</td>
</tr>
<tr>
<td>FRAC(1), FRAC(2) ..., FRAC(V), FRACZ</td>
<td></td>
<td>6E12.5</td>
</tr>
<tr>
<td>TOTMS</td>
<td></td>
<td>E12.5</td>
</tr>
<tr>
<td>FRAC(V+1), FRAC(V+2) ..., FRAC(V+S)</td>
<td></td>
<td>6E12.5</td>
</tr>
<tr>
<td>IXSCOR, AXS, BXS</td>
<td></td>
<td>15, 2E12.5</td>
</tr>
<tr>
<td>TOTMC(V+S+1) ..., TOTMC(V+S+C)</td>
<td></td>
<td>6E12.5</td>
</tr>
</tbody>
</table>
Table B.2

Description of Input Variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE (20)</td>
<td>80 Character data set title</td>
</tr>
<tr>
<td>E</td>
<td>Number of elements (E ≤ 13)</td>
</tr>
<tr>
<td>V</td>
<td>Number of vapor species excluding the inert</td>
</tr>
<tr>
<td>S</td>
<td>Number of solution species</td>
</tr>
<tr>
<td>C</td>
<td>Number of pure condensed phases</td>
</tr>
<tr>
<td>T</td>
<td>System Temperature (K)</td>
</tr>
<tr>
<td>P</td>
<td>System Pressure (Pa)</td>
</tr>
<tr>
<td>TO</td>
<td>Reference Temperature for $\Delta H$ and $\Delta S$ formation</td>
</tr>
<tr>
<td>PO</td>
<td>Reference Pressure for $\Delta H$ and $\Delta S$ formation</td>
</tr>
</tbody>
</table>

| ELMNT (13) | 2 character symbol for each element (right justified) |
| SPECIE (50, 3) | 12 character symbol for each species |
| A (50, 13) | Elemental abundance matrix |
| DHO (50) | Enthalpy of formation (kcal/g-mole) for each species at Temperature TO and Pressure PO. |
| DSO (50) | Entropy of formation (kcal/g-mole-K) for each species 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

<table>
<thead>
<tr>
<th>ICP (1)</th>
<th>A2 (1)</th>
<th>A3 (1)</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>kcal-K/g-mole</td>
<td>kcal/g-mole-K$^2$n(k)</td>
<td>AO+A1<em>T+A2</em>T$^2$+A3*T$^3$</td>
</tr>
<tr>
<td>1</td>
<td>kcal/g-mole-K$^3$</td>
<td>kcal/g-mole-K$^4$</td>
<td>AO+A1<em>T+A2</em>T$^2$+A3*T$^3$</td>
</tr>
</tbody>
</table>
INERT(3)  12 Character name for inert vapor species

OHOZ  Inert Specie enthalpy of formation

DSOZ  Inert Specie entropy of formation

A0Z  Inert Specie heat capacity correlation parameter
A1Z
A2Z
A3Z
ICPZ

IDEBUG  Debugging Output parameter
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 matrices and vectors D, DPRME, KEQ and Q for each iteration

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

ISS  Source Zone Steady State Option Parameter
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.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IWRAP</td>
<td>Data output write parameter</td>
</tr>
<tr>
<td>0</td>
<td>Writes input data, execution diagnostics and results to printer</td>
</tr>
<tr>
<td>1</td>
<td>(IWRAP) function plus writes-out a concise wrap-up file</td>
</tr>
<tr>
<td>2</td>
<td>No printer output, just a wrap-up file</td>
</tr>
<tr>
<td>3</td>
<td>Writes a result to the printer</td>
</tr>
<tr>
<td>MAXIT</td>
<td>Maximum number of iterations allowed for the equilibrium composition to converge</td>
</tr>
<tr>
<td>NMAX</td>
<td>Maximum number of loops allowed for the IOP7 parameter</td>
</tr>
<tr>
<td>CNVG</td>
<td>Convergence criterion</td>
</tr>
<tr>
<td>TINC</td>
<td>Temperature increment for each loop if IOP1=1</td>
</tr>
<tr>
<td>PINC</td>
<td>Pressure increment for each loop if IOP1=2</td>
</tr>
<tr>
<td>TOTMV</td>
<td>Total moles in the vapor phase</td>
</tr>
<tr>
<td>TOTMS</td>
<td>Total moles in the solution phase</td>
</tr>
<tr>
<td>TOTMC(I)</td>
<td>Total moles in each pure condensed phase</td>
</tr>
<tr>
<td>FRAC(I)</td>
<td>Mol fraction of specie I in vapor (I&lt;K(V)</td>
</tr>
<tr>
<td>FRACZ</td>
<td>Mol fraction of inert in vapor</td>
</tr>
<tr>
<td>IXSCOR</td>
<td>Activity coefficient correlation parameter for the solution phase</td>
</tr>
<tr>
<td>0</td>
<td>Ideal solution</td>
</tr>
<tr>
<td>1</td>
<td>Binary single solution</td>
</tr>
<tr>
<td>2</td>
<td>Henry's law</td>
</tr>
<tr>
<td>AXS, BXS</td>
<td>Activity coefficient correlation coefficient for the solution phase</td>
</tr>
<tr>
<td>0</td>
<td>Ideal solution</td>
</tr>
<tr>
<td>1</td>
<td>( G = (AXS + BXS \times T) \times X1 \times X2 )</td>
</tr>
<tr>
<td>2</td>
<td>( H = AXS \times \exp(BXS/T) )</td>
</tr>
<tr>
<td>PLYMIN</td>
<td>Minimum value of the convergence force</td>
</tr>
</tbody>
</table>
Following the data for each individual specie is a record describing the various options available and numerical methods information. Parameter IDBUG 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. \textit{MAX} 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.

\textit{MAXIT} sets the maximum number of iterations to be performed for calculating the equilibrium compositions. Typically \textit{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 \textit{CNVG}. A typical value for \textit{CNVG} is \( 10^{-9} \).

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 enthalpy of formation, entropy of formation and heat capacity correlation data are then written to SWRT 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 ESTMT 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 ICHNG 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 forcing is calculated in subroutine CNVFRC and the molar amounts of each species 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 463 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 (IOPF>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 (Ni < 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 species 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 iterative procedure to continue over unusually intricate contours on the Gibbs Free Energy surface. If the solution has not diverged, i.e. the last iteration 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

1 C MCNPSEC...STOIC ... MULTICOMP...ANT MULTIPHASE EQUILIBRIUM : DE
2 C STOICICHEMICAL FORMULATION
3 C
4 C
5 DIMENSION A(5,13),ACCEF(90),AO(50),AI(50),AJ(50),AI2(50),A3(50),
6 & B(13),SCALC(13),CHMFT(50),CCEF(6),
7 & D(13,13),DINV(13,13),DG(50),D00(50),DS0(50),
8 & DZETA(50),FAC(50),FRAQ(50),GAM(50),
9 & ICP(50),IDBAS(13),INEX(50),INEAT(3),U(50),STOCP(50),
10 & TOTMC(50),TMA(50),
11 INTEGER 8SPCE(50,5),ISPCE(50,5),PHASE(50,3),SPECIE(50,3),
12 & STRING(5,4),TITLE(20),V,S,C,E,VPSL,VPSL1,VPSL2,VSC,VSCF,
13 & BQUES(50),QUEST(50),QUEST1? , QUEST2?? /
14 & ELMNT(13),/13" */VAPC(3)/" V"/AFC'/* F" ,
15 & SCLN(3)/"SCL'"UTI'"CN"/CCND(3)/"CCN'"CEN'"SDE'/,
16 & RPSPC/* */AFAC*/<"/RPL*/" */SSPS/* */F,
17 & BLMKS/* */F/P/*/*
18 REAL KEQ(50),NV,NS,LAMDA
19 REAL*8 DD,DINV,DKA,N(50),DESTN(50),NTEMP(50),DPRME(13,13),OZETA
20 C
21 C A(I,J) : ELEMENTAL ABUNDANCE MATRIX
22 C B(I,J) : TOTAL NUMBER OF GRAM-MOLES CF ELEMENT J
23 C DH0(I) : ENTHALPY CF FORMATION CF SPECIES I
24 C DS0(I) : ENTROPY CF FORMATION CF SPECIES I
25 C STOCP(I) : STANDARD CHEMICAL POTENTIAL CF SPECIES I
26 C
27 C **************** HEAT CAPACITY CF RELATIONS ****************
28 C ICP(I)=0 : CP(I) = AO(I) + AI(I)*T + A2(I)*T**2 + A3(I)*T**3
29 C ICP(I)=1 : CP(I) = AO(I) + A1(I)*T + A2(I)*T**2 + A3(I)*T**3
30 C
31 C
32 C IRD=5
33 & IWT=6
34 & IFILE=2
35 & IDIM1=50
36 & IDIM2=13
37 & FRZIN=0.0
38 & DHO2=0.0
39 & DSQ2=0.0
40 & AJZ=0.0
41 & AZ=0.0
42 & A2Z=0.0
43 & A3Z=0.0
44 & TOTNV=0.0
45 C
46 C SUPPRESS PRINTING OF OVERFLOW, UNDERFLOW, DIVIDE BY ZERO
47 C AND EXPONENTIAL ARGUMENT ERROR MESSAGES
48 C
49 C CALL ERFSET (207,0,-1.0,0,209)
50 C CALL ERFSET (252,-1.0,0,253)
51 C
52 C READ TITLE
53 C
54 C READ (IRD,5) (TITLE(K),K=1,20)
55  S FORMAT(2344)
56 C
57 C NUMBER OF ELEMENTS, VAPOR SPECIES, SOLUTION SPECIES,
58 C CONDENSED PURE PHASES, SYSTEM TEMPERATURE (K) AND PRESSURE (PA)
59 C
60 READ(IRD,10) EL,V,3,C,T,F,T,P0
61 10 FORMAT(4I5,4F12.0)
62 VPI=V+1
63 VPS=V+S
64 VPSP1=V+S+1
65 VSC=V+S+C
66 VSCC=V+S+C+C
67 C
68 C READ ELEMENTS
69 C
70 READ(IRD,15) (ELWNT(J),J=1,5)
71 15 FORMAT(13(1X,A2))
72 C
73 C VAPOR SPECIES INFORMATION
74 C
75 IF(V.EQ.0) GO TO 118
76 DO 110 I=1,V
77 READ(IRD,20) (SPECIE(I,K),K=1,3),CH0(I),DS0(I)
78 READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
79 REAL(IRD,22) (A(I,J),J=1,13)
80 20 FORMAT(3A4,2E12.5)
81 21 FORMAT(4E12.5,15)
82 22 FORMAT(13(F5.2,1X))
83 DO 110 J=1,3
84 PHASE(I,J)=VAPCR(J)
85 110 CONTINUE
86 C
87 C INERT SPECIES
88 C
89 READ(IRD,20) (INERT(I),K=1,3),CH0Z,DS0Z
90 READ(IRD,21) A0Z,A1Z,A2Z,A3Z,ICPZ
91 READ(IRD,22) DUMMY
92 118 CONTINUE
93 C
94 C SOLUTION SPECIES INFORMATION
95 C
96 IF(S.EQ.0) GO TO 125
97 DC 120 I=VP1,VPS
98 READ(IRD,20) (SPECIE(I,K),K=1,3),CH0(I),DS0(I)
99 READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
100 READ(IRD,22) (A(I,J),J=1,13)
101 DC 120 J=1,3
102 PHASE(I,J)=SOLN(I)
103 120 CONTINUE
104 125 CONTINUE
105 C
106 C CONDENSED PHASE DATA
107 C
108 IF(C.EQ.0) GO TO 135
DO 130 I=VPSPI,VSC
READ(IR0,20) (SPECIE(I,K),K=1,3),DHJ(I),D3J(I)
READ(IFO,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
READ(IR0,22) (A(I,J),J=1,13)
FRAC(I)=1.0
FRAC(I)=1.0
DO 130 J=1,3
PHASE(I,J)=CONC(J)
CONTINUE
CONTINUE

C MAXIMUM NUMBER OF ITERATIONS, CONVERGENCE CRITERION AND OPTIONS
READ(IR0,136) IMAX,ITLAP,MAIP,MAXIT,MAXN,CONV,TPAP,PINC,
& RLXMIN
136 FORMAT(15,4F10.4)
IF(ITLAP.EQ.3) IFILE=1*RT

C SET THE LOOP LIMITS FOR THE TEMPERATURE, PRESSURE AND COMPOSITION
LOCPS. THE COMPOSITION LOOP STARTS HERE.

NCMP=1
NTP=1
IF(ICPT.EQ.1.OR.ICPT.EQ.2) NTP=NMAX
IF(ICPT.EQ.3) NCMP=NMAX
DO 2000 ICMP=1,NCMP
INPUT=0

C TOTAL NUMBER OF MOLES OF VAPOR AND MOLE FRACTIONS
IF(V.EQ.0) GO TO 138
READ(IR0,137) TOTMV
READ(IR0,137) (FRACIN(I),I=1,V),FRCZ1N
137 FORMAT(6E225)

C TOTAL NUMBER OF MGLES OF SOLUTION SPECIES, MOLE FRACTIONS
ASIC EXCESS FREE ENERGY CORRELATION PARAMETERS

138 CONTINUE
IF(S.EQ.0) GO TO 140
READ(IR0,137) TOTMS
READ(IR0,137) (FRACIN(I),I=VFI,VPS)
READ(IR0,139) IXSCOR,AXS,EXS
139 FORMAT(15,2E12.5)

C TOTAL NUMBER OF MGLES IN PURE CONDENSED PHASES
IF(C.EQ.0) GO TO 142
READ(IR0,137) (TOMC(I),I=VPSPI,VSC)
142 CONTINUE

C SAVE THE ORIGINAL SPECIE ORDER SC THE PROBLEM
CAN BE PLACED IN THIS ORDER AFTER THE ITERATIVE PROCEDURE
DO 165 I=1,VSC
DO 165 K=1,3
ISPEC(I,K)=SPECIE(I,K)
CONTINUE
IF (ICMP.GT.1.OR.IWRAP.EQ.1) GC TC 187
C WRITE-OUT SOME OF THE INPUT DATA
IPAGE=1
WRITE(IWRT,430) (TITLE(K),K=1,20),IPAGE
WRITE(IWRT,170) T,P
IF (IWRAP.GT.1) GC TC 187
WRITE(IWRT,170)
FORMAT('**HEAT CAPACITY CORRELATION COEFFICIENTS**
**ENTHALPY CORRELATION COEFFICIENTS**
**REFERENCE TEMPERATURE AND PRESSURE ARE 298.15 K**
**MAXIMUM NUMBER OF ITERATIONS *15**
**CONVERGENCE CRITERION *1.0E-12**
**INPUT PARAMETER ICEBUG = *0**
**2X**
**EXCESS FREE ENERGIE CORRELATION DATA :
**2X**
**AT EQUILIBRIUM WITH THE III-V STEICHIOMETRIC SOLID**
CONTINUE
THE TEMPERATURE AND PRESSURE LCP'S BEGIN HERE
DC 2030 IPT=1,NTP
IF (IPT.EQ.2.AND.ITP.GT.1) TAT+TINC
IF (IPT.EQ.2.AND.ITP.GT.1) PEP+PINC
CALCULATE THE STANDARD STATE CHEMICAL POTENTIALS
AND AN INITIAL ESTIMATE OF THE EQUILIBRIUM COMPOSITIONS
B23

217 C
218 CALL STSCP(AJ,A1,A2,A3,AQ1,AL1,AL2,A37,A3L,CH1,CH2,H2Z,SO2,STSCP, I)
219 & STSCP(1C=1CZ,T,T,1D11,T',Y,3,C)
220 IF(1TP,GT,1.0)IS5=1.0) GC TC 195
221 GC 19J 1=1.VPS
222 FRAC(I)=FRACIN(I)
223 CONTINUE
224 FRACZ=FRACIN
225 CALL ESTMDT(JUTMZ,TCTMS,TCTMC,FRAC,FRACZ,2V,
226 & IDIM1,V,SC)
227 CONTINUE
228 C
229 C SOURCE ZONE STEADY-STATE LIQUID COMPOSITION MODEL
230 C
231 IF(IS5,GT,0) CALL STEADY(SPECIE,A,STSCP,ELMAT,X11,T,T,TO,V,SC.
232 & IDIM1,IDIM2,IS5,IRT)
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(I,J)=BCALC(J)
242 CONTINUE
243 IF(I*RAP,GT,1) GC TC 476
244 IF(I*RAP,LT,1) GC TC 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 C IPAGE=IPAGE+1
250 WRITE(IWRT,430) (TITLE(K),K=1,20),IPAGE
251 400 FORMAT('1',I10,'/','0/','T34','STCICICEMTRIC FORMULATION FOR DETERMINING',.
252 & ' EQUILIBRIUM COMPOSITIONS','/','0/','T30,2044,T120,
253 & ','PAGE','I2',
254 WRITE(IWRT,417) T,P
255 410 FORMAT('O','T43','TEMPERATURE = '+F6.1,' K','5X','PRESSURE = '+E12.5,
256 & ',PA')
257 WRITE(IWRT,420) (ELNMT(K),K=1,13)
258 420 FORMAT('O','T48','INPUT DATA AND INITIAL COMPOSITION ESTIMATES',.
259 & ',',0/','T29','INITIAL','T43','STANDARD','/','1X,T27','COMPOSITION',.
260 & ',',T43,'CHEMICAL','/','1X,T4','SPECIE','T29','ESTIMATE','T42','POTENTIAL',.
261 & ',',T72,'ELEMENTAL ABUNDANCE MATRIX','/','1X,T4','SYMBOL','T17','PHASE',.
262 & ',',T28,'(G-MOLE)╝','T40','(KCAL/G-MOLE)╝','T55,13(A2,4X),/','**',.
263 & ',12(                                                                       )','T15,5(                                                                       )','T25,14(                                                                       )','T40,13(                                                                       )','T55,7(                                                                       )
264 DO 440 I=1,VSC
265 WRITE(IWRT,420) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),IM1
266 & STSCP(I)*A(I,J),J=1,E
267 IF(I*20>V) WRITE(IWRT,430) (INPUT(K),K=1,3),(PHASE(I,K),K=1,3),
268 & JV,STSCP/
269 430 FORMAT('1X,3A4,T15,3A,T25,C14,T42,FI,3,55,13(6F7.1'))
270 CONTINUE
IF(ISGEJ.0) WRITE(1MT,445) XI1
DETERMINE THE OPTIMUM SET OF PHASES.


CALL DQUSD(IN, IC, PC, D, Q, T, I, M, A, T, 2, P).

IF (IC > 2) GO TO 504.

IF (IC = 2) GO TO 500.

CALL IPVEC(IDXAS, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2).

CALL FMAT(A, ICIM1, ICIM2, VSC, C, F, T).

CALL FMAT(D, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2).

CALL OPMAT(DPRL, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2).

CONTINUE

CALCULATE THE STOICHIOMETRIC COEFFICIENTS AND THE EQUILIBRIUM CONSTANTS.

CALL EQCON(A, ICIM1, ICIM2, VSC, C, F, T, 1).

CALL STEPC(IDXAS, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2).

IF (IC > 3) GO TO 504.

CALL IPVEC(IDXAS, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2).

CALL FMAT(G, ICIM1, ICIM2, VSC, C, F, T, 1).

CALL FMAT(N, ICIM1, ICIM2, VSC, C, F, T, 1).

CALL FVVEC(KN, ICIM1, VSC, C, F, T, 1).

CONTINUE

CALCULATE THE ACTIVITY COEFFICIENTS.

CALL ACTCOF(FRAZ, ACCEF, SPECIES, SPECIES, INDEX, ICIM1, RELMAX, W, V, C, T, 1).

CALL STEPC(IDXAS, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2).

CALL EQCON(A, ICIM1, ICIM2, VSC, C, F, T, 1).

CALL STEPC(IDXAS, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2, ICIM2).

CALCULATE THE EQUILIBRIUM CONSTANTS FROM THE CURRENT COMPOSITION.


CALCULATE THE CMEM BETWEEN THE EQUILIBRIUM CONSTANTS.

CALCULATE BY THE COMPOSITIONS AND THE EQUILIBRIUM CONSTANTS.

CALCULATE FROM THE SIGMA FREE ENERGY CHANGE.

RELMAX = 0.

DO 590 J = 1, VSC.

DO 567 K = 1, VSC.

QUS(1) = BLKKS.

DO 570 J = 1, E.

IF (K = 0, J = 0) GO TO 590.

CONTINUE

570 CONTINUE

RELREL = (QUS(1) - QUS(1)) / QUS(1).

ASSIGN "?" TO QUS(1) IF THE CONVERGENCE CRITERION IS NOT MET.

ASSIGN "?" TO QUS(1) IF THERE IS LESS THAN THE SIGNIFICANT FIG.

IF (ABS(RELREL) < 0.0001) QUS(1) = QUS(1).

IF (ABS(RELREL) > 0.0001) QUS(1) = QUS(1).

IF (ABS(RELREL) > 0.0001) QUS(1) = QUS(1).

END
590 CONTINUE
381 C KEEP THE BEST ESTIMATE TO THE EQUILIBRIUM SOLUTION
382 C IN CASE THE NUMERICAL PROCEDURE DIVERGES
383 C
384 C IF(ITER=0T.1ANU.RELMAX GT.VESTCVG) GO TO 594
385 BVESTCVG=RELMAX
386 IF(ITER=ITZ) GO TO 598
387 DO 593 IBEST=1,VSC
388 QUES(IBEST)=QUES(IBEST)
389 BESTN(IBEST)=N(IBEST)
390 593 CONTINUE
391 594 CONTINUE
392 IF(RELMAX.LE.CVNGV) GO TO 610
393 IF(IEEEECG.EQ.2) CALL PVSC(FRAC,ICIM1,VSC,EPFPAC ,INFT)
394 IF(IEEEECG.EQ.1) CALL PVSC(Q,ICIM1,VSC,EP2C ,INFT)
395 IF(ITER.EQ.MAXIT) GO TO 595
396 595 IF(ITER.LT.MAXIT) GO TO 597
397 C MAKE ADJUSTMENTS TO THE EXTENTS OF REACTION
398 C TO THE EQUILIBRIUM SOLUTION FROM VECTOR BESTN INTO N.
399 C
400 CALL ADJEXT(N,KEQ,G,GNU,DZETA,IDXAS,COND,PHASE,ICIM1,ICIM2,
401 & VSC,C,E,IVRT)
402 CALL CNVFHC(N,TEMP,STCCP,ACQEF,DZETA,GNU,IDXAS,VAPOR,COND,
403 & SCLN,PHASE,ZV,RT,P,P0,FLXMIN,LAGCMV,ICIM1,ICIM2,VSC,C,E)
404 CALL CNVLIL(N,DZETA,GNU,IDXAS,ICIM1,ICIM2,LAGCMV,VSC,C,E)
405 596 IF(ITER.LT.MAXIT) GO TO 597
406 C IF THE SOLUTION DID NOT CONVERGE TRANSFER THE BEST ESTIMATE
407 C TO THE EQUILIBRIUM SOLUTION FROM VECTOR BESTN INTO N.
408 C
409 C DO 596 IBEST=1,VSC
410 QUES(IBEST)=QUES(IBEST)
411 N(IBEST)=BESTN(IBEST)
412 596 CONTINUE
413 597 CONTINUE
414 CALL CALCO(NU,N,ACQEF,FRAC,PHASE,VAPOR,SCLN,IDXAS,IVRT)
415 & ZV,FRACZ,PO,V,SC,E,ICIM1,ICIM2 ,INFT)
416 IF(CEBUG.EQ.0) GO TO 600
417 CALL GIBE(N,STCCP,STCPZ,ACQEF,FRAC,ZV,FRACZ,COND,SCLN,PHASE,
418 & RT,P,P0,ICIM1,VSC,C,E)
419 CALL GEBUS(N,DZETA,VSC,ICIM1,ITER,LAMBDA,C,E,RELMAX,IVRT)
420 600 CONTINUE
421 601 CONTINUE
422 634 CONTINUE
423 IF(IW=AP.LT.3) WRITE(IWFT,605)MAXIT,RELMAX,VESTCVG,ITACT
424 605 FORMAT('**** Iteration for equilibrium composition',
425 & '**** Did not converge *****,
426 & '**** After',IT,' Iterations. RELMAX =',RELMAX,E12.5','
427 & '**** Last CONV. RC=1.E-12,E-5 AT Iteration',IT)
428 611 CONTINUE
429 CALL GIBE(N,STCCP,STCPZ,ACQEF,FRAC,ZV,FRACZ,COND,SCLN,PHASE,
430 & RT,P,P0,ICIM1,VSC,C,E)
431 C CALCULATE THE GRAY-VALUES OF EACH ELEMENT AFTER THE ITERATION:
432 C
DO 800 J=1,5.

B3CALC(J)= J.

DO 700 I=1,VSC

B3CALC(J)=B3CALC(J)*=(I,J)*N(I)

700 CONTINUE

C CALCULATE THE CHEMICAL POTENTIAL OF EACH SPECIE

C

DO 800 I=1,VSC

PPJ=1.*

IF(FACT(J)*EQ.VAFCH(I)) FPD=F/PD

ARG=FRAC(I)*ACOF(I)+PPD

CHMPT(J)=AT*(STDCPZ*ACLEG(ARG))

800 CONTINUE

ARG=1.*

IF(FRAZ*GT.J.*J) AGF=FRAZ*P/PD

CHMPT=RT*(STDCPZ*ACLEG(ARG))

DO 810 I=1.VSC

DO 810 K=1,3

B3PCE(I,K)=SPECIE(I,K)

810 CONTINUE

C PUT THE MATRICES AND VECTORS INTO THE ORIGINAL PROBLEM STATEMENT CODE

C

CALL CLSME(ISPEC, SPECIE, PHESE, A, STCPZ, J,AT, RT, PP, ID1, ID2, ID3, ID4, ID5)

CALC, CHMPT, ACLEG, FRAC, QUES, DG, KEQ, ICNP, IDIM1, IDIM2, F, VSC, EIMRT

CALL TRED1(A, ELMNT, FRAC, N, SITCT, SIMF, ACTNS, T, P, IDIM1, IDIM2, V, E)

CALL RATCT(A, ELMNT, FRAC, N, STCPZ, ACTGAS, ACTINS, ACTGAS, ACTNS, ACLEG)

& RAT1, GA, INFTR, T, P, IDIM1, IDIM2, V, E

IF(I*RAP*GT.1) GE TC 571

C WRITE OUT THE RESULTS

C

IF(ACME=IPAGE+1

WRITE(I*RT,40) (TITLE(K),K=1,20), IPAGE

WRITE(I*RT,41) T,P

WRITE(I*RT,30) ITBST, CFF, 2STCVG, CAVG, LAMDA

900 FORMAT(10*'/', 1X, T45, 'EQUILIBRIUM COMPOSITIONS AFTER * 9S.

6* ITERATIONS*/', T45, 'SYSTEM GIVES FREE ENERGY = ', T45, '+

6* (KCAL/)

KCOEF.*KRELATIVE ERROR = * E12.5, SX, 'CONVERGENCE CRITERION = '

E12.5, SX, 'RELAXATION PARAMETER AT LAST ITERATION = *, E12.5, SX

E12.5, SX, 'COMPOSITION *', T45, 'CHEMICAL

E12.5, SX, 'SPECIES *', T45, 'LATENCY *', T45, 'COMPOSITION *', T45

E12.5, SX, 'UNCERTAINTY *', T45, 'POSSIBILITY *', T45

E12.5, SX, 'EQUILIBRIUM *', T45, 'POSSIBILITY *', T45

E12.5, SX, 'EQUILIBRIUM *', T45, 'POSSIBILITY ', T45

E12.5, SX, 'EQUILIBRIUM *', T45, 'POSSIBILITY ', T45

E12.5, SX, 'EQUILIBRIUM *', T45, 'POSSIBILITY ', T45
B28

497 IF(14(.E1,P7,.X9,14(.E1,P7,.X9,12(.E1)))

498 ZETAT=0.0

499 ZACT=1.0

500 DQ 920 1=1,VSC

501 WRITE(IWTR,910) (SPEC(I,I,K),K=1,2), (PM(I,P,K),K=1,2), F(I)

502 & (N(I),Z2:14(I),CH&RT(I),ACTRSS(I))

503 IF(1,EG,V) WRITE(IWTR,916) (INERT(K),K=1,2), (PM(I,P,K),K=1,2)

504 & (N(I),Z2:14(I),CH&RT(I),ACTRSS(I))

505 910 FORMAT(I1,X,3A4,T15,3A3,T24,E12.5,T37,E14/7,T53,E14/7,T92,E12.5)

506 & (E10,.E12.5)

507 920 CONTINUE

508 IF(1,ES,GT,0) WRITE(IWTR,945) XIII

509 WRITE(IWTR,930) SIVF

510 & *VAPOR PHASE = *912.5)

511 & *VAPOR PHASE = *912.5)

512 WRITE(IWTR,940) RIVIV

513 940 FORMAT(*91,TS0,*III/IVSTATIC IN THE VAPOR PHASE = *912.5)

514 WRITE(IWTR,950)

515 950 FORMAT(*91,TS0,*III/IV TOTAL GRAM-MOLES OF EACH ELEMENT FROM INP."

516 & INPUT DATA*91,TS0,*AND AS CALCULATED FROM THE EQUILIBRIUM."

517 & *COMPOSITIONS*91,TS0,*INPUT DATA*91,TS0,*CALCULATED*91,TS0,*EX))

518 & *CALCULATED*91,TS0,*EX))

519 NPRT=7/4

520 NCHK=NPRT+4

521 IF(NCHK,NE,2) NPRT=NPRT+1

522 ISTAT=1

523 DC 970 K=1,NPRT

524 NEND=ISTRT+3

525 IF(NEND,GT,2) NEND=3

526 WRITE(IWTR,960) ((UNIV(J),E(J),CALC(J),J=,1ST-7,N,12)

527 ISTAT=NEND+1

528 963 CONTINUE

529 IF(IWAP,GT,2) CALL AND congratulations TITLESPECIC K=1,20), IMAGE

530 WRITE(IWTR,961)

531 WRITE(IWTR,980)

532 980 FORMAT(*91,TS4,*A SET OF INDEPENDENT REACTION EQUATIONS FOR *

533 & *THIS SYSTEM IS AS FOLLOWS:*91,TS4*)

534 IF(IWAP,GT,10) IMAGE(1X,I=1,DIV)

535 C

536 C WRITE OUT THE INDEPENDENT REACTION EQUATIONS

537 C

538 IPAGE=1PAGE+1

539 WRITE(IWTR,900) (TITLE(I),K=1,20), IMAGE

540 WRITE(IWTR,910) TIP

541 WRITE(IWTR,980)

542 980 FORMAT(*91,TS4,*A SET OF INDEPENDENT REACTION EQUATIONS FOR *

543 & *THIS SYSTEM IS AS FOLLOWS:*91,TS4*)

544 IF(IWAP,GT,10) IMAGE(I=1,DIV)

545 C

546 C DETERMINE THE NUMBER OF SPECIES SPECIES IN EACH EQUATION EQUATION

547 C

548 NSPEC=0

549 DO 990 K=1,2

550 IF(IWAP,GT,RAIS(K)) GO TO 110

551 C

552 C
IF(AESGN(I,IBASE)) .LT. 1.0E-6) GO TO 999

C FILL THE CHARACTER ARRAY "STRING" WITH THE COMPOSITION SPECIES

C

NLCCF = 1
IF(NSPEC.GT.4) NLCCF = FLCAT(NSPEC)/4.0+4
DC IDJ = 1,3
STRING(I,K) = JSPCE(I,K)
1000 CONTINUE
STRING(1,4) = APAJ
CCEFF(I) = 1.0
IST = 1
ICNT = 0
DO 1060 ILCCF = 1, NLCCF
NCNT = NSPEC - ICNT + 1
IF(NCNT.GT.5) NCNT = 5
DO 1070 IDX = 2, NCNT
ICNT = ICNT + 1
DC;
1010 K = 1,3
STRING(I,K) = ESPCE(I,IDX,K)
1010 CONTINUE
CCEFF(IDX) = GNUM(I, IBASE)
STRING(I,4) = RSPS
GO TO 1010
1015 CONTINUE
IST = 1; AS +1
1020 CONTINUE
STRING(NCNT,4) = RPSL
IF(ILCCF.EQ.1) WRITE(I*FT,1041)(LP,CCEFF(IJK),)
& (STRIH(IJK,K), K=1,4, JJK=1, NCNT)
1040 FOR 4AT(I*F,11,FS,2,.44,4, (41,21,0,3,44))
1050 FOR 4AT(I*F,20,.4,.4, (41,21,0,3,44))
GO TO 1060
1060 CONTINUE
1070 CONTINUE
C WRITE-OUT A COMPARISON BETWEEN THE EQUILIBRIUM CONSTANTS
C AS CALCULATED BY THE Gibbs FREE ENERGY CHANGE AND BY COMPOSITION
C

PAGE = PAGE + 1
WRITE(I*FT,40) (TITLE(K), K=1,20), PAGE
WRITE(I*FT,40) T,T
WRITE(I*FT,1110)
1110 FOR-4AT(I*F,11,FS,2,.44,4, (41,21,0,3,44))
& EQUILIBRIUM CONSTANTS FOR THE REACTION */
& REACTION PRODUCT*/ T25/* (CALC/ OXIDE)*/ T25/* = SOL. TEMP */
& EQUILIBRIUM CONSTANT*/ 1.14
& EQUILIBRIUM PRODUCT*/ T25/* (CALC/ OXIDE)*/ T25/* = SOL. TEMP */
& EQUILIBRIUM PRODUCT*/ T25/* (CALC/ OXIDE)*/ T25/* = SOL. TEMP */
595 624('i'), T45, 'B('i'), T73, 2c('i'))
596 DL 1200 I=1, Y30
597 IF(N(i),ST1.,J=21) WRITE(IWT, 1120) (SPECIE(:n:i), K=1,3) 
598 & K=0(I),O(I)
599 IF(N(i),LE1.,J=21) WRITE(IWT, 1121) (SPECIE(:n:i), K=1,3) , 
600 & K=0(I),O(I)
601 1120 FORMAT(1X,3X,2d,E2.3, T51, E12.5, T77, E12.5)
602 1121 FORMAT(1X,3X,2d,E2.3, T51, E12.5, T77, E12.5, 8X ,*(AGT BINDING)) * 
603 1200 CONTINUE 
604 IF(ISSGT, 3) WRITE(IMAT, 445) 
605 1900 IF(I55CP. EQ.1) GC TC 3000 
606 2000 CONTINUE 
607 3000 WRITE(IMAT, 3001) 
608 3001 FORMAT(*1s, ** * 
609 STOP 
610 END
B.3 A Description of the Major Variables in MCMPS3,STOIC

Variables which are used in the IMSL subroutines LIV1F, LEQT1F, LUDATF and LUELMF are not included in this list. FORTRAN default typing applies unless otherwise specified.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (I,J)</td>
<td>elemental abundance matrix</td>
<td>atoms of element j atoms of molecule of specie i</td>
</tr>
<tr>
<td>ACOEF (I)</td>
<td>activity coefficient of specie i</td>
<td>-</td>
</tr>
<tr>
<td>AMAX</td>
<td>maximum value the convergence forcer may attain</td>
<td>-</td>
</tr>
<tr>
<td>AMIN</td>
<td>minimum value the convergence forcer may attain</td>
<td>-</td>
</tr>
<tr>
<td>AXS</td>
<td>activity coefficient correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>AO (I)</td>
<td>heat capacity correlation parameter</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>AI (I)</td>
<td>heat capacity correlation parameter</td>
<td>kcal/g-mole-K^2</td>
</tr>
<tr>
<td>A2 (I)</td>
<td>heat capacity correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>A3 (I)</td>
<td>heat capacity correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>AOZ</td>
<td>inert specie heat capacity correlation parameter</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>A1Z</td>
<td>inert specie heat capacity correlation parameter</td>
<td>kcal/g-mole-K^2</td>
</tr>
<tr>
<td>A2Z</td>
<td>inert specie heat capacity correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>A3Z</td>
<td>inert specie heat capacity correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>B (J)</td>
<td>moles of element J specified in the system</td>
<td>g-moles</td>
</tr>
<tr>
<td>BCALC (J)</td>
<td>moles of element J as calculated by algorithm</td>
<td>g-moles</td>
</tr>
<tr>
<td>BESTN</td>
<td>The best estimate to the equilibrium mole numbers</td>
<td>g-moles</td>
</tr>
<tr>
<td>BXS</td>
<td>activity coefficient correlation parameter</td>
<td>variable</td>
</tr>
<tr>
<td>C</td>
<td>number of pure condensed phases (integer)</td>
<td>-</td>
</tr>
<tr>
<td>CHMPT (I)</td>
<td>chemical potential of specie i</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>CHMPTZ</td>
<td>chemical potential of the inert</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>CNVG</td>
<td>composition convergence criterion</td>
<td>-</td>
</tr>
<tr>
<td>COND (3)</td>
<td>vector containing the character string 'CONDENSED'</td>
<td>-</td>
</tr>
<tr>
<td>D (I, J)</td>
<td>matrix of basis species</td>
<td>atoms of j molecule of i</td>
</tr>
<tr>
<td>DELH</td>
<td>total enthalpy change</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>DELN (I)</td>
<td>change in moles of specie i</td>
<td>g-mole</td>
</tr>
<tr>
<td>DELS</td>
<td>total entropy change</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>DG (I)</td>
<td>Gibbs Free Energy change of reaction i</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>DGDL</td>
<td>change in system Gibbs Free Energy with respect to the convergence forcer</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td>DHO (I)</td>
<td>enthalpy of formation of specie i</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>DHOZ</td>
<td>enthalpy of formation of the inert specie</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>DINV (I, J)</td>
<td>inverse of matrix D</td>
<td>-</td>
</tr>
<tr>
<td>DPRME (I, J)</td>
<td>Gram-Schmidt orthogonalization of matrix D</td>
<td>-</td>
</tr>
<tr>
<td>DSO (I)</td>
<td>entropy of formation of specie i</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>DSOZ</td>
<td>entropy of formation of the inert specie</td>
<td>kcal/g-mole-K</td>
</tr>
<tr>
<td>DJZETA(I)</td>
<td>change in reaction extent for specie</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>number of elements in the system</td>
<td>(integer)</td>
</tr>
<tr>
<td>ELIII (K)</td>
<td>vector containing character string of group III elements</td>
<td>-</td>
</tr>
<tr>
<td>ELMNT (J)</td>
<td>vector containing character strings of the elements present in the system</td>
<td>-</td>
</tr>
<tr>
<td>ELV (K)</td>
<td>vector containing character strings of group V element</td>
<td>-</td>
</tr>
<tr>
<td>EPCP2</td>
<td>E + C + 2 (integer)</td>
<td>-</td>
</tr>
<tr>
<td>EP3</td>
<td>E + 3 (integer)</td>
<td>-</td>
</tr>
<tr>
<td>EP3PC</td>
<td>E + 3 + C (integer)</td>
<td>-</td>
</tr>
<tr>
<td>FRAC (I)</td>
<td>mole fraction of specie i in its phase</td>
<td>-</td>
</tr>
<tr>
<td>FRACZ</td>
<td>mole fraction of inert in the vapor</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>------------</td>
<td>------------------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>GNU (I, J)</td>
<td>formation reaction coefficient matrix</td>
<td>g-mole</td>
</tr>
<tr>
<td>GFE</td>
<td>Gibbs free energy of the system</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>GSTAR</td>
<td>GFE divided by RT</td>
<td>-</td>
</tr>
<tr>
<td>IACFF</td>
<td>activity coefficient switch</td>
<td>-</td>
</tr>
<tr>
<td>IALG</td>
<td>convergence forcer algorithm switch</td>
<td>-</td>
</tr>
<tr>
<td>ICHNG</td>
<td>parameter which indicates whether or not the basis species have changed</td>
<td>-</td>
</tr>
<tr>
<td>ICMP</td>
<td>index for the composition loop</td>
<td>-</td>
</tr>
<tr>
<td>ICP (I)</td>
<td>heat capacity correlation parameter</td>
<td>-</td>
</tr>
<tr>
<td>IDATA</td>
<td>switch used with the wrap-up file</td>
<td>-</td>
</tr>
<tr>
<td>IDGT</td>
<td>number of significant figures in each matrix element</td>
<td>-</td>
</tr>
<tr>
<td>IDIM1</td>
<td>maximum number of species allowed in system</td>
<td>-</td>
</tr>
<tr>
<td>IDIM2</td>
<td>maximum number of elements allowed in system</td>
<td>-</td>
</tr>
<tr>
<td>IDEBUG</td>
<td>option to aid in trouble-shooting</td>
<td>-</td>
</tr>
<tr>
<td>IDXBAS (J)</td>
<td>vector containing the index of each basis specie</td>
<td>-</td>
</tr>
<tr>
<td>IFILE</td>
<td>logical unit designator of the wrap-up file</td>
<td>-</td>
</tr>
<tr>
<td>INERT (3)</td>
<td>vector containing the inert specie name</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>IOPT</td>
<td>parameter to allow various computational options</td>
<td>-</td>
</tr>
<tr>
<td>IOUT</td>
<td>number of pure condensed phases removed by subroutine ADDRMOV</td>
<td>-</td>
</tr>
<tr>
<td>IRD</td>
<td>logical unit designator for data input</td>
<td>-</td>
</tr>
<tr>
<td>ISPCE(i,j)</td>
<td>array containing the original specie order</td>
<td>-</td>
</tr>
<tr>
<td>ISS</td>
<td>steady state option parameter</td>
<td>-</td>
</tr>
<tr>
<td>ISTOP</td>
<td>switch which halts the computation if problems develop</td>
<td>-</td>
</tr>
<tr>
<td>ITER</td>
<td>current iteration number in the equilibrium calculation</td>
<td>-</td>
</tr>
<tr>
<td>ITP</td>
<td>index for the temperature and pressure loop</td>
<td>-</td>
</tr>
<tr>
<td>ITST</td>
<td>parameter which indicates linear dependence in the basis specie matrix</td>
<td>-</td>
</tr>
<tr>
<td>IWRAP</td>
<td>switch used with the wrap-up file</td>
<td>-</td>
</tr>
<tr>
<td>IWRT</td>
<td>logical unit designator for data output</td>
<td>-</td>
</tr>
<tr>
<td>IXSCOR</td>
<td>parameter which chooses the solution phase activity coefficient model</td>
<td>-</td>
</tr>
<tr>
<td>KEQ(I)</td>
<td>equilibrium constant for formation reaction i as calculated from the Gibbs Free Energy change (real)</td>
<td>-</td>
</tr>
<tr>
<td>LAMIN</td>
<td>convergence forcer (real)</td>
<td>-</td>
</tr>
<tr>
<td>MAXIT</td>
<td>maximum number of iterations to be used</td>
<td>-</td>
</tr>
<tr>
<td>N(I)</td>
<td>moles of specie i (real)</td>
<td>g-moles</td>
</tr>
<tr>
<td>NMAX</td>
<td>total number of loops to be made in the composition or temperature and pressure loops</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>NS</td>
<td>total moles in solution (real)</td>
<td>g-moles</td>
</tr>
<tr>
<td>NSPEC</td>
<td>number of species in the formation reaction</td>
<td>-</td>
</tr>
<tr>
<td>NV</td>
<td>total moles in the vapor (real)</td>
<td>g-moles</td>
</tr>
<tr>
<td>P</td>
<td>system pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>PHASE (I, 3)</td>
<td>matrix containing a character string to denote the phase of each species</td>
<td>-</td>
</tr>
<tr>
<td>PINC</td>
<td>pressure increment for each loop</td>
<td>Pa</td>
</tr>
<tr>
<td>PO</td>
<td>formation data reference pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>Q(I)</td>
<td>equilibrium constant for formation reaction i as calculated from composition</td>
<td>-</td>
</tr>
<tr>
<td>RELERR</td>
<td>fractional change between KEQ(I) and Q(I)</td>
<td>-</td>
</tr>
<tr>
<td>RELMAX</td>
<td>maximum value of RELERR during an iteration</td>
<td>-</td>
</tr>
<tr>
<td>RLXMIN</td>
<td>The minimum allowable value of the convergence forcer</td>
<td>-</td>
</tr>
<tr>
<td>RIIIIV</td>
<td>vapor phase III/V atomic ratio</td>
<td>-</td>
</tr>
<tr>
<td>RT</td>
<td>product of the ideal gas constant and the temperature</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>S</td>
<td>total number of species in the solution phase</td>
<td>-</td>
</tr>
<tr>
<td>SIMF</td>
<td>mole fraction of silicon species in the vapor</td>
<td>-</td>
</tr>
<tr>
<td>SITOT</td>
<td>moles of silicon species in the vapor</td>
<td>g-moles</td>
</tr>
<tr>
<td>SOLN (3)</td>
<td>vector containing the character string 'SOLUTION'</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>SPECIE (I, 3)</td>
<td>matrix of character strings containing the names of each species</td>
<td>-</td>
</tr>
<tr>
<td>STDCP (I)</td>
<td>standard chemical potential of specie i</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>STDCPZ</td>
<td>standard chemical potential of the inert</td>
<td>kcal/g-mole</td>
</tr>
<tr>
<td>SUMIII</td>
<td>total moles of group III atoms in the vapor</td>
<td>g-mole</td>
</tr>
<tr>
<td>SUMV</td>
<td>total moles of group V atoms in the vapor</td>
<td>g-mole</td>
</tr>
<tr>
<td>T</td>
<td>system temperature</td>
<td>K</td>
</tr>
<tr>
<td>TITLE (K)</td>
<td>vector containing an 80 character title</td>
<td>-</td>
</tr>
<tr>
<td>TINC</td>
<td>temperature increment for each loop</td>
<td>K</td>
</tr>
<tr>
<td>TOTMC (I)</td>
<td>total moles of pure condensed phase i as input</td>
<td>g-moles</td>
</tr>
<tr>
<td>TOTMOL</td>
<td>total moles in a single phase</td>
<td>g-moles</td>
</tr>
<tr>
<td>TOTSMS</td>
<td>total moles in the solution phase</td>
<td>g-moles</td>
</tr>
<tr>
<td>TOTMV</td>
<td>total moles in the vapor phase</td>
<td>g-moles</td>
</tr>
<tr>
<td>TO</td>
<td>formation data reference temperature</td>
<td>K</td>
</tr>
<tr>
<td>V</td>
<td>total number of species in the vapor (integer)</td>
<td>-</td>
</tr>
<tr>
<td>VAPOR (3)</td>
<td>vector containing the character string 'VAPOR'</td>
<td>-</td>
</tr>
<tr>
<td>Variable</td>
<td>Description</td>
<td>Units</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>WKA</td>
<td>work area for LEQT1F</td>
<td></td>
</tr>
<tr>
<td>WKAL</td>
<td>work area for LINV1F</td>
<td></td>
</tr>
<tr>
<td>XIII</td>
<td>group III specie fraction in the steady state liquid &quot;pure&quot; condensed phase</td>
<td></td>
</tr>
<tr>
<td>ZV</td>
<td>moles of inert in the system</td>
<td>g-moles</td>
</tr>
<tr>
<td>ZACT</td>
<td>activity coefficient of the inert</td>
<td>-</td>
</tr>
</tbody>
</table>
B.4 Descriptions of the Subroutines

The subroutine structure of MCMPCS.STOC 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, LUELME 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 STSCP

A listing of subroutine STSCP is shown in Figure B3. STSCP calculates the standard state chemical potential for each species in the system. The reference state is the system temperature $T$, the formation pressure $P_0$, and pure component in the phase in which the species is present.

The pure component Gibbs Free Energy (standard chemical potential) of species $i$ at temperature $T_0$ and pressure $P_0$ is:

$$
\omega_i(T_0, P_0) = G_i^0 = \Delta H_f^0 - T_0 \Delta S_f^0
$$

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

$$
\omega_i(T, P_0) = \Delta H_f(T_0) + \int_{T_0}^{T} C_p^i \, dT - T \left[ \Delta S_f(T_0) + \int_{T_0}^{T} \frac{C_p^i}{T} \, dT \right]
$$

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

<table>
<thead>
<tr>
<th>ICP</th>
<th>Heat Capacity Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$C_p(T) = a_0 + a_1 T + a_2 T^{-2} + a_3 \ln(T)$</td>
</tr>
<tr>
<td>1</td>
<td>$C_p(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3$</td>
</tr>
</tbody>
</table>
Figure 8.2
Subprogram Structure of CMPEC,STEM

MAIN PROGRAM

- ERRSET
  suppresses printing of arithmetic overflow error messages.

- STSTOP
  calculates standard chemical potentials.

- ESTIMATE
  calculates an initial estimate to the equilibrium composition.

- STEAM
  inserts a steady state composition liquid phase if ISS=0.

- TOTSL
  determines the total moles of silicon species in the vapor phase.

- RATIO
  determines the III/V atom ratio in the vapor phase.

- WRAP
  writes-out temperatures, pressure and composition data to the wrap-up file when WRAP=0.

- OPTBAS
  determines the optimum set of basis species for constructing a set of independent formation reaction equations.

- TEST
  entry for testing.
IPVE:
writes out integer vectors when IDEBUG>1.

PMAT:
writes out single precision matrices when IDEBUG>1.

PMAT:

PMAT:

EOCN:
calculates the stoichiometric coefficients for a set of independent formation reactions and the equilibrium constants for these reactions.

LINMOD:
inputs the matrix of basis species.

DPMAT:
writes-out double precision matrices when IDEBUG>1.

PMAT:

PMAT:

PVE:
writes out real vectors when IDEBUG>1.

ACTOP:
calculates the species activity coefficients.

MAT:
calculates the formation reaction equilibrium constants, from composition.
ADJEXT
adjusts the reaction extents to yield a closer approximation to the equilibrium composition.

CNVUSHK calculates the convergence factor.

DGOLAM calculates the derivative of the Gibbs Free Energy with respect to the convergence factor.

CORMOL corrects the molar amounts of each species based on the adjusted extents of each formation reaction.

CALCO (executed when IDERIG>0)

GIBBS calculates the Gibbs Free Energy of the system when IDERIG>0.
SUBROUTINE STSTCP(A0, A1, A2, A3, A7, A12, A13, A19, D0, I5, DS, DO, D5, I5, I5, I5)

C STOC, STOC2, ICP, ICPZ, TO, T, IDIM1, V, S, C

C THIS SUBROUTINE CALCULATES THE STANDARD STATE CHEMICAL POTENTIALS
C AT TEMPERATURE T.

DIMENSION AO(IDIM1), A1(IDIM1), A2(IDIM1), A3(IDIM1), D0(IDIM1),
C IDIM1, STOC(IDIM1), ICP(IDIM1), IDIM1,
C VSC=V+S+C

INTEGER V, S, C, VSC

DT = T - TO

DT2 = T**2 - TO**2

DT3 = T**3 - TO**3

DT4 = T**4 - TO**4

DTML = 1.0 / T - 1.0 / TO

DLNT = ALOG(T) - ALOG(TO)

DLNT2 = ALOG(T)**2 - ALOG(TO)**2

DTLNT = ALOG(T) - T * ALOG(TO)

CHEMICAL POTENTIALS FOR THE VAPOR, SOLUTION AND CONDENSED PHASES

DO 100 I=1, VSC


STOC(I) = D0(I) + DELH - T * (D0(I) + DELS)

100 CONTINUE

CHEMICAL POTENTIAL FOR THE INERT COMPONENT IN THE VAPOR PHASE


STOCZ = D0Z + DELH - T * (D0Z + 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, STOCP(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 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.

### 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 In/IP 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.

\[
(1-x)\text{III}(s) = (1-x)\text{III}(l) \\
x\text{V}(s) = x \text{V}(l) \\
(1-x)\text{III}(l) + x\text{V}(l) = \text{III}_{1-x} \text{V}_x \\
(1-x)\text{III}(s) + x\text{V}(s) = \text{III}_{1-x} \text{V}_x
\]

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.

\[
G_1 = (1-x) [ S_m^{\text{III}}(T_m - T) + \Delta C_p^{\text{III}}(T-T_m - \frac{T_{m}}{T}) ] \\
G_2 = x [ S_m^{\text{V}}(T_m - T) + \Delta C_p^{\text{V}}(T-T_m - \frac{T_{m}}{T}) ]
\]
Figure B4: Subroutine ESTMTE

SUBROUTINE ESTMTE(TCTMV,TCTMS,TCTMC,FRAc,NC,FRAcZ,ZV,IDIM1,VS,C)

C THIS SUBROUTINE CALCULATES AN INITIAL ESTIMATE
C TO THE SYSTEM EQUILIBRIUM COMPOSITIONS

DIMENSION TCTMC(IDIM1),FRAc(IDIM1)
INTEGER VS,C,VS1,VSC
REAL*E N(IDIM1)
VS=VS+S
VS1=VS*S
VSC=VS+S+C
TCTMCL=TCTMV
DC EG I=1,VS
IF(I.GT.V) TCTMCL=TCTMV
N(I)=TCTMCL*FRAc(I)
50 CONTINUE
ZV=FRAcZ*TCTMV
IF(C.EQ.0) RETURN
DC 60 I=VS1,VSC
N(I)=TCTMC(I)
60 CONTINUE
RETURN
END
Where it has been assumed that $\Delta C_p$, 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]:

$$G_3 = RT\left[ x \ln x + (1-x) \ln(1-x) \right] + \left( A_{xS} + B_{xS} T \right) x(1-x)$$  \hspace{1cm} (7)

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

$$G_4 = G_1 + G_2 + G_3$$  \hspace{1cm} (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.

$$T^{\text{IIIIV}} = \frac{S_{m}^{\text{IIIIV}} - A_{xS} (2x-2x^2-0.5)}{S_{m}^{\text{IIIIV}} - R \ln 4x(1-x) + B_{xS} (2x-2x^2-0.5)}$$  \hspace{1cm} (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**

<table>
<thead>
<tr>
<th></th>
<th>$\Delta S_m$ (Cal/g-mole-K)</th>
<th>$T_m$ (K)</th>
<th>$\Delta C_p$ (Cal/g-mole-K)</th>
<th>$A_{xS}$ (Cal/g-mole)</th>
<th>$B_{xS}$ (Cal/g-mole-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>4.411</td>
<td>302.9</td>
<td>-0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>4.7</td>
<td>1090</td>
<td>1.0</td>
<td>4665</td>
<td>-8.741</td>
</tr>
<tr>
<td>GaAs</td>
<td>16.64</td>
<td>1511</td>
<td>0</td>
<td>32750</td>
<td>-23.95</td>
</tr>
<tr>
<td>In</td>
<td>1.815</td>
<td>429.8</td>
<td>-0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.5011</td>
<td>313.3</td>
<td>0.47</td>
<td>32750</td>
<td>-23.95</td>
</tr>
<tr>
<td>InP</td>
<td>10.01</td>
<td>1332.2</td>
<td>0</td>
<td>32750</td>
<td>-23.95</td>
</tr>
</tbody>
</table>
Figure 2a
The LiAs System Liquid Line
(Data refs. 1, 3, 11)

Figure 2b
The InP System Liquid Line
(Data refs. 8, 9, 13, 11)
A listing of subroutine STADY is shown in Figure B7. Lines 15 and 17 define a statement function which corresponds to the right hand side of equation 9. Hollerith strings are assigned to the species 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/Ga systems are assigned in lines 29 through 54.

An "interval halving" root finding algorithm for solving the implicit equations 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 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 (SPECILE, SPEC1, SPEC2, SYST, Y, T, ..., S)!

C SUBROUTINE TO CALCULATE THE BILATERAL-GOAL FUNCTION Y FOR USE IN THE STEADY-STATE APPROXIMATION IN THE MODEL.

C ISS SYSTEM

C 1 G(NL)-SL(L)/GA-AS (5)

C 2 IN(L)-P(L)/IN-P (3)

DIMENSION A(DIM1, DIM2), STOCP(101)

INTEGER SPECILE(DIM1, 2), DCMT(DIM2), DCML(DIM2), Y, V, ..., W

C G = T

C SPECILE(G, V) = Y

C SPECILE(G, W) = VCL(LSS)

C SPECILE(G, T) = LAST

C DT = T - TO

C DT2 = T**2 - TO**2

C DTM1 = 1.0/T - 1.0/TO

C DTM2 = 1.0/T**2 - 1.0/TO**2

C DLNT = ALC0(T/TO)

C IF(LSS, 20, P) GC TO 50

C GA-AS SYSTEM

C TM11 = 3.091.9

C TMV = 10.50

C TMIV = 15.11

C DSV = 3.03.04 + 11

C DIV = 0.15

C DSIV = 0.75 + 0.1

C DCIV = 0.75 + 0.1

C DO = 0.1

C AX = 0.5

C AXS = 0.35 + 0.1

C GC TO 60

C IN-P SYSTEM

C TM11 = 31.3

C TMV = 31.3

C TMIV = 13.11

C DIV = 0.15 + 0.11

C DSIV = 0.75 + 0.1

C DCIV = 0.75 + 0.1

C DO = 0.1

C AX = 0.5

C AXS = 0.35 + 0.1

C GC TO 60
55 DO CONTINUE
56 C DINAR-ALT FINDING SOLUTION-NEXT THE SOURCE SOL. FOR NEW
57 C
58 C
59 XV=0.0
60 XMIN=0.0
61 XMAX=1.0
62 F=0.0319 + 72
63 THET=T
64 XLOD=0.4
65 TMLOD=THET/2(XXLOD)
66 DO PDO = 1,5
67 THET2 = THET-2(XXLOD)
68 EFT = (THET2-THET1)/(THET1)
69 IF (XNO(X2=THET2+0.01) .OR. T .LT .0)
70 SMOP = (THET2-THET1)/(XW-XXLOD)
71 TMLOD = THET2
72 XLOD = XV
73 IF (SMOP .LT 0.3) AND (THET2 .LT THET1) GO TO 30
74 IF (SMOP .LT 0.3) AND (THET2 .GT THET1) GO TO 50
75 XV = MAX = XV
76 XV = MIN = XV
77 GC TO 100
78 B) XV = MIN = XV
79 DO PDO = 1,5
80 XV = 0.0(5)X(XMAX+XV)
81 CONTINUE
82 WRITE (10, T, L, N)
83 DO 120 FORMAT (64), 64 = (*CONVERGENCE NOT CONVERGED*)
84 CONTINUE
85 C CALCULATE THE STAND H-CHICAL PERTH OF THE SOURCE SOLUION
86 C
87 DOX = (1.0-XV) .B (1.0) * (TV1/T3-1) + XV * (1.0-XV) .B (1.0) * (TV1/T3-1)
88 DOX = XV * (1.0-TW-T) * (TV-T) + XV * (TV-T) * (1.0-TW-T)
89 DOX = (XV+XW/XW-1) .B XV * (1.0-XV) .B (1.0-XV) .B XV * ALG (XW-XV)
90 STOC = (VX) .B (VX) .B (VX)
91 C LOCATE THE GROUP III AND V ELEMENTS IN THE ELEMENTAL ABUNDANCE ARRAY
92 C AND INSERT THE CALCULATED ABUNDANCES INTO THIS ARRAY
93 C
94 DO I = 1,5
95 DO X = 300.0, 10.0, 10.0
96 IF (XIAN(I) .LT THET2) GO TO 200
97 IF (XIAN(I) .LT THET1) GO TO 200
98 IF (XIAN(I) .LT THET) GO TO 200
99 IF (XIAN(I) .LT THET) GO TO 200
100 CONTINUE
101 CONTINUE
102 CONTINUE
103 CONTINUE
104 CONTINUE
105 C CONTINUE
106 A(I, C+1) = (1.0-XV)
107 A(I+1, D) = XV
108 CONTINUE
109 RETURN
110 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,

\[ \text{Si} (s) = \text{Si} (v) \quad (1) \]

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

\[ a_s = \frac{s_{\text{Si}}}{K \cdot Po} \quad (2) \]

where: \( P_{\text{Si}} \) = partial pressure of Si(v) 
\( Po \) = reference state pressure 
\( a_s \) = 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

\[ R_{\text{SAT}} = \frac{P_{\text{III}}}{K \cdot P_{\text{IV}}} \quad (1) \]

where the equilibrium constant, \( K_{\text{III/V}} \) is calculated from the Gibbs Free Energy change of the reaction

\[ \text{III} \text{V} (s) = \text{III}(v) + \text{V}(v) \quad (2) \]
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 $RSAT > 1$.

### B.4.5 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, DOS, AO, Al, 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 species 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 species 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 TESTJ 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.
SUBROUTINE TOTSI((ELMT,J,E),RT,JNT,J,L,T,U,S1,DC,KS)  
C      SUBROUTINE TO CALCULATE THE TOTAL SI IN THE VALED WATER, 
C      AND THE ACTIVITY OF SI IN A SOLIC L SOLUTION.  
C      DIMENSION (ELMT,IE),FRAC(I,E),FRAC(I,E)  
C      INTEGER ELMT(I),E,FRAC(I,E)  
C      REAL KS(I,E)  
C      T=255.15  
C      PD=101325.0  
C      RT=J.3015372X7  
C      DETERMINE THE TOTAL AMOUNT OF SILICON IN THE VALED WATER.  
C      S1(1,J,E)  
C      SIMF=0.0  
C      ACTI=0.  
C      DC 100 CONTINUE  
C      GC TO 300  
C      130 CONTINUE  
C      DC 140 I=1.1  
C      IF(A(I,KS1,E).LT.1001) GC TO 150  
C      SITC=SITC+N(1)  
C      SIMF=SIMF+FRAC(I)  
C      140 CONTINUE  
C      FIND SI(V) AND CALCULATE THE ACTIVITY OF SOLIC SI IN SOLUTION.  
C      DC 200 I=1.1  
C      ICNT=0  
C      IF(A(I,KS1,E).LT.0.011) GC TO 230  
C      DC 150 J=1.1  
C      IF(A(I,J,E).LT.100) GC TO 160  
C      ICNT=ICNT+1  
C      150 CONTINUE  
C      IF(ICNT.GT.14) GC TO 200  
C      DG=1.0-0.030J(17-T)-5.0J11E-7/2.*(T*2-T*2-T*2+1)*1.*4.*R(17-17.0)  
C      E = (-T*(0.30637-2.372.0+1.411E-7+1.3+7.0))  
C      E = -127.3*(17+2-1/T+2.0)  
C      ACTS1=FRAC(I)+PD*EXP(E/RT)  
C      IF(N(I,J,E).LT.1) ACTS1=0.  
C      GC TO 300  
C      200 CONTINUE  
C      300 CONTINUE  
C      ACTOUT  
C      END
Figure B9. Subroutine RATIO

```fortran
SUBROUTINE RATIO (X1, X2, X3, X4, X5, X6, X7, X8, X9, X10, X11, X12)

DIMENSION A(I),I(J),I(K)
REAL*8 X, Y, Z

CALL SUBRUTE RATIO (X, Y, Z)
```

This subroutine calculates the value of X/Y.

It calculates the ratio of X and Y for various columns and species.

1. **Dimension**: The subroutine first declares the dimensions of arrays `A`, `I`, and `J`, and initializes `X`, `Y`, and `Z` to real numbers.

2. **Call**: The subroutine then calls itself recursively to handle the calculation for various columns and species.

3. **Calculation**: The calculation logic involves iterative calls to itself and uses arrays `A`, `I`, and `J` for storing and manipulating data as required.

This subroutine is designed to handle complex calculations involving ratios and is likely part of a larger program or simulation.
54 C KAS=0
55 C KIN=0
56 C KPE=0
57 C
58 C G A D A T A
59 C
60 C
61 C KSPC=KIII(3)
62 C A1=3.0373
63 C A2=0.0301
64 C A3=3.0637
65 C A4=3.3386
66 C A5=6.0
67 C A6=0.04
68 C AX=1.3850
69 C GC AT (1, 21, 23, 24)
70 C
71 C
72 C I N C L U M D A T A
73 C
74 C 213 KSPC=KIII(4)
75 C A1=3.0150
76 C A2=1.6141
77 C A3=0.0
78 C A4=0.0
79 C A5=1.6441
80 C OH=67.3
81 C O1=0.3270
82 C GC AT (4)
83 C
84 C P R E S = H U C ( I ) ( R ) D A T A
85 C
86 C 230 KSPC=KIV(2)
87 C A1=1.0107
88 C A2=0.0
89 C A3=0.0
90 C A4=0.0
91 C A5=0.0
92 C OH=75.0
93 C O1=0.3290
94 C GC AT (2)
95 C
96 C A R S E N I C (AS) D A T A
97 C
98 C 240 KSPC=KV(3)
99 C A1=0.003
100 C A2=1.525
101 C A3=15.34
102 C A4=0.393
103 C A5=0.0
104 C OH=77
105 C O1=0.328
106 C GC AT (3)
107 C IGN=0
108 C

Figure B17. Subroutine SCIV01
109 IF(A1<0) GOTO 123
110 CT = 0
111 IF(A1<0) GOTO 120 D = 1.209
112 CONTINUE
113 235 CONTINUE
114 IF( A2<0 ) GOTO 130
115 IF( A3<0 ) GOTO 120 D = 1.200
116 DT = FR*(T)
117 A = ACT( V )= AL( 1 )= M Y( S )= X( C X Y( T )
118 IF( A1<0 ) GOTO 120 D = 1.200
119 IF( A1<0 ) GOTO 120 D = 1.200
120 IF( A1<0 ) GOTO 120 D = 1.200
121 IF( A1<0 ) GOTO 120 D = 1.200
122 IF( A1<0 ) GOTO 120 D = 1.200
123 IF( A1<0 ) GOTO 120 D = 1.200
124 IF( A1<0 ) GOTO 120 D = 1.200
125 IF( A1<0 ) GOTO 120 D = 1.200
126 GOTO 400
127 300 CONTINUE
128 400 CONTINUE
129 C
130 C CALCULATE THE SATURATION RATIOS FOR GA-AS AND IN-P.
131 C
132 RGAS = J.
133 RIN = J.
134 C
135 C GA-AS SYSTEM SATURATION RATIO
136 C
137 A1=3.101-6
138 A2=2.101-6
139 A3=0.
140 A4=0.
141 A5=0.
142 DH=-1.52
143 DT=-1.10244
144 K3=4.6
145 K4=4.6
146 OUT 300 1=1.2
147 IF( A3<0.0 ) GOTO 120 D = 1.200
148 IF( (K2)LT.1.035-6 ) GOTO 120 D = 1.200
149 D = DT*K3*PLP(K3)*(PLP(K3))*K4/COG(T)/FT
150 RGAS=K6=CG(K3)*PLP(K3)*CG(K3)*CG(K3)*CG(K3)/COG(T)
151 IF( A1<0 ) GOTO 120 D = 1.200
152 IF( A1<0 ) GOTO 120 D = 1.200
153 C
154 C IN-P SYSTEM SATURATION RATIO
155 C
156 472 A1=3.1012
157 X3=0.
158 A2=-1.14
159 D=-1.9
160 K3=1.5
161 C3=5
162 806 CONTINUE
Figure B10. Subroutine OPTBAS

SUBROUTINE OPTBAS(N, J, ICP, OPT, IC, IC1, L, LIMIT)

C THIS SUBROUTINE DETERMINES THE OPTIMUM SET OF ELEMENTS
C
C DIMENSION A(IDCIM1, IDCIM2), IC1(IDCIM1), IC2(IDCIM2),
C &
C & STOCP(IDCIM1), A0(IDCIM1), A1(IDCIM1), A2(IDCIM1), A3(IDCIM1),
C &
C & RH(IDCIM1), SC(IDCIM1), IC(IDCIM1), IC1(IDCIM1), IC2(IDCIM1),
C &
C & TEMP(IDCIM1), BESTN(IDCIM1), OPTIC(IDCIM1, 3), PHASE(IDCIM1, 3), ENSN(IDCIM1), V, S, C, E, VEC
C &
C &
C & ISTOP=0
C &
C & ICHNG=0
C &
C & VEC=W+VEC
C &
C & VEC=M+VEC-1
C &
C JUPELE SORT THE N ELEMENTS INTO DESCENDING ORDER
C &
C AND ORDER 1CP, A, A0, A1, A2, A3, OPTIC, PHASE
C &
C AND ICP CORRESPONDINGLY
C &
C DO 300 I = 1, VECM1
C &
C IP1 = I + 1
C &
C DO 200 II = IP1, VEC
C &
C IF(N(I) .LE. N(II)) GO TO 200
C &
C ICHNG = 1
C &
C TEMP = N(II)
C &
C N(II) = N(I)
C &
C N(I) = TEMP
C &
C TEMP = BESTN(I)
C &
C BESTN(I) = BESTN(II)
C &
C BESTN(II) = TEMP
C &
C TEMP = STOCP(I)
C &
C STOCP(I) = STOCP(II)
C &
C STOCP(II) = TEMP
C &
C TEMP = A0(I)
C &
C A0(I) = A0(II)
C &
C A0(II) = TEMP
C &
C TEMP = A1(I)
C &
C A1(I) = A1(II)
C &
C A1(II) = TEMP
C &
C TEMP = A2(I)
C &
C A2(I) = A2(II)
C &
C A2(II) = TEMP
C &
C TEMP = A3(I)
C &
C A3(I) = A3(II)
C &
C A3(II) = TEMP
C &
C TEMP = RH(I)
C &
C RH(I) = RH(II)
C &
C RH(II) = TEMP
C &
C TEMP = SC(I)
C &
C SC(I) = SC(II)
C &
C SC(II) = TEMP
C &
C ICP = ICP - 1
C &
C GO TO 300
C &
C END
55  IQUES(I)=IQUE(S(I,2))
56  IQUES(I)=ITMP
57  ITMP=ICP(I)
58  ICP(I)=ICP(S(I,1))
59  ICP(S(I,1))=ITMP
60  DO 50 J=1,3
61  ITMP=SPECIE(I,J)
62  SPECIE(I,J)=SPECIE(S(I,1),J)
63  SPECIE(S(I,1),J)=ITMP
64  ITMP=PHASE(I,J)
65  PHASE(I,J)=PHASE(S(I,1),J)
66  PHASE(S(I,1),J)=ITMP
67  50 CONTINUE
68  DO 100 J=1,3
69  TEMPS=AT(I,J)
70  AT(I,J)=AT(S(I,1),J)
71  AT(S(I,1),J)=TEMPS
72  100 CONTINUE
73  200 CONTINUE
74  300 CONTINUE
75  C IF THE PREVIOUSLY USED BASIS IS STILL THE OPTIMUM BASIS
76  C SKIP THE REST OF THIS SUBROUTINE AND CONTINUE WITH THE CALCULATIONS
77  C
78  C IF (INTERST.1 LT.1CINHNG.3) GO TO 420
79  C
80  C BUILD THE D MATRIX WHICH WILL CONTAIN THE OPTIMUM BASIS
81  C
82  C
83  DO 320 J=1,3
84  DPHASE(I,J)=S(I,J)
85  320 CONTINUE
86  MA=0
87  DO 400 ND=1,5
88  400 MA=MA+1
89  IF (MA. LT. VSC) GO TO 450
90  DO 350 J=1,3
91  O(MA,J)=S(MA,J)
92  350 CONTINUE
93  IDX=MA+(J-1)
94  IF (IDX. LT. 1) GO TO 400
95  CALL TESTS(D,DPHASE,ND,IDX,1,MED,TST)
96  IF (ITST. EQ. 0) GO TO 340
97  400 CONTINUE
98  GO TO 490
99  450 WRITE(10,460) ITMP
100  460 FORMAT('***** iteration ',I5,' in optimum set of basis
101  ***** SPECIES could not be found for this system in computing optimum
102  *****)
103  490 RETURN
104  END
Figure B11. Subroutine TESTD

```
SUBROUTINE TESTD(C,CPAME,MC,E,IDIM2,ITST)

C THIS SUBROUTINE TESTS THE D-MATRIX FOR LINEAR DEPENDENCE
C USING A GRAM-SCHMIDT ORTHONORALIZATION ALGORITHM

DIMENSION D(IDIM2,IDIM2)
REAL*8 CPAME(IDIM2,IDIM2),ANLM,CENC
INTEGER E
ITST=0
DC 100 J=1,E
DCRME(MC,J)=C(MD,J)
100 CONTINUE
MD1=M0-1
DC 400 L=1,MD1
ANL=0.0
DC 200 K=1,E
DCRME(MC,J)=DCRME(MC,J)+DCRME(L,K)*CPAME(L,K)
200 CONTINUE
DC 300 J=1,E
DCRME(MC,J)=DCRME(MC,J)-DCRME(L,J)*ANLM/DENC
300 CONTINUE
400 CONTINUE
C TEST FOR "ZERO'S" ON THE NEW RCM
500 CONTINUE
500 RETURN
END
```
B.4.8 EOCON

Subroutine EOCON, 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 LINLIF. 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 LINLIF 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 species, 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 applicable to binary solutions only. The activity coefficient for species i is given by:

\[
\gamma_i = \exp [(A_{xs} + B_{xs}T)(1-X_i)^2/RT] \tag{1}
\]

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

\[
\gamma_{V+1} = H = A_{xs} \exp[B_{xs}/T] \tag{2}
\]

The vapor phase is always assumed to be ideal.

B.4.10 CALCO

A listing of CALCO 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.

\[
Q_i = \sum_{k=1}^{E} \gamma_i X_i p_i / \pi (\gamma_k X_k p_k)^{v_{ik}} \tag{1}
\]

where:
- \(\gamma_i\) = activity coefficient
- \(X_i\) = mole fraction
- \(v_{ik}\) = stoichiometric coefficient
- \(p_i = {P/P_o}\) vapor species
- \(\pi = 1\) condensed phases
Figure B12. Subroutine EQCON

SUBROUTINE EQCON(A,CC,CINV,CC,CAL,STCP,KEG,IDXAS,IXA,
& RT,ITR,IDI1,IC1M2,VS,C,E,ISTCP,IFRT)

THIS SUBROUTINE CALCULATES THE REACTION COEFFICIENT MATRIX
AND THE EQUILIBRIUM CONSTANTS FOR THE FORMATION REACTIONS

DIMENSION (IOD1,IC1M2),D(IC1M2,IC1M2),CC(1M2,1M2),
& DINV(1M2,IC1M2),DC(1M1,1M1),GNU(1M1,1M2),
& IDXAS(1M2),STCP(1M1),IXA(1M2)

DOUBLE PRECISION CC,CINV,IXA

INTEGER V,SC,E,VSC

REAL K,EC,STCP

DO I=1,E

DO J=1,E

DC(I,J)=D(I,J)

END

CONTINUE

INVERT MATRIX DD USING IMSL SUBROUTINE LINVIF

CALL LINVIF(CC,E,IC1M2,CINV,IDG,T,AX,IER)

IF(IER.EQ.34) WRITE(11,110) IER

110 FORMAT('E*SUBROUTINE LINVIF DURING MATRIX INVERSION E* IOGT=*12)

IF(IER.EQ.129) WRITE(11,120) 1ER

120 FORMAT('E*SUBROUTINE EQCON E* IN SUBROUTINE EQCON E* E* E* IN E* E* E* IN E* E*

IF(IER.EQ.129) ISTCP=1

IF(ISTCP.EQ.1) GC TO 610

CALCULATE THE REACTION COEFFICIENT MATRIX

DC 300 I=1,E

DC 3CJ J=1,E

TEMP=0.0

DC 200 JJ=1,E

TEMP=TEMP+A(I,J)*CINV(J,J)

200 CONTINUE

GNU(I,J)=TEMP

300 CONTINUE

CALCULATE THE EQUILIBRIUM CONSTANTS FOR THE FORMATION REACTIONS

DC 500 I=1,E

ARG=(-1.0)*STCP(I)

DC 400 K=1,E

IDXK=1C*K

ARG=ARG*GNU(I,K)*STCP(IDXK)

400 CONTINUE
55 DGI = (-1.0) * ARG * RT
56 KEQ(I) = EXP(ARG)
57 500 CONTINUE
58 600 RETURN
59 END
Figure B13. Subroutine ACTCOF

1 SUBROUTINE ACTCCF(FRAC,ACCEF,ISPCE,SPECIE,INDEX-IDIMZ,VELMAX,
2 & IXSCCP,AXS,EXST,IACF,F,VSC,CMRT)
3 C
4 C SUBROUTINE TO CALCULATE ACTIVITY COEFFICIENTS FOR THE SOLUTION PHASE.
5 C
6 C IXSCCM ALGORITHM
7 C 1 BINARY SIMPLE SOLUTION THEORY GE=(AXS+8X5*T)*X1*X2
8 C 2 HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE F=AXS*EXP(8X5/T)
9 C
10 DIMENSION ACCEF(IDIM1),FRAC(IDIM1),INDEX(IDIM1)
11 INTEGER ISPCE(IDIM1,3),SPECIE(IDIM1,3),VSC,C,VSC
12 VSC=V+E+C
13 DC 100 I=1,VSC
14 ACCEF(I)=1.0
15 C CONTINUE
16 IF((ACCEF(I)==0.0)) IACFF=1
17 IF((IXSCCP.EQ.0)) IACFF=1
18 IF((IXSCCP.EQ.0)) IACFF=1
19 IF((IXSCCP.EQ.0)) IACFF=1
20 RT=0.0015672*T
21 C IDENTIFY THE SOLUTION SPECIES
22 C
23 DO 150 J=1,S
24 K=V+j
25 DC 150 I=1,VSC
26 IF((SPECIE(I,1).EQ.ISPCE(K,1)) AND.
27 & SPECIE(I,2).EQ.ISPCE(K,2)) AND.
28 & SPECIE(I,3).EQ.ISPCE(K,3)) INDEX(J)=1
29 C CONTINUE
30 C TEST=1
31 IF((INDEX(J)<LT.0.0)) TEST=0
32 IF((INDEX(J)<GT.0.0)) TEST=0
33 IF((INDEX(J)<EQ.0.0)) TEST=0
34 C CONTINUE
35 IF((TEST.EQ.0)) WRITE(IVRT,150)
36 IF((INDEX(J)<EQ.0)) WRITE(IVRT,150)
37 C BINARY SIMPLE SOLUTION THEORY
38 C
39 ICX=INDEX(1)
40 ICX2=INDEX(2)
41 X1=FRAC(ICX1)
42 X2=1.0-X1
43 ARG1=(AXS+8X5*T)*X2**2/RT
44 ARG2=(AXS+8X5*T)*X1**2/RT
45 X1=EXP(ARG1)
46 X2=EXP(ARG2)
47 GC TC 500
48 C HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIES
49 C
50 DC 200 ICX=INDEX(1)
51 ICX2=INDEX(2)
52 ACCEF(ICX)=AXS*EXP(8X5/T)
53 C RETURN
54 C
Figure B14. Subroutine CALQQ

```plaintext
SUBROUTINE CALQQ(GNU, N, ACCEF, FRAC, PHASE, VAFCF, SCLN, IDXBASE, G,
NZ, FRACZ, P, PJ, V, E, C, E, IDIM1, IDIM2, IWAT)
C
SUBROUTINE TO CALCULATE EQUILIBRIUM CONSTANTS FROM COMPOSITION
C
DIMENSION GNU(IDIM1, IDIM2), ACCEF(IDIM1), FRAC(IDIM1), IDXBASE(IDIM2),
& Q(IDIM1)
INTEGER VS, C, E, VSC, PHASE(IDIM1, 3), VAFCF(3), SCLN(3)
REAL*8 N(IDIM1), NV, NS
VSC = V + S + C

CALCULATE THE TOTAL NUMBER OF MCGS IN EACH PHASE
NS = 0.
NV = 2V
DO 100 I = 1, VSC
100 CONTINUE
CALCULATE THE MCG FRACTIONS
DC 200 I = 1, VSC
FRAC(I) = 1.0
DO 250 I = 1, VSC
FRAC(I) = N(I)/NV
250 CONTINUE
CALCULATE THE EQUILIBRIUM CONSTANTS
DC 400 I = 1, VSC
PP0 = 1.0
IF(PHASE(I, 1) .EQ. VAFCF(I)) PP3 = F/P0
Q(I) = ACCEF(I) * FRAC(I) * PP0
DC 200 J = 1, E
K = IDXBASE(J)
PPJ = 1.0
IF(PHASE(K, 1) .EQ. VAFCF(I)) PP3 = F/P0
Q(I) = Q(I) / (ACCEF(K) * FRAC(K) * PP0) ** 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 \( \Delta g_i \) 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 CNVFRG and DGOlam

Listings of subroutine CNVFRG and function subprogram DGOlam are shown in Figure B16. Subroutine CNVFRG calculates a convergence forcing \( \lambda \), 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 forcing to 1.0 and \( Rlx 0 \) respectively.

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

\[
\frac{dG}{d\lambda} = RT \sum_{i=1}^{\nu_{sc}} (n_{r,i} - n_{i}) \ln \left( \frac{n_{r,i}p_i}{n_{i}} \right) + \ln \left( \frac{n_{r,i}p_i}{n_{i}} \right)
\]

where: 
- \( n_r \) = total moles in the phase 
- \( n_i \) = equations 9 and 10 section B.5 
- \( p_i \) = \( p/p_0 \) vapor phase 
- \( p_i \) = \( 1 \) condensed phases

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 \( 1.65 \times 10^{-24} \) moles (one molecule).
SUBROUTINE ADJEXT(KEC,C,CNU,DZETA,IDBAS,CNJ,PHASE,IC1M1,IC1M2,N,VSCE,IFRT)

SUBROUTINE TO ADJUST THE EXTENTS OF REACTION

DIMENSION IDBAS(IC1M2),C0(0IC1M1),CNJ(0IC1M1,0IC1M2)
INTEGER CCND(3),PHASE(0IC1M1,3),VSCE,VS
REAL KEC(0IC1M1),DZETA(0IC1M1),DENCM,TCTON

VSC=VSCE

CALCULATE THE CHANGE IN REACTION EXTENT FOR EACH REACTION

DC 200 I=1,VSC
DELI=1.0
IF(PHASE(I,1).EQ.CCND(1)) DELI=0.0
DENCM=DELI/IN(1)
DZETA(I)=0.0
DC 100 J=1,E
K=IDBAS(J)
IF(I.EQ.K) GO TO 200
DELCM=0.0
IF(PHASE(K,1).EQ.CCND(1)) DELCM=0.0
DENCM=DENCM-DELCM*GNL(I,J)*42/N(K)
100 CONTINUE

IF(DENCM.EQ.G0,0) DENCM=ALCG(KEC(I))-ALCG(G(I))
DZETA(I)=(ALCG(KEC(I))-ALCG(G(I)))/CABS(DENCM)
IF((N(I).LT.1.66E-24.AND.DZETA(I).LT.0.1) OR DZETA(I).GT.1.)
IF(DZETA(I).LT.0.0.AND.DADE(GzetA(1)).LT.K(1))
DZETA(I)=1.0*KN(I)
200 CONTINUE
200 CONTINUE

LIMIT THE MAXIMUM ALLOWABLE DZETA VALUES

AKAPA=1.0
DC 400 J=1,E
K=IDBAS(J)
TCTON=0.0
DC 300 I=1,VSC
TCTON=TCTON*GNL(I,J)*DZETA(I)
300 CONTINUE
300 CONTINUE
TEST=K(K)*TCTON*AKAPA
400 CONTINUE

400 CONTINUE
DC 500 I=1,VSC
DC 450 J=1,E
IF(I.EQ.IDBAS(J)) GO TO 500
450 CONTINUE
DZETA(I)=DZETA(I)*AKAPA
500 CONTINUE
500 CONTINUE
RETURN
END
Figure B16. Subroutine CNVFRC

SUBROUTINE CNVFRC(NM, T, VM, STCP, ACCEF, BETA, CM, VM, V, IC, I1, I2)
C
C SUBROUTINE TO CALCULATE THE CONVERGENCE FUNCTION CM
C
C DIMENSION IDX(9,3), CM(1,1), CM(1,1)
C
C INTEGER VAPJ(3), CNJ(3), SCEN(3), PHASE(1,1,1), I1, I2, I3, VSC
C
C REAL CM
C
C REAL CM(1,1), CM(1,1), CM(1,1), CM(1,1), CM(1,1), CM(1,1)
C
C VSC = V + C
C
C CALCULATE CM AT LAM = 1.0
C
LAMBDA = 1.0
DC 100 I = 1, VSC
100 CM(I) = CM(I)
100 CONTINUE
CALL CCMOL(NSTD, CM, CM, CM, CM, CM, CM, CM, CM, CM, CM)
GDEL = GDLAM(NSTD, CM, CM, CM, CM, CM, CM, CM, CM, CM, CM)
& GDEL = GDLAM(NSTD, CM, CM, CM, CM, CM, CM, CM, CM, CM, CM)
& IF (GDEL.LT.0.0) GO TO 999
C
C CALCULATE CM AT LAM = 0.0
C
GDEL = (-1.0) * GDLAM(NSTD, CM, CM, CM, CM, CM, CM, CM, CM, CM, CM)
& GDEL = (-1.0) * GDLAM(NSTD, CM, CM, CM, CM, CM, CM, CM, CM, CM, CM)
& IF (GDEL.LE.0.0) GDEL = 0.0
LAM = CM / (GDEL - GDEL)
IF (LAM.LT.0.0) LAM = 1.0
IF (LAM.LT.0.0) LAM = 1.0
500 CONTINUE
RETURN
END

FUNCTION GDLAM(NSTD, CM, CM, CM, CM, CM, CM, CM, CM, CM, CM)
S
S
C
C SUBROUTINE TO CALCULATE CM
C
C DIMENSION ACCEF(1,1), STCP(1,1)
C
C INTEGER PHASE(1,1,1), VARCH(3), SCEN(3), VSC
C
C REAL CM(1,1), CM(1,1), CM(1,1), CM(1,1), CM(1,1), CM(1,1)
C
C NV = 0.0
C
DC 100 I = 1, VSC
100 IF (PHASE(1,1,1) .GT. VARCH(1,1)) NV = NV + 1
100 CONTINUE

C CALCULATE THE TOTAL NUMBER OF MESES IN THE SOLUTION AND VARCH PHASE
C
C NV = 0.0
C
DC 100 I = 1, VSC
100 IF (PHASE(1,1,1) .GT. VARCH(1,1)) NV = NV + 1
100 CONTINUE

C CALCULATE CM

C
C

DO CL=1,2

DO 100 I=1,5

AFG=1.0

IF(NAME(I,1),2.*ASCF(I),A=0.0,CF(I)*NP(I))=V

IF(NAME(I,1),2.*SCLN(I),ARG=ACCF(I)*NP(I)/N)

DGCL=DGCL+(CL(I)-N(I))*(STOR(I)+LGS(AFG))

100 CONTINUE

DGCL=AC*DGCL*T

RETURN

END
Figure B17. Subroutine CORRCL

```
SUBROUTINE CORRCL(N,ZETA,GNU,IDXAS,IDIX1,IDIX2,LAMDA,VSC,E)
C
SUBROUTINE TO CORRECT THE POLAR AMOUNTS OF EACH SPECIE
C
DIMENSION GNU(IDIX1,IDIX2),IDXAS(IDIX2)
REAL LAMDA
REAL*8 N(IDIX1),ZETA(IDIX1)
INTEGER VSC,E
C
C CORRECT EACH NONBASIS SPECIE
10 DC 200 I=1,VSC
11 DC 100 J=1,E
12 IF(I.EQ.IDXAS(J)) GO TO 200
13 103 CONTINUE
14 N(I)=N(I)*ZETA(I)*LAMDA
15 IF(N(I).LT.1.0E-24) N(I)=1.0E-24
16 200 CONTINUE
C
C CORRECT EACH BASIS SPECIE
20 DC 400 J=1,E
21 K=IDXAS(J)
22 DC 300 I=1,VSC
23 N(K)=N(K)-GNU(I,J)*ZETA(I)*LAMDA
24 300 CONTINUE
25 IF(N(K).LT.1.0E-24) N(K)=1.0E-24
26 400 CONTINUE
27 RETURN
28 END
```
A COMPARATIVE THERMODYNAMIC ANALYSIS OF IMPURITY INCORPORATION IN VAPOR P. (U) FLORIDA UNIV GAINESVILLE DEPT OF CHEMICAL ENGINEERING T J ANDERSON ET AL.
UNCLASSIFIED 31 OCT 83 AFOSR-TR-83-1108 AFOSR-81-0164 F/G 20/12 NL
B.4.14 ORDER

A listing of subroutine ORDER is shown in Figure 318. Subroutine ORDER places arrays N, STOC, A0, A1, A2, A3, DHO, DSO, IC0, DZTA, CHMPT, ACOEF, FRAC, DG, Q, KEO, SPECIE, PHASE and A into the specie order of the original problem statement. This makes the output readily accessible and also is necessary for the correct operation of the composition logging option (IOPT=3).

B.4.15 WRAPUP

Subroutine WRAPUP, shown in Figure 819 writes a wrap-up file to logical unit designator IFIELD. This subroutine is accessed when parameter IWRAP>0. For IWRAP=1 or 2 the value of IFIELD is set at 2. For IWRAP=3 IFIELD 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

\[ G = RT \sum_{i=1}^{\nu_{SC}} \left( n_i f_{i}^{0} + \ln \left( \gamma_i X_i P_i \right) \right) \]  

where:
- \( \gamma_i \) = activity coefficient
- \( X_i \) = mole fraction of \( i \)
- \( P_{vi} \) = P/P0 vapor phase
- \( P_{\text{condense phases}} \)

B.4.18 PMAT, DPMAT, PVEC, and IPVEC

Subroutines PMAT, DPMAT, PVEC and IPVEC are used to write out single precision, double precision matrices, and single precision and integer vectors when the debugging option is active. Listings of these subroutines are shown in Figure B22 through B25.
SUBROUTINE ORDER(ISPCE, SPECIE, PHASE, A, STDCP, N, A, A2, A3, PHA)

& DSO, DZETA, CHMPT, ACCEF, FRAC, QUSS, DG, G, KEC, ICP, DIM, IDIM, VSC, & WRT)

SUBROUTINE ORDER TO ORDER THE ARRAYS BACK TO THE ORIGINAL ORDER
OF THE PROBLEM STATEMENT

DIMENSION A(IDIM1, IDIM2), STDCP(IDIM1), AO(IDIM1), A1(IDIM1),
A2(IDIM1), A3(IDIM1), CHMPT(IDIM1), ACCEF(IDIM1), OSHJ(IDIM1),
& DSO(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(II, 1) .EQ. SPECIE(II, 1)) .AND.
& ISPCE(II, 2) .EQ. SPECIE(II, 2)) .AND.
& ISPCE(II, 3) .EQ. SPECIE(II, 3)) GO TO 50
GO TO 200
50 TEMP = N(I)
N(I) = N(I)
N(I) = TEMP
STDCP(I) = STDCP(I)
STDCP(I) = TEMP
AO(I) = AO(I)
AO(I) = TEMP
A1(I) = A1(I)
A1(I) = TEMP
A2(I) = A2(I)
A2(I) = TEMP
A3(I) = A3(I)
A3(I) = TEMP
A3(I) = A3(I)
A3(I) = TEMP
DHQ(I) = DHQ(I)
DHQ(I) = TEMP
CSO(I) = TEMP
CSO(I) = TEMP
DSO(I) = DSO(I)
DSO(I) = TEMP
ICP(I) = ICP(I)
ICP(I) = TEMP
TEMP = DZETA(I)
DZETA(I) = DZETA(I)
DZETA(I) = TEMP
DZETA(I) = TEMP
CHMPT(I) = CHMPT(I)
CHMPT(I) = TEMP
E = PHASE(I, 3), E, VSC, VSCM1
55 \text{CHMPT}(II) = \text{TEMP} \\
56 \text{TEMP} = \text{ACCEF}(I) \\
57 \text{ACCEF}(I) = \text{ACCEF}(II) \\
58 \text{ACCEF}(II) = \text{TEMP} \\
59 \text{TEMP} = \text{FRAC}(I) \\
60 \text{FRAC}(I) = \text{FRAC}(II) \\
61 \text{FRAC}(II) = \text{TEMP} \\
62 \text{ITEMP} = \text{GUES}(I) \\
63 \text{GUES}(I) = \text{GUES}(II) \\
64 \text{GUES}(II) = \text{ITEMP} \\
65 \text{TEMP} = \text{DG}(I) \\
66 \text{DG}(I) = \text{DG}(II) \\
67 \text{DG}(II) = \text{TEMP} \\
68 \text{TEMP} = \text{G}(I) \\
69 \text{G}(I) = \text{G}(II) \\
70 \text{G}(II) = \text{TEMP} \\
71 \text{TEMP} = \text{KEQ}(I) \\
72 \text{KEQ}(I) = \text{KEQ}(II) \\
73 \text{KEQ}(II) = \text{TEMP} \\
74 \text{DO} 60 \ J = 1, 3 \\
75 \text{ITEMP} = \text{SPECIE}(I, J) \\
76 \text{SPECIE}(I, J) = \text{SPECIE}(II, J) \\
77 \text{SPECIE}(II, J) = \text{ITEMP} \\
78 \text{ITEMP} = \text{PHASE}(I, J) \\
79 \text{PHASE}(I, J) = \text{PHASE}(II, J) \\
80 \text{PHASE}(II, J) = \text{ITEMP} \\
81 \text{DO} 60 \ CONTINUE \\
82 \text{DO} 100 \ J = 1, 5 \\
83 \text{TEMP} = \text{A}(I, J) \\
84 \text{A}(I, J) = \text{A}(II, J) \\
85 \text{A}(II, J) = \text{TEMP} \\
86 \text{DO} 100 \ CONTINUE \\
87 \text{DO} 200 \ CONTINUE \\
88 \text{DO} 300 \ CONTINUE \\
89 \text{RETURN} \\
90 \text{END}
SUBROUTINE WRAPUP(TITLE, SPECIE, ACTSC, ACIGAS, ACTIN, ACTPS, ACIGAV, ELMAX, CNVG, IES, XI, IST, MINV, VMAX, VEC)

C SUBROUTINE TO WRITE OUT A SUMMARY OF THE RESULTS TO A FILE

DIMENSION INRT(3), FRA(10)
INTEGER TITLE(20), SPECIE(10), GUES(10), VMAX, VEC
REAL*8 N,IDIM1
IF(IDATA.GE.10) WRITE(1 FILE, 50)(TITLE(K), K=1,20)
C FORMAT(2044)
WRITE(1 FILE, 55) T,P
C FORMAT(*TEMPERATURE = 7#1, K*, PRESSURE = 7.12,5, PA*)
IF(AES(AELMAX).GT.CNVG AND IDATA.NE.0) WRITE(1 FILE, 53) AELMAX, CNVG, IES, XI, IST
C FORMAT(*50*1, /, 13, 5X, *ITERATION FOR EQUILIBRUM COMPOSITION * & * DID NOT CONVERGE, 5X, * /, 1X, *MAX=VMAX & )
IF (IDATA.EQ.0) WRITE(1 FILE, 60)
C FORMAT(13X, *INITIAL COMPOSITION*)
IF (IDATA.EQ.0) WRITE(1 FILE, 70)
C FORMAT(13X, *EQUILIBRUM COMPOSITION*)
IF (IDATA.EQ.0) WRITE(1 FILE, 80)
C FORMAT(*SPECIE, 7X, *MCLE FRACTION, 4X, *GRAM VOLS*)
DO 200 I=1, VEC
WRITE(1 FILE, 100)(SPECIE(I,K), K=1,3), FRA(I), N(I), GUE3(I)
IF (I.NE.0) GC TC 200
WRITE(1 FILE, 100)(INRT(K), K=1,2), FRAZ, ZY
C FORMAT(34A, 2X, E12.5, 2X, E12.5, 1X, A4)
IF (RIIV, GT, 0) AND RIIVL, LT, 1, 0EC) WRITE(1 FILE, 105) RIIV
C FORMAT(*VAPOR 11X/V * 10X,F9.4)
C FORMAT(*SITCT, GT, 0) WRITE(1 FILE, 110) SITCT
C FORMAT(*31 IN VAPOR 2X, E12.5, 2X, E12.5)
IF (ACTS.GT.0) WRITE(1 FILE, 120) ACTS
C FORMAT(*ACTIVITY*13X, E12.5)
IF (ACIGAV.GT.0) WRITE(1 FILE, 120) ACIGAV
C FORMAT(*ACTIVITY*13X, E12.5)
IF (ACTPS.GT.0) WRITE(1 FILE, 120) ACTPS
C FORMAT(*ACTIVITY*13X, E12.5)
IF (ACTS.GT.0) WRITE(1 FILE, 120) ACTS
C FORMAT(*ACTIVITY*13X, E12.5)
C FORMAT(*GAN-GAS SATURATION RATIC * E12.5)
IF (FINP.GT.0) WRITE(1 FILE, 135) RINF
C FORMAT(* IN-P SATURATION RATIC * E12.5)
C FORMAT(*13X, *F0.4)
WRITE(1 FILE, 210)
C FORMAT(* *)
ICATA=1
RETURN
END
SUBROUTINE DEBUG(N,ZETA,VSC,ICIM1,ITER,ALMCEA,GFE,
        RMX,IMRT)
C ROUTINE TO WRITE-OUT N, CZETA, ALMCEA DURING THE ITERATION PROCESS
C
REAL*8 N(ICIM1),ZETA(ICIM1)
INTEGER VSC
WRITE(IMRT,10) ITER,ALMCEA,GFE,RMX
1) FORMAT(*'ITERATION = ',5X,*'LAMCEA = ',E14.7,
       5X,'GIBBS FREE ENERGY = ',E14.7,*' KCAI',
       5X,'RELATIVE ERROR = ',E12.5,*'1X',
       5X,'N-VALUES',T2J,'DELTA-ZETA VALUES')
DC 50 I=1,VSC
WRITE(IMRT,20) N(I),ZETA(I)
2) FORMAT(1X,E14.7,T2C,E14.7)
50 CONTINUE
RETURN
END
SUBROUTINE GIBBS(N,STDCF,STDCPZ,ACCEF,FRAC,Z,V,FRACZ,CCNO,SCLN,PHASE,F1,P,PJ,IC1,I1,V,S,C,CFE)

SUBROUTINE TO CALCULATE THE GIBBS FREE ENERGY OF THE SYSTEM

DIMENSION STDCP(IDIM1),FRAC(ICI*1),ACCEF(I*1)
REAL*8 *IDIM1)
INTEGER CCNO(J),SCLN(J),PHASE(I*1,J),V,S,C,VSC
VSC=V+S+C
GAS CONSTANT IS IN UNITS OF: KCAL/G-ML=K

ARG=1.0
IF(FRACZ*GT.0.0) AFG=FRACZ*F/F0
GSTAR=ZV*(STDCPZ+ALCC(AFG))
DC 1=0 I=1,VSC
ARG=ACCEF(I)*FRAC(I)*P/P0
IF(PHASE(I,1)*EQ.CCND(I)) ARG=1
GSTAR=GSTAR+N(I)*(STCCF(I)+ALCC(AFG))
15J CONTINUE
GFE=GSTAR*RT
RETURN
END
Figure B22. Subroutine PMAT

```
1 SUBROUTINE PMAT(Matrix,NDIM1,NDIM2,L1,L2,NAME,IWRIT)
2       INTEGER NAME(3)
3       REAL MATRIX(NDIM1,NDIM2)
4       WRITE(IWRIT,10) (NAME(J),J=1,3)
5       FORMAT(*10,*MATRIX*,3A2)
6       DO 10 I=1,L1
7       WRITE(IWRIT,20) (MATRIX(I,J),J=1,L2)
8       10 FORMAT(1X,10(E11.4,2X))
9       100 CONTINUE
10      RETURN
11      END
```

Figure B23 Subroutine DPMAT

```
1 SUBROUTINE DPMAT(DMTRIX,NDIM1,NDIM2,L1,L2,NAME,IWRIT)
2       INTEGER NAME(3)
3       DOUBLE PRECISION DMTRIX(NDIM1,NDIM2)
4       WRITE(IWRIT,10) (NAME(J),J=1,3)
5       FORMAT(*10,*MATRIX*,3A2)
6       DO 10 I=1,L1
7       WRITE(IWRIT,20) (DMTRIX(I,J),J=1,L2)
8       10 FORMAT(1X,10(E11.4,2X))
9       100 CONTINUE
10      RETURN
11      END
```
Figure B24. Subroutine PVEC

```fortran
SUBROUTINE PVEC(VECTOR, NDIM, L, NAME, IWRIT)
C
C SUBROUTINE TO WRITE-OUT REAL VECTORS
C
5 DIMENSION VECTOR(NDIM)
6 INTEGER*2 NAME(3)
7 WRITE(IWRIT,10) (NAME(J),J=1,3)
8 10 FORMAT(*0*,'THE TRANSPSCED ',3A2,' VECTOR IS: ')
9 WRITE(IWRIT,20) (VECTOR(J),J=1,L)
10 20 FORMAT(1X,10(E11.4,2X))
11 RETURN
12 END
```

Figure B25. Subroutine IPVEC

```fortran
SUBROUTINE IPVEC(IVCTR, NDIM, L, NAME, IWRIT)
C
C SUBROUTINE TO WRITE-OUT INTEGER VECTORS
C
5 DIMENSION IVCTR(NDIM)
6 INTEGER*2 NAME(3)
7 WRITE(IWRIT,10) (NAME(J),J=1,3)
8 10 FORMAT(*0*,'THE TRANSPSCED ',3A2,' VECTOR IS: ')
9 WRITE(IWRIT,20) (IVCTR(J),J=1,L)
10 20 FORMAT(1X,10(I11,2X))
11 RETURN
12 END
```
B.4.19 IMSL Subroutines LINVIF, LEQTIF, LVELMF, and LVIDATF.

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 matrices by placing ones on the diagonal of matrix B and then calling LEQTIF to solve the matrix problem

\[ AX = B \]  

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.
**IMSL Subroutine Calling Sequence**

**LINVIF**: Driver program to invert matrix A. This subroutine puts ones on the diagonal of matrix B for LEOTIF.

**LEOTIF**: Driver program to solve the matrix problem A*X=B for matrix X.

**LUDATE**: Performs an LU decomposition of matrix A with partial pivoting.

**LUELMA**: Performs appropriate substitutions to obtain the X matrix and writes the X matrix into B.
SUBROUTINE LINVIF (A,N,IA,AINV,IDGT,KAREA,IER)

IMSL SUBROUTINE FOR INVERTING REAL MATRICES

DOUBLE PRECISION A(IA,N),AINV(IA,N),KAREA(1),ZERC,CNE

DATA ZERC/J0000,CNE/L000/

IER=0

DC 1C I=1,N

DC 5 J=1,N

AINV(I,J) = ZERC

CONTINUE

AINV(I,I) = CNE

CONTINUE

CALL LECTIF (A,N,IA,AINV,IDGT,KAREA,IER)

IF (IER .EQ. 0) GC TC 5005

5005 CONTINUE

5005 RETURN

END

SUBROUTINE LECTIF (A,N,IA,B,IDGT,KAREA,IER)

IMSL SUBROUTINE LECTIF FOR SOLVING THE MATRIX PROBLEM A*X = B

DIMENSION A(IA,1),E(IA,1),KAREA(1)

DOUBLE PRECISION A,E,KAREA,D1,D2,WA

IER=0

DECCLOSE A

CALL LUCATF (A,N,IA,IDGT,D1,D2,KAREA,KAREA,WA,IER)

IF (IER .GT. 128) GC TC 5005

CALL SUBROUTINE LUELMF (FORWARD AND BACKWARD SUBSTITUTIONS)

DC 10 J=1,N

CALL LUELMF (A,B(1,J),KAREA,IA,E(1,J))

CONTINUE

5005 RETURN

END
SUBROUTINE LUCATF (A, LU, N, IA, IC, C1, C2, IFVT, IEU, L, IER)

C THIS SUBROUTINE IS USED WITH SUBROUTINE LECTIF

DIMENSION A(IA+1), LU(IA+1), IFVT(1), IEU(1)

DOUBLE PRECISION A, LU, CL, C2, IEU, L, N, TEST, EIC

DATA ZER, CN, FC, SIN, SIXT, SINX, SINH1, COSH, SIN, COS, TAN, SECH, COT

C FIRST EXECUTABLE STATEMENT

IER = 0

RA = N

WREL = ZER

DI = CN

D2 = ZER

BIGA = ZER

DC 10 I = 1, N

BIG = ZER

DC 5 J = 1, N

F = A(I, J)

LU(I, J) = P

F = DABS(F)

IF (P * GT. BIG) BIG = P

CONTINUE

IF (BIGA * GT. CN)BIGA = BIG

IF (BIGA * EQ. ZER) GC TC 119

EICLI(I) = CN/EIG

CONTINUE

DC 10 CONTINUE

DC 100 J = 1, N

JMI = J - 1

IF (JMI * LT. 1) GC TC 40

CCMFLTE U(I, J), I = 1, ..., J - 1

DC 35 I = 1, JM1

SLW = LU(I, J)

IM1 = I - 1

IF (10GT. EQ. 0) GC TC 25

C WITH ACCURACY TEST

AI = DABS(SUM)

MI = ZER

IF (IM1 * LT. 1) GC TC 20

DC 15 K = 1, IM1

T = LU(I, K) + LU(K, J)

SUM = SUM - T

MI = MI + DABS(T)

CONTINUE

LU(I, J) = SUM

MI = MI + DABS(SLW)

IF (AI * EQ. ZER) AI = EIC

TEST = MI/AI

IF (TEST * GT. WREL) WREL = TEST

GC TC 25

C WITHOUT ACCURACY

IF (IM1 * LT. 1) GC TC 35
55  CC 30 K=1,1M1
56  SUM = SUM-LU(I,K)*LU(K,J)
57  30  CCCONTINUE
58  LU(I,J) = SUM
59  35  CCCONTINUE
60  40  P = ZERC
61  CC 70 I=J1N
62  SLU = LU(I,J)
63  IF (IDGT .EG. 0) GC TC 6E
64  65  CCWHITEMACCURACY TEER
65  AI = DAES(SUM)
66  WI = ZERC
67  IF (JM1 .LT. 1) GC TC EC
68  CC 45 K=1,1M1
69  T = LU(I,K)*LU(K,J)
70  SUM = SUM-T
71  WI = WiDAES(T)
72  45  CCCONTINUE
73  LL(I,J) = SLU
74  55  CCWHITEMACCURACY TEER
75  WI = WI+DAES(SUM)
76  IF (AI .EG. ZERC) AI = EICA
77  TEST = WI/AI
78  IF (TEST .GT. WREL) WREL = TEST
79  GC TC ES
80  CCWITHEOUTACCURACY TEER
81  55  IF (JM1 .LT. 1) GC TC ES
82  CC 60 K=1,1M1
83  SUM = SUM-LU(I,K)*LU(K,J)
84  60  CCCONTINUE
85  LU(I,J) = SUM
86  65  GC = EQUI(L(I))*DAES(SUM)
87  IF (P .LT. C) GC TC 7c
88  F = 0
89  IMAX = 1
90  70  CCCONTINUE
91  CCTEST FOR ALGORITHMIC SINGULARITY
92  IF (FN+F .EG. Fn) GC TC 11)
93  IF (J .EG. IMAX) GC TC 80
94  CCINTERCHANGE RCMES J AND IMAX
95  D1 = -D1
96  CC 70 K=1,N
97  F = LU(IMAX,K)
98  LU(IMAX,K) = LU(J,K)
99  LL(J,K) = P
100  75  CCCONTINUE
101  EQLIL(IMAX) = EQLIL(J)
102  80  IF(VT(J)) = IMAX
103  D1 = C1*LU(J,J)
104  85  IF (CABS(D1) .LE. CNE) GC TC S3
105  D1 = C1+SIXTP
106  C2 = C2*FCUP
107  GC TC ES
108  90  IF (CABS(D1) .GE. SIXTP) GC TC SS
105      D1 = D1*SIXTN
110      D2 = C2-FCUK
111      GC TC 90
112      95      CONTINUE
113      JFI = J+1
114      IF (JFI GT N) GC TC 105
115      C      DIVIDE BY Pivot ELEMENT U(J,J)
116      P = LL(J,J)
117      DC 100 1=JP1.N
118      LL(I,J) = LU(I,J)/P
119      100      CONTINUE
120      105      CONTINUE
121      C      PERFORMANCE ACCURACY TEST
122      IF (ICGT *EQ. 0) GC TC 5005
123      P = 3*K+3
124      WA = F*FEL
125      IF (WA<10.D0/*(-10*GT) *NE. WA) GC TC 5005
126      IER = 34
127      GC TC 5005
128      C      ALGORITHMIC SINGULARITY
129      110      IER = 125
130      D1 = ZERF
131      D2 = ZERF
132      5005      RETURN
133      END
SUBROUTINE LUELMF (A, B, IPVT, N, IA, X)

C THIS SUBROUTINE IS USED WITH SUBROUTINE LECTIF

C DIMENSION A(IA+1), B(1), IPVT(1), x(1)

DOUBLE PRECISION A, B, X, SLW

C FIRST EXECUTABLE STATEMENT

C Solve L Y = E for Y

C DC L I=1,N

C X(I) = E(I)

C Iw = 0

C DC 20 I=1,N

C IF = IPVT(I)

C SLW = X(IP)

C X(IP) = X(I)

C IF (Iw .NE. 0) GC TC 15

C Iw1 = I-1

C DC 10 J=Iw, Im1

C SUM = SUM-A(I,J)*X(J)

C CONTINUE

C GC TC 20

C IF (SUM .NE. 0.0) Iw = I

C X(I) = SLW

C Solve L X = Y for X

C DC 30 I=1,N

C I = N+1-I2

C IP1 = I+1

C SLW = X(I)

C IF (IP1 .GT. N) GC TC 30

C DC 25 J=IP1,N

C SUM = SUM-A(I,J)*X(J)

C CONTINUE

C X(I) = SLW/A(I,1)

RETURN

END
B.5 Theoretical Development of the Stoichiometric Algorithm

The stoichiometric algorithms employed by Cruise [1] and Smith and Misser [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

$$S_i = \sum_{k=1}^{E} v_{ik} s_k^b$$

(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 $v_{ik}$ 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 equilibrium composition of the system.

The discrete formulation of this algorithm, applied to a system consisting of a vapor phase have $V$ species, 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.
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.

\[
A^T N = R
\]  

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 \((n_1 > n_2 > ... > n)\) 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 is 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].
\[ d'_{ij} = d_{ij} \]

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

where: \( i = 2, 3, \ldots, \text{md} \)
\( j = 1, 2, \ldots, E \)
\( \text{md} = \text{current row in matrix D} \)

A linear dependence between row \( \text{md} \) of \( D \) and the remaining rows in \( D \) exists if row \( \text{md} \) of \( D' \) contains all zeros.

The matrix containing the stoichiometric coefficients for all of the formation reactions is given by:

\[ N = \begin{pmatrix} v_{11} & \cdots & v_{1E} \\ \vdots & & \vdots \\ v_{\text{sc},1} & \cdots & v_{\text{sc},E} \end{pmatrix} = A D^{-1} \]

Equilibrium constants may now be calculated for each of the formation reaction equations using the Gibbs Free Energy change of each reaction.

\[ \ln K_{\text{eqi}} = \frac{1}{RT} \left( \sum_{k=1}^{E} v_{ik} \mu^*_k - \mu^*_i \right) \]

where: \( \mu^*_i = \text{standard chemical potential of specie } i \)
\( \mu^*_k = \text{standard chemical potential of basis specie } k \)

An "equilibrium constant" for each formation reaction may also be calculated from the current estimate to the equilibrium composition.

\[ \ln Q_i = \ln a_i - \sum_{k=1}^{E} v_{ik} \ln a_k \]

where: \( a_i = \gamma_i n_i p_i / n_T \) (activity of specie \( i \))
\( \gamma_i = \text{activity coefficient} \)
\( n_T = \text{total moles of species in the same phase as specie } i \)
\( p_i = \frac{(P/P_0)}{(1)} \) vapor species
\( p_i = \) (nonvapor species)
Defining the extent of reaction, $\xi_i$, as

$$\xi_i = (n'_j - n_j)/n_j$$

where: $n'_j = \text{composition of specie } j \text{ at reaction extent } \xi_i$

the "equilibrium constant" as calculated from the current composition may be written as

$$\ln Q_i = \ln [\beta_i(n_i + \xi_i)] - \sum_{k=1}^{E} \gamma_{ik} \xi_{ik}(n_k + \nu_{ik}\xi_i)$$

where: $\beta_i = \gamma_i \frac{P_i}{n_T}$

As an approximation assume that $\beta_i$ and $\nu_{ik}$ are constant for small changes in $\xi_i$. Introducing a function $\delta_i$ 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.

$$\frac{\ln K_{eq} - \ln Q_i}{\Delta \xi_i} \approx \frac{d \ln Q_i}{d \xi_i} \approx \frac{\xi_i}{n_i} - \sum_{k=1}^{E} \delta_{ik} \Delta \xi_i$$

where: $\delta_i, \delta_k = 1 \text{ vapor phase}$

Thus the difference between the equilibrium constant for formation reaction $i$ as calculated from the Gibbs Free Energy ($K_{eq}$) 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 occurrence of negative molar amounts the effect of $\Delta \xi_i$ on the new composition must be tested. Thus, for the nonbasis species:

$$n'_i = n_i \Delta \xi_i$$

and for the basis species

$$n'_k = n_k - \sum_{i=1}^{vsc} \nu_{ik} \Delta \xi_i$$

where: $\Delta \xi_i = \Delta \xi_i$

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

$$\kappa = -n_k / \sum_{i=1}^{vsc} (-\nu_{ik} \Delta \xi_i)$$
to each of the basis species in the system and choosing the smallest positive value of $\kappa$ which results while $\kappa$ is constrained to be no greater than unity.

In order to assure convergence of the numerical scheme it is necessary to apply a convergence force. The Gibbs Free Energy of the system is given by

$$G = \sum_{i=1}^{vsc} n_i [u_i^* + RT \ln a_i]$$

(11)

The procedure used for determining the value of the convergence force, $\lambda$, is as follows.

1) Evaluate the derivative:

$$\left( \frac{dG}{d\lambda} \right)_{\lambda=1} = \frac{vsc}{\sum_{i=1}^{vsc} n_i \left[ u_i^* + R \ln a_i \right]}$$

where: $u_i^* = \beta_i n_i$

$$\Delta n_i = n_i^0 - n_i$$

If $\left( \frac{dG}{d\lambda} \right)_{\lambda=1} < 0$ then set $\lambda = 1$.

2) If $\left( \frac{dG}{d\lambda} \right)_{\lambda=1} > 0$ then evaluate:

$$\left( \frac{dG}{d\lambda} \right)_{\lambda=0} = \sum_{i=1}^{vsc} \Delta n_i [u_i^* + R \ln a_i]$$

(13)

The optimum value of $\lambda$ is then approximated by:

$$\lambda = \frac{\left( \frac{dG}{d\lambda} \right)_{\lambda=0}}{\left( \frac{dG}{d\lambda} \right)_{\lambda=1}}$$

Equation 14 represents a single step of a Regula-Falsi root finding algorithm which yields a sufficiently accurate estimate of the optimum value of the convergence force. Infrequently, equation 14 will predict a negative value for $\lambda$ and in this case $\lambda$ is set to 0.01 in order to allow the iterative solution to continue.
B.6 Example Calculation: The Gas Chloride System Source Zone

The results of an equilibrium calculation for the gas 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 700°C and 1 atm pressure. The inlet gas composition was 1% AsCl₃ and 99% H₂. The steady state liquid option (ISS=1) was active and excess solid SiO₂ 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

**STOCHIOMETRIC FORMULATION FOR DETERMINING EQUILIBRIUM COMPOSITIONS**

**THE GaAs CHLORIDE SYSTEM SOURCE ZONE: A TEST OF MCPEC 820C**

<table>
<thead>
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<th>HEAT CAPACITY CORRELATION COEFFICIENTS</th>
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<tbody>
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<td></td>
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<td>DRY NUCLEUS (KCAL/MOL-K)</td>
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<td>-0.0327000</td>
</tr>
<tr>
<td>Cl</td>
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<td>0.0327000</td>
</tr>
</tbody>
</table>

**TEMPERATURE:** 298 K

**PRESSURE:** 0.1013250 PA

The entropy and enthalpy of formation reference temperature and pressure are 298 K and 0.1013250 PA, respectively.

Maximun number of iterations allowed: 1000

Convergence criterion: 0.00000003

Output parameters: 0

The III-V liquid solution is at equilibrium with the III-V stoichiometric solid.
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**TOTAL GRAM-MOLAR OF EACH ELEMENT FROM INPUT DATA AND AS CALCULATED FROM THE INITIAL COMPOSITION ESTIMATES**

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<th>Element</th>
<th>Input Data</th>
<th>Calculated</th>
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<td>0.01590E+01</td>
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**INPUT DATA AND INITIAL COMPOSITION ESTIMATES**

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<tr>
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<th>Input Data</th>
<th>Calculated</th>
</tr>
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<tbody>
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<td>H</td>
<td>0.01590E+01</td>
<td>0.01590E+01</td>
</tr>
<tr>
<td>O</td>
<td>0.01590E+01</td>
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<tr>
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<tr>
<td>Si</td>
<td>0.01590E+01</td>
<td>0.01590E+01</td>
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<tr>
<td>Ca</td>
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STOICHIOMETRIC FORMULATION FOR DETERMINING EQUILIBRIUM COMPOSITIONS
THE GA/AS CHLORIDE SYSTEM SOURCE ZONE. A TEST OF HOMPEC.STOIC.

TEMPERATURE = 973.1 K
PRESSURE = 0.10133E+06 PA

EXECUTION DIAGNOSTICS
### Equilibrium Compositions for Calculated and Input Data

<table>
<thead>
<tr>
<th>Species</th>
<th>Phase</th>
<th>Mol Fraction</th>
<th>Eq Mol Fraction</th>
<th>Estimated Composition Uncertainty</th>
<th>Chemical Potential (kcal/6-mole)</th>
<th>Activity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1V1</td>
<td>VAPOR</td>
<td>0.71626E-09</td>
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#### Total ppm-moles of Each Element from Input Data

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<th>Calculated</th>
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#### Mol Fraction of Silicon Species in Vapour Phase

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<th>Mol Fraction</th>
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<td>1V2</td>
<td>0.13058E-01</td>
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<tr>
<td>1V3</td>
<td>0.34903E-04</td>
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<tr>
<td>1V5</td>
<td>0.12579E-02</td>
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<tr>
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<td>0.57979E-10</td>
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<tr>
<td>2V2</td>
<td>0.34039E-21</td>
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<tr>
<td>2V3</td>
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<tr>
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#### Summary

- **Temperature**: 973.2 K
- **Pressure**: 0.101332566020517517525E+01 Pa

---

**Note:** The document contains a table with equilibrium compositions presented in a tabular format. The calculations are related to chemical potential and activity coefficients for various species, indicating a detailed analysis of equilibrium states under specific conditions.
A SET OF INDEPENDENT REACTION EQUATIONS FOR THIS SYSTEM IS AS FOLLOWS:

<table>
<thead>
<tr>
<th>Equation</th>
<th>Reaction</th>
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<tbody>
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<td>1.00 AS2 (V)</td>
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<tr>
<td>1.00 AS3 (V)</td>
<td>(-0.750E+00) AS4 (V)</td>
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<tr>
<td>1.00 H CL (V)</td>
<td>(-0.500E+00) H2 (V)</td>
</tr>
<tr>
<td>1.00 GA-CL (V)</td>
<td>(-0.101E+01) GA-AS1 (X) + (0.100E+01) GA-CL (V)</td>
</tr>
<tr>
<td>1.00 AS-H3 (V)</td>
<td>(-0.150E+01) H2 (V)</td>
</tr>
<tr>
<td>1.00 GA-CL3 (V)</td>
<td>(-0.201E+01) GA-AS1 (X) + (0.100E+01) GA-CL (V)</td>
</tr>
<tr>
<td>1.00 GA (V)</td>
<td>(-0.101E+01) GA-AS1 (X) + (-0.131E+02) AS4 (V)</td>
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<td>(-0.500E+00) H2 (V) + (0.250E+00) AS4 (V)</td>
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<td>1.00 SI-H4 (V)</td>
<td>(-0.100E+01) SI-02 (S) + (0.400E+01) H2 (V) + (-0.200E+01) H2-O (V)</td>
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<td>1.00 H (V)</td>
<td>(-0.500E+00) H2 (V)</td>
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<td>1.00 SI-H3-CL</td>
<td>(-0.101E+01) SI-02 (S) + (0.150E+01) SI-02 (S) + (-0.201E+01) GA-AS1 (X) + (0.100E+01) GA-CL (V)</td>
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<td>1.00 AS (V)</td>
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<tr>
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<tr>
<td>1.00 CL (V)</td>
<td>(-0.101E+01) GA-AS1 (X) + (0.100E+01) GA-CL (V)</td>
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<tr>
<td>1.00 SI-CL4</td>
<td>(-0.100E+01) SI-02 (S) + (0.250E+01) H2 (V)</td>
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<tr>
<td>1.00 SI-CL3</td>
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</tr>
<tr>
<td>1.00 SI-CL2</td>
<td>(-0.100E+01) SI-02 (S) + (0.250E+01) H2 (V)</td>
</tr>
</tbody>
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1.20 AS-CL (V) = (-0.19E+01 SAX-AS(1-X)) + ( 0.50E+01 GA-CL (V) ) + ( -0.25E+00 AS4 (V) )
1.20 SI (V) = (-0.19E+01 SAX-AS(1-X)) + ( 0.79E+01 H2 (V) ) + ( -0.20E+01 H2-D (V) )
1.20 CL2 (V) = (-0.20E+01 SAX-AS(1-X)) + ( 0.50E+01 GA-CL (V) ) + ( 0.17E-02 AS4 (V) )
1.20 O-M (V) = (-0.50E+00 H2 (V) ) + ( 0.10E+01 H2-O (V) )
1.20 SI-CL2 (V) = (-0.20E+01 SAX-AS(1-X)) + ( 0.79E+01 GA-CL (V) ) + ( 0.25E+00 AS4 (V) )
1.20 SI-CL (V) = (-0.19E+01 SAX-AS(1-X)) + ( 0.20E+01 H2 (V) ) + ( -0.20E+01 H2-0 (V) )
1.20 SI2-CL (V) = (-0.20E+01 SAX-AS(1-X)) + ( 0.40E+01 H2 (V) ) + ( -0.40E+01 SAX-AS(1-X)) + ( 0.60E+01 GA-CL (V) )
1.20 O (V) = (-0.10E+01 H2 (V) ) + ( 0.10E+01 H2-O (V) )
1.20 O2 (V) = (-0.20E+01 H2 (V) ) + ( 0.20E+01 H2-O (V) )
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**Figure B29. The Wrap-up File**
Figure B30. The Data File
References
