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ON PHASE EQUILIBRIA
PHASE 2 - BINARY TWO-PHASE SOLIDS

July 1976

RESEARCH DEPARTMENT



GRUMMAN AEROSPACE CORPORATION
BETHPAGE NEW YORK

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ON PHASE EQUILIBRIA

PART 2 - BINARY TWO-PHASE SOLIDS

RM-622

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ABSTRACT

Analysis of the Skylab M553 Experiment samples resulted in the hypothesis that the reduced gravity environment was altering some of the melting and solidification reactions. The present analytical study was conducted to identify those physical phenomena, properties, and experimental conditions which induce such changes. This report considers two-phase solids and eutectic, monotectic, peritectic, and syntectic reactions.

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1. INTRODUCTION

There is little doubt that exploration of the orbital low-*g* environment will lead to new products. Past experience has shown that every new working environment that has been discovered and explored has resulted in new products based on new technology. At the time a new environment is discovered or becomes readily accessible, investigators usually find it difficult to predict the kinds of products that will eventually result. This is because the environment has not been fully characterized, investigators have not experienced it first hand, nor have the processes of research, development, and pilot-plant operations yet matured. Most useful products stem from this sequence rather than from strictly theoretical considerations.

On the basis of our first-hand experience with Skylab II Space Processing experiments, we have characterized the low-*g* environment in terms of the physical phenomena, phase reactions, and phase diagrams fundamental to all materials processing. We anticipate that this characterization will provide immediate benefits to scientists intending to work with the low-*g* environment.

A previous report summarized our analysis of altered phase equilibria in low-*g* for simple systems. This report completes the phase diagram analysis for more complex systems and considers potential applications to processes and products.

2. ANALYTICAL RESULTS AND DISCUSSION

2.1 Effects of Gravity Dependent Pressure Reduction

As shown in the Phase 1 report (Ref. 1), a typical metallic liquid sample in a vacuum will experience a pressure reduction of approximately two to three orders of magnitude on transport from the one-g to the low-g environment. The total internal pressure within a typical metal drop is then reduced to approximately 10^{-1} mm Mg. Although this pressure drop was shown to have an insignificant effect on solid/liquid and liquid/liquid behavior, it could significantly affect liquid/vapor, liquid/liquid/vapor, or solid/liquid/vapor behavior. The possible effects are illustrated in Fig. 1 for a binary eutectic system, A-B. It is assumed in this diagram that at one-g the internal pressure is P_1 and at low-g the internal pressure is P_0 . At P_1 , the alloy can be heated above the melting point of the higher melting component A by an increment ΔT_1 before the more volatile component B would cavitate (i. e., cross the GL_B boundary), if localization persisted into the liquid state. At pressure P_0 the situation is quite different; the B component would melt first, at T_{QB} , but before reaching the

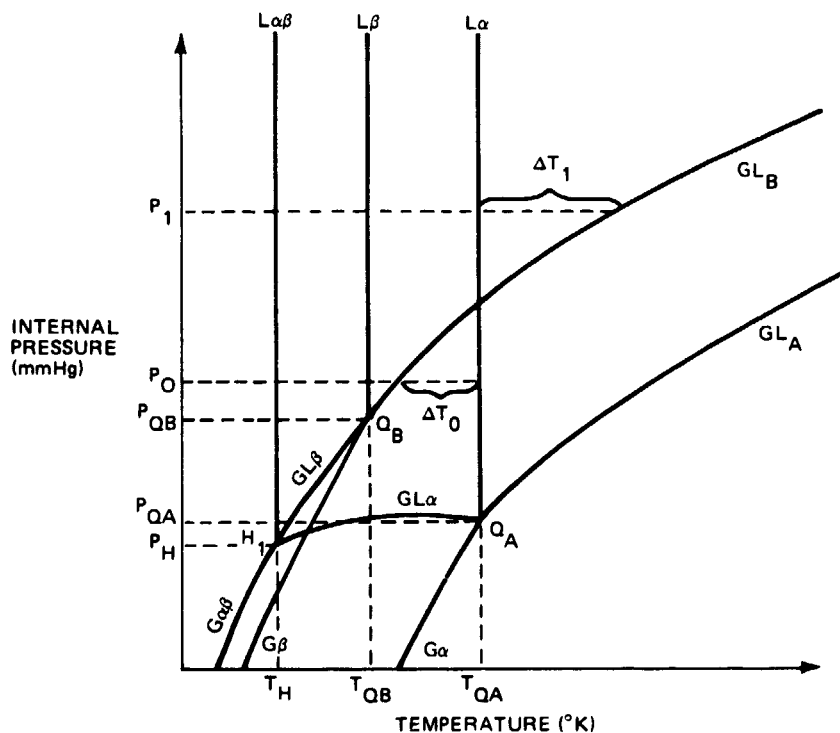


Fig. 1 Pressure - Temperature Protection For A Eutectic System A-B.

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melting point of the other binary phase (the $L\alpha$ line), the liquid would cavitate. Metallic gas bubbles of composition B would form, at a temperature T_0 below the melting point (T_{QA}) of component A.

If the internal pressure is lowered further and P_0 falls below P_{QB} , then the two-phase equilibria are superseded by a three phase reaction. Changes in phase reactions will differ depending on the magnitude of the internal pressure relative to the specific Pressure-Temperature (P-T) projection and the type of phase reaction. These changes will be dealt with specifically in subsequent sections.

It is important to note from the preceding that phase equilibria may realistically be expected to be modified in orbit because of gravity dependent pressure reductions within the liquid samples. It is of equal importance to note that in situations where the type of reaction remains unchanged in low-g, the onset temperatures of these reactions (e.g. cavitation) may be appreciably lowered. This greatly reduces the experimental tolerance to superheat and demands consideration in experiment planning or experiment design that will avoid such effects. Since this experimental design is straightforward and readily accomplished, the exploitation of these reactions is very attractive. We may utilize them directly, suppress them, or induce them at will which gives us total reaction control.

Finally, it is important to recognize that factors other than gravitationally dependent pressure reductions may affect solidification morphology. The near-absence of buoyancy forces and gravitationally driven convection makes possible solidification of arrays of disparate, immiscible materials that would demonstrate appreciable macroscopic segregation in one-g.

Alteration of morphology does not depend on reaction alteration alone and can exist in solid/liquid, liquid/liquid, liquid/vapor, and three phase reaction. Systems involving reaction alteration, and formation of a gaseous metallic phase, are, by nature of the density difference between the vapor and liquid or solid, ideal systems in which to demonstrate these effects.

2.2 Mathematical Terminology

Because of the large number of variations within one phase reaction type, it is necessary to approach the reaction possibilities systematically. This is best done mathematically and with reference to Fig. 1 the following notation will be used throughout this report: triple

points will be noted by Q with subscripts identifying the component (as Q_A and Q_B in Fig. 1). Quadruple points will be denoted by H with subscripts (as H_1 in Fig. 1); temperatures and pressures at these points will be denoted by T_{QA} , T_{QB} , and T_{H1} , P_{QA} , P_{QB} , and P_{H1} , respectively. The location of the quadruple point relative to the triple points will vary from system to system and for the case illustrated would be noted: $T_{QA} > T_{QB} > T_{H1}$ and $P_{QB} > P_{QA} > P_{H1}$.

2.3 Clausius-Clapeyron and Phase Rule Considerations

The Clausius-Clapeyron equation, as given below, is useful in estimating the volume fraction of reacting phase.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

This affords an opportunity to draw more realistic Temperature-Composition (T-X) phase diagrams from isobaric sections of P-T projections. This is particularly true when a gaseous phase is involved as the volume of the gas is so much greater than that of either the solid or liquid. In all of our cases we will treat heat of reactions (ΔH) as positive endothermic on heating, T as positive, and dP/dT as defined by the slope of the appropriate curve on the P-T projection at the point of interest. We may then infer the sign of ΔV for the reaction in question. For example, Fig. 2 shows a $GL\beta$ line of positive dP/dT , whereas the $GL\alpha$ line is of negative slope. Considering that H and T are positive for both cases, then V must be of opposite sign for these two cases (positive for $GL\beta$ and negative for $GL\alpha$). This means that for the $GL\beta$ reaction $V_G > V_\beta + V_L$ and for the $GL\alpha$ reaction $V_L < V_\alpha + V_G$. Both of these volumetric criteria are reasonable physically and thus the reaction could take place. When numerical substitutions are made, relative volumes of phases may be estimated.

The P-T projection for a binary system includes the univariant (two phase) and invariant (three phase) equilibria of the separate components as well as the univariant (three phase) and invariant (four phase) equilibria of the binary reactions. The sequence of univariant, three phase, reactions about an invariant, four phase, quadruple point has a relationship dependent upon the solute content of the phases (Ref. 2). The phases are numbered 1, 2, 3, 4 in order of increasing or decreasing solute content. The three phase reactions about a quadruple point are then numbered by the phase that is missing, e.g., reaction between phases 2, 3, 4 is numbered 1. The metastable extension is primed, and the sequence, either clockwise or counterclockwise, must be 1-2'-3-4'-1'-2-3'-4. Eutectic and monotectic reactions

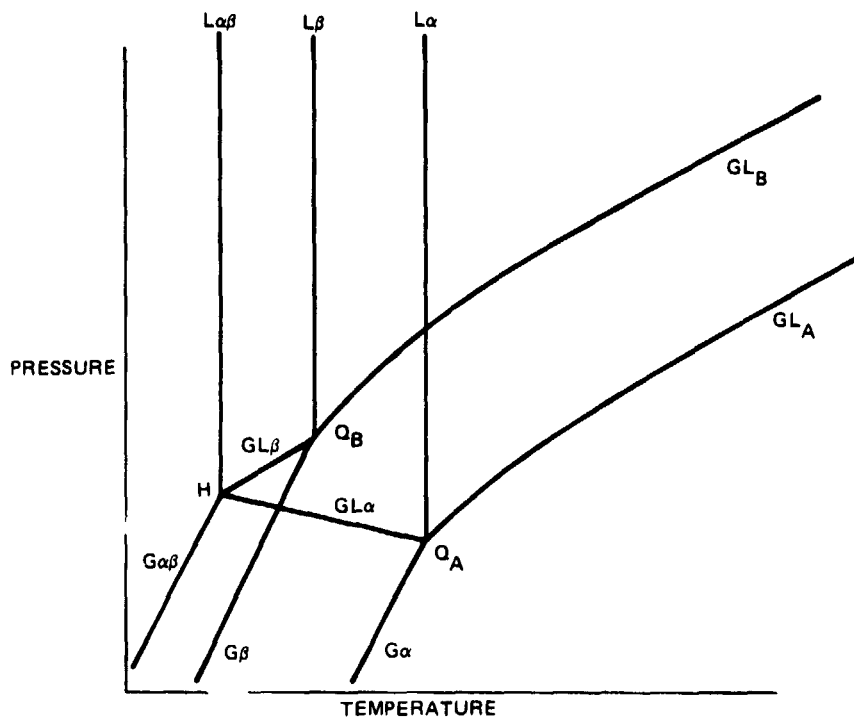


Fig. 2 Pressure Temperature Protection For A Eutectic System A-B.

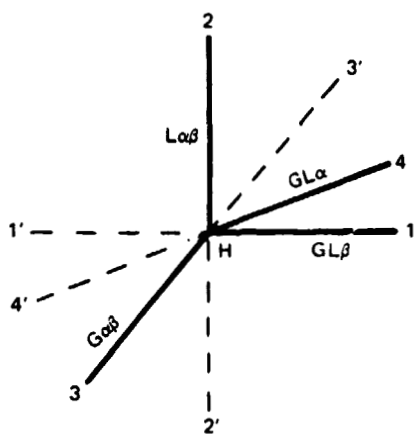
are such that two of the univariant lines proceed toward higher temperatures, one is near-vertical, and one proceeds to lower temperatures (Fig. 3a, b). In peritectic and syntectic reactions, arrangements of the univariant lines are reversed and one is near-vertical, two proceed to lower temperatures, and one toward higher temperature (Fig. 3c, d). This simple check is based on thermodynamics and the phase rule and serves the purpose of defining possible variations in the disposition of univariant lines (dP/dT) about quadruple points in the hypothetical P-T projections. Thus, all of the mathematically defined P-T possibilities may be checked in a direct manner against thermodynamic criteria.

2.4 Phase Relations: Two-Phase Solids

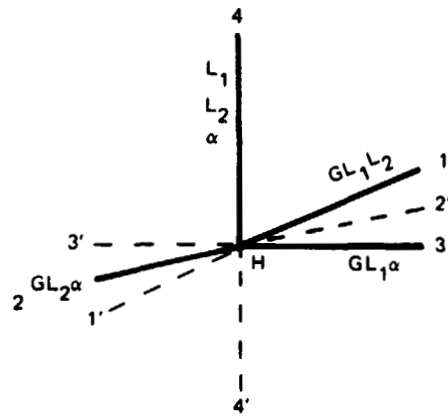
The effects of pressure reduction are presented systematically by reaction types in the following sequence: eutectic, peritectic, monotectic, and syntectic. Low pressure reactions will be presented in tabulated equation form, and only selected reactions will be illustrated.

2.4.1 Eutectic

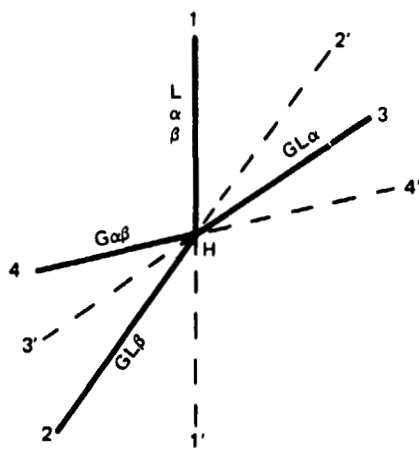
The eutectic quadruple point involves equilibria between the G, L, α , and β phases. For



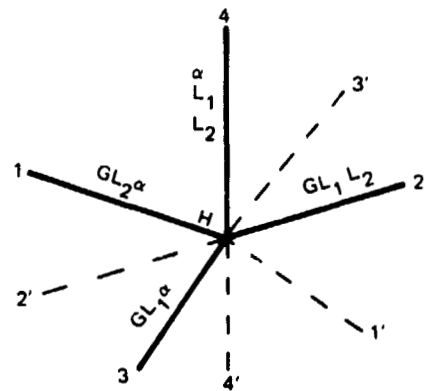
(a) Eutectic ($\alpha = 1, G = 2, L = 3, \beta = 4$)



(b) Monotectic ($\alpha = 1, L_1 = 2, L_2 = 3, G = 4$)



(c) Peritectic ($G = 1, \alpha = 2, \beta = 3, L = 4$)



(d) Syntectic ($L_1 = 1, \alpha = 2, L_2 = 3, G = 4$)

Fig. 3 Schematic Representation of Arrangement of Univariant Lines About a Quadruple Point H, for Binary Reactions With Two Solid Phases.

each P-T projection there are four pressure ranges that will give discretely different isobaric sections. Each of these isobaric sections will be characteristic of its pressure range. The four pressure ranges may be qualitatively described as being P_1 above both triple points and the quadruple point, P_2 below the uppermost critical point but above the other two, P_3 below the two uppermost points but above the third, and P_4 below all three critical points. In all binary eutectic systems, internal pressures in the range P_1 will result in an isobaric T-X diagram that is simply a eutectic solid/liquid reaction with a discrete gas envelope at higher temperatures, while the range P_4 will always result in a eutectic evaporative reaction. At the intermediate pressures P_2 and P_3 the relative positions of the triple points and the quadruple point will determine the isobaric reaction.

All possible relative positions are tabulated in Table 1. The intermediate reactions are listed in Table 2. All possible isobaric sections are illustrated in Figs. 4-9 and each invariant reaction is indicated adjacent to the T-X diagram.

Figures 4-9 show that cavitation can occur below the melting point of one or both of the constituent elements, at reduced internal pressures. This is an important concept in space processing since the $L\alpha G$ and $L\beta G$ reactions are sensitive to pressure changes and the reaction temperatures can be lowered significantly by pressure reduction. It has been shown that the orbital environment can reduce the internal pressure in liquids (Ref. 1) which may result in significant shifts in reaction temperature.

Figures 6 and 8 illustrate unusual reactions where a liquid decomposes to a solid plus a vapor on cooling and Fig. 9 shows a more complex reaction with the same behavior. Both offer the possibility of fabricating controlled arrays of second phase gas bubbles during solidification. Alignment of such arrays have been shown to retard creep (Ref. 3).

Off-eutectic compositions will also benefit from space processing since the proeutectic constituent frequently segregates due to specific weight differences in 1-g. In the near absence of buoyancy forces and gravitationally driven convection, segregation of the proeutectic phase is minimized and a uniform morphology should result. This concept may also be an important consideration in the solution growth of single crystals as nucleated crystallites could grow without interaction with the surface, sidewalls, or bottom of container, without a

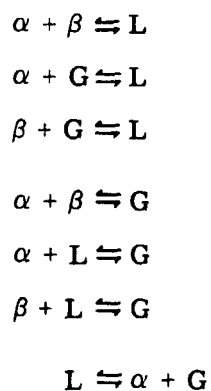
TABLE 1 VARIATION OF RELATIVE POSITIONS OF THE TRIPLE POINTS AND THE QUADRUPLE POINT WITHIN BINARY EUTECTIC PRESSURE-TEMPERATURE PROJECTIONS

-
1. $T_{QA} > T_{QB} > T_H$; $P_{QB} > P_{QA}$
 - a. $P_{QB} > P_{QA} > P_H$
 - b. $P_{QB} > P_H > P_{QA}$
 - c. $P_H > P_{QB} > P_{QA}$

 2. $T_{QA} > T_{QB} > T_H$; $P_{QA} > P_{QB}$
 - a. $P_{QA} > P_{QB} > P_H$
 - b. $P_{QA} > P_H > P_{QB}$
 - c. $P_H > P_{QA} > P_{QB}$

 3. $T_{QA} > T_{QB} > T_H$; $P_{QA} > P_{GLB}$ at $T_{QA} > P_{QB}$
 - a. $P_{QA} > P_{QB} > P_H$
 - b. $P_{QA} > P_H > P_{QB}$
 - c. $P_H > P_{QA} > P_{QB}$
-

TABLE 2 POSSIBLE REACTIONS OCCURRING WITHIN PRESSURE-TEMPERATURE PROJECTIONS OF BINARY EUTECTIC SYSTEMS



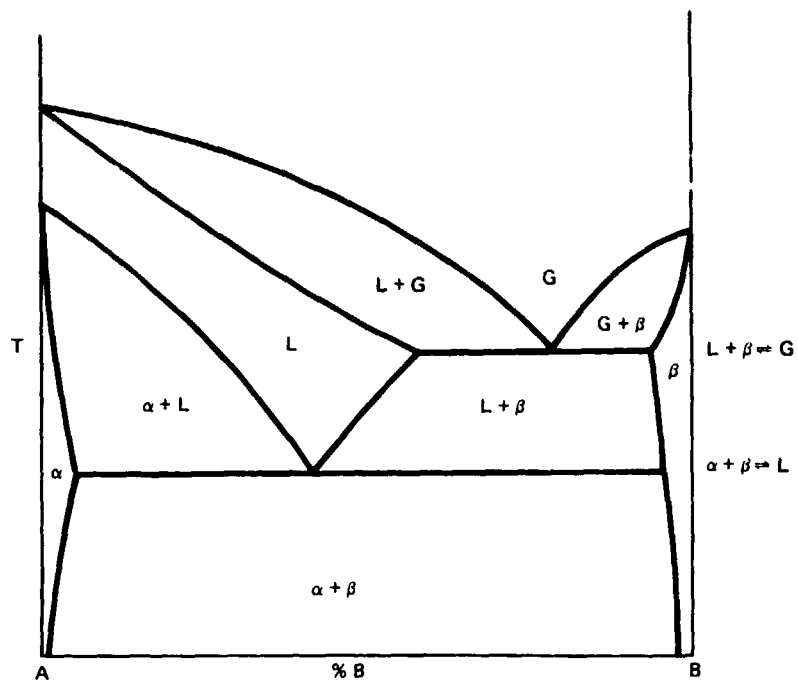


Fig. 4 T-X Diagram Incorporating $L\beta G$ and $\alpha\beta L$ Reactions

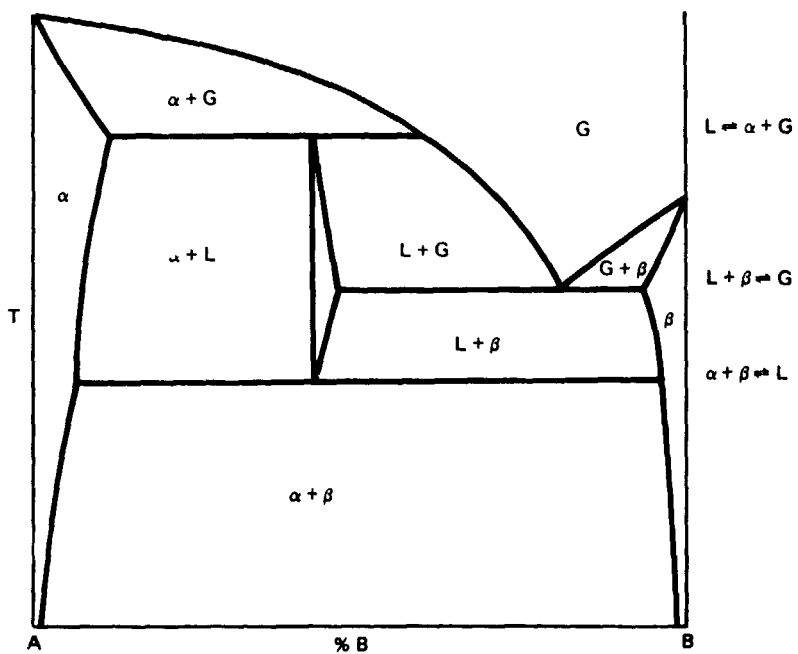


Fig. 5. -T-X Diagram Showing Above Reactions (Fig. 4) plus a $L \rightleftharpoons \alpha + G$ Reaction At Higher Temperatures

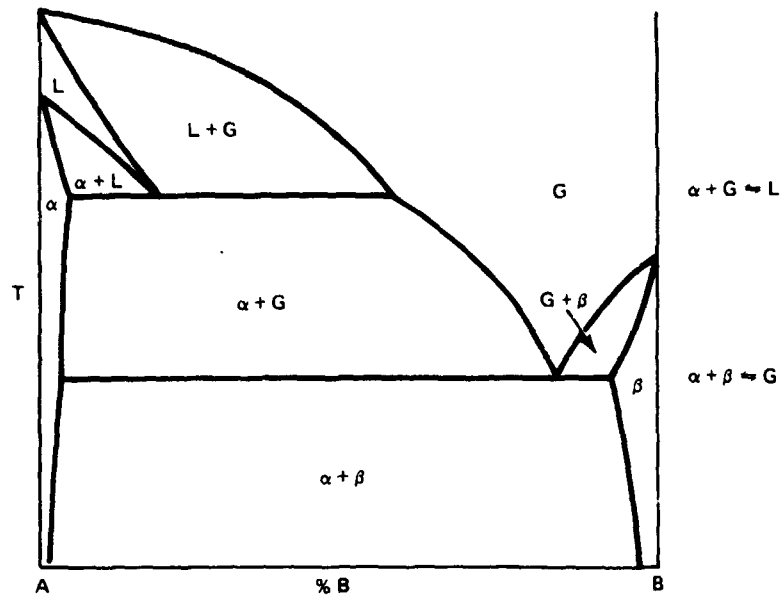


Fig. 6. - T-X Diagram Showing $\alpha\beta G$ and αGL Reactions

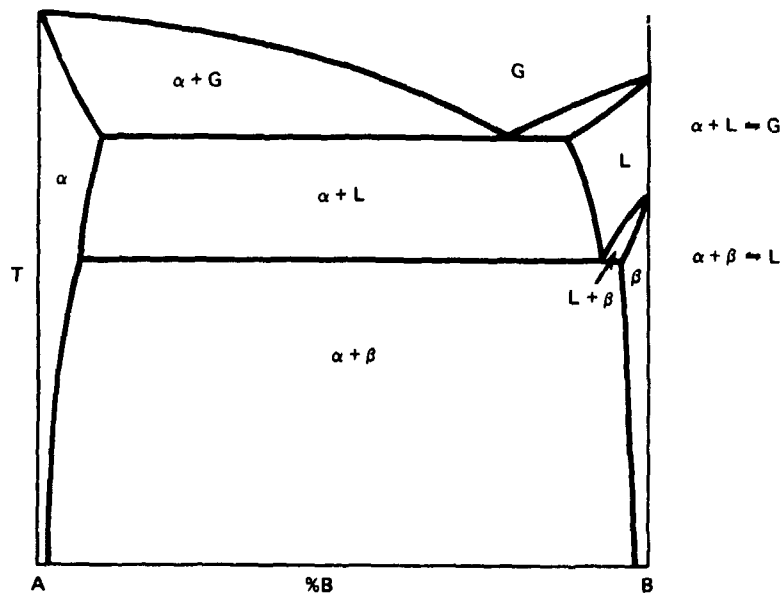


Fig. 7. - T-X Diagram Showing $\alpha\beta L$ and αLG Reactions

pedestal or sting.

In summary, we may conclude that eutectic systems may demonstrate reaction modification in the low-g environment or may simply demonstrate significant alteration of reaction temperature. Even if reaction modification does not take place in low-g, morphological modification is likely, because of the absence of buoyancy forces resulting from weight differences in coexisting phase.

2.4.2 Peritectic

The peritectic quadruple point involves G, L, α and β equilibria. All possible variations, of the quadruple point and triple point within peritectic binary systems, are presented in Table 3. As described in the previous section, there are four discretely different pressure ranges within each peritectic P-T projection. These pressure ranges were described in the previous section. For peritectic type systems, pressure range P_1 represents a peritectic

TABLE 3 VARIATION OF RELATIVE POSITIONS OF THE TRIPLE POINTS AND THE QUADRUPLE POINT WITHIN BINARY PERITECTIC PRESSURE-TEMPERATURE PROJECTIONS

-
1. $T_{QA} > T_H > T_{QB}; P_{QB} > P_{QA}$
 - a. $P_{QB} > P_{QA} > P_H$
 - b. $P_{QB} > P_H > P_{QA}$
 - c. $P_H > P_{QB} > P_{QA}$ (forbidden by sequential rule)
 - d. $P_H > P_{GLB} | T_H > P_{QB} > P_{QA}$ (forbidden by sequential rule)

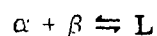
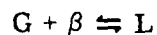
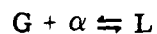
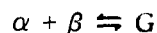
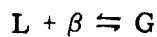
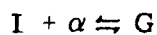
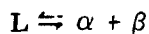
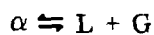
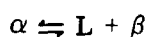
 2. $T_{QA} > T_H > T_{QB}; P_{QA} > P_{QB}$
 - a. $P_{QA} > P_{QB} > P_H$
 - b. $P_{QA} > P_H > P_{QB}$
 - c. $P_H > P_{QA} > P_{QB}$
 - d. $P_H > P_{GLB} | T_H > P_{QA} > P_{QB}$

 3. $T_{QA} > T_H > T_{QB}; P_{QA} > P_{GLB} | T_{QA} > P_{QB}$
 - a. $P_{QA} > P_{QB} > P_H$
 - b. $P_{QA} > P_H > P_{QB}$
 - c. $P_{QA} > P_H > P_{GLB} | T_H > P_{QB}$
 - d. $P_H > P_{QA} > P_{QB}$
-

reaction, with a discrete gas envelope at higher temperature, and in range P_4 a peritectic evaporative reaction occurs. The number of possible reactions is greater than that for the eutectic systems and these possibilities are listed in Table 4. It should be noted that the last six reactions listed in Table 4 are eutectic-type reactions; this demonstrates that the peritectic projection is unstable in P-T space. Eutectic systems by comparison demonstrated only one peritectic reaction, which is indicative of a reduced tendency toward instability in P-T space. Specific reactions, of a cavitative nature, are illustrated in Figs. 10-14. These are of interest, once again, because of their pressure sensitivity and the potential for creating controlled arrays of second phase bubbles during solidification in low-g.

Each of these isobaric T-X diagrams also illustrates the possibility of cavitation occurring at a temperature below the absolute melting point of one of the components; perhaps in the orbital environment it may be possible to control cavitation on melting as well as solidification. Such control offers another possibility of creating stable arrays of disparate phases. The problem of uniform nucleation on melting is not an insignificant one, however.

TABLE 4 REACTIONS OCCURRING IN BINARY PERITECTIC SYSTEMS, THROUGHOUT PRESSURE-TEMPERATURE SPACE



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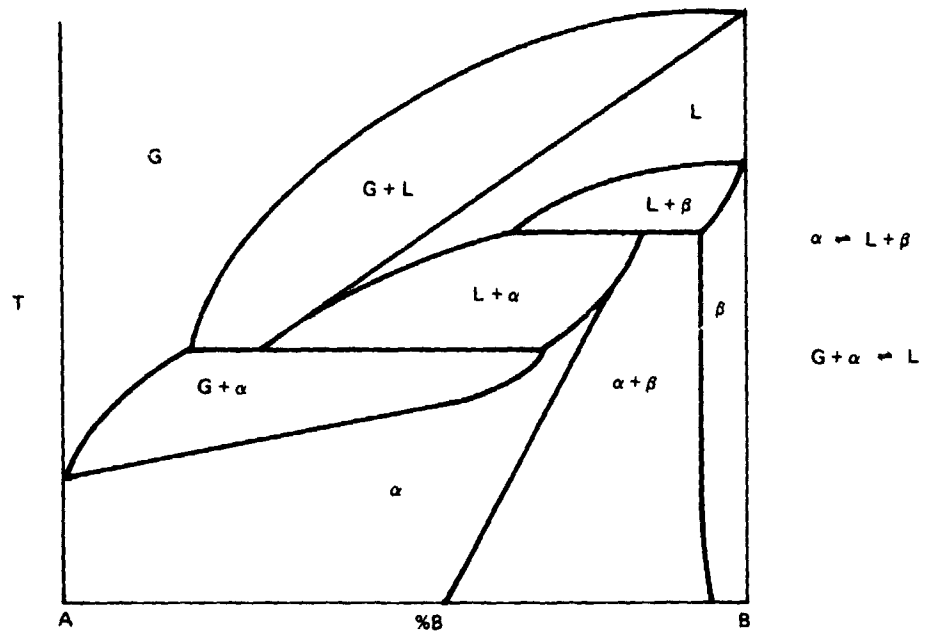


Fig. 10. - T-X Diagram Showing αGL and $\alpha L\beta$ Reactions

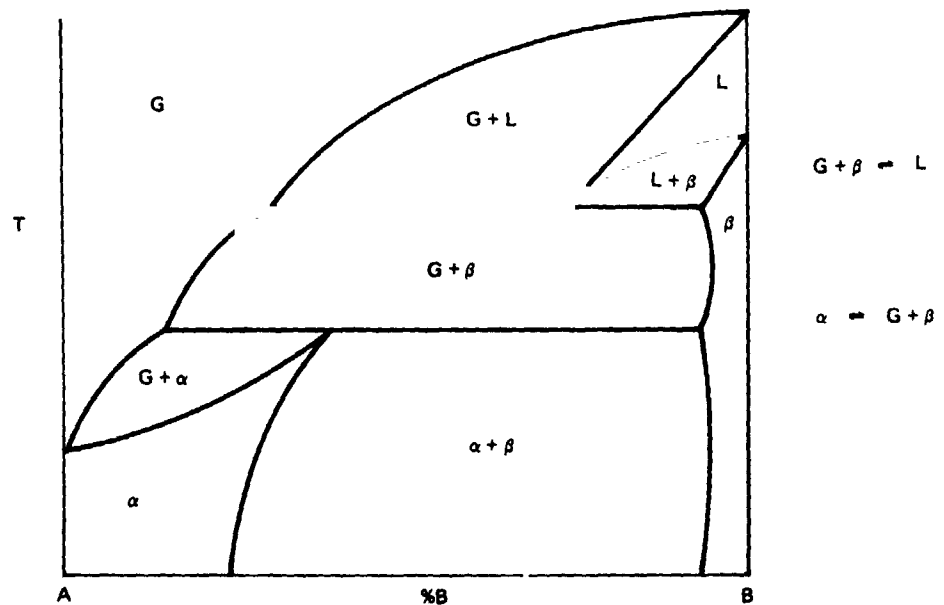


Fig. 11. - T-X Diagram Showing $\alpha G\beta$ and $G\beta L$ Reactions

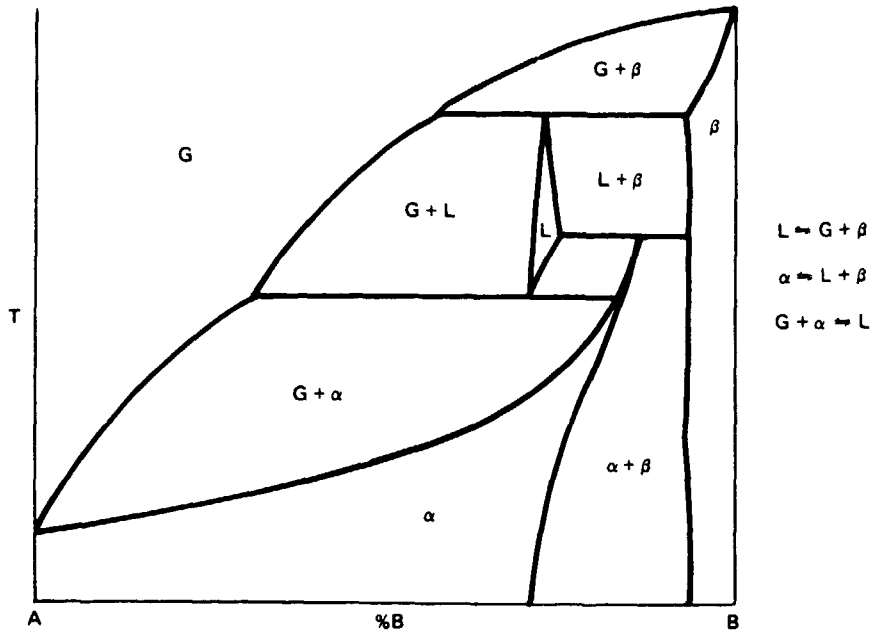


Fig. 12. — Complex T-X Diagram Showing $G\alpha L$, and $\alpha L\beta$, and $L G\beta$ Reactions

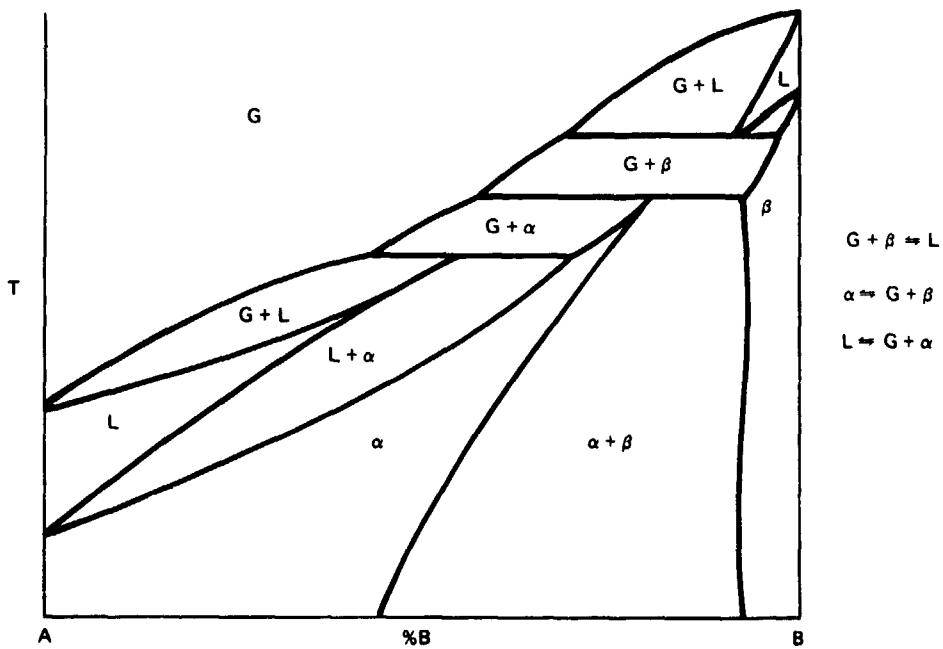


Fig. 13. — Complex T-X Diagram Showing $L G\alpha$, $\alpha G\beta$, and $G\beta L$ Reactions

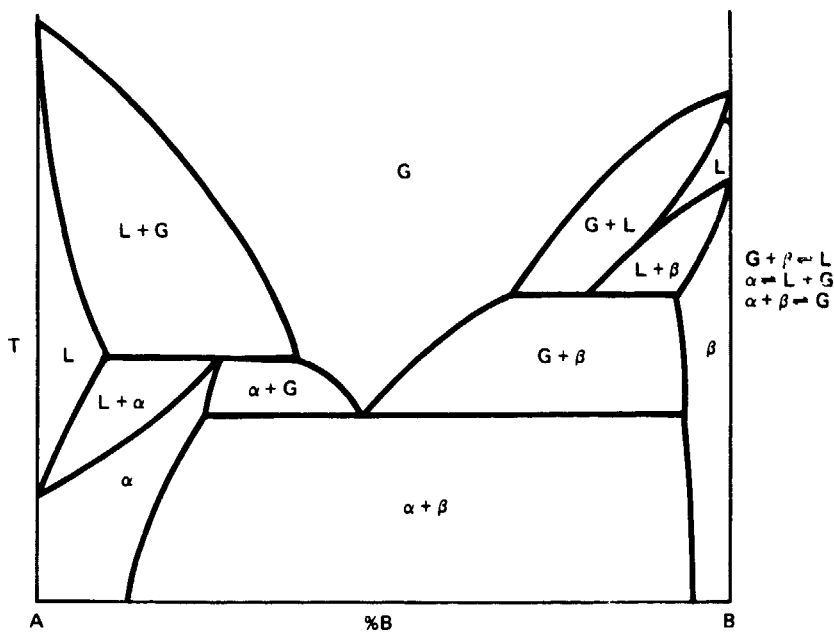


Fig. 14. - Complex T-X Diagram Showing $\alpha\beta G$, αLG , and $G\beta L$ Reactions.

The concept of morphological control in the orbital environment is particularly appropriate for peritectic systems because in each reaction shown in Table 3, a single phase, on heating, decomposes into two distinctly different phases. These phases are prone to gravitational segregation in one-g, whereas in the orbital environment segregation would be minimal or absent. The major question inherent in the concept of controlled cavitation is one of uniform nucleation and rate of gaseous agglomeration. If these phenomena can be experimentally controlled, then new morphologies can be created on both heating and cooling of peritectic systems. The control of nucleation and growth of bubbles during solidification is appreciably easier than during melting.

2.4.3 Monotectic

A monotectic is a eutectic-class reaction and in our considerations consists of a eutectic P-T projection (Fig. 1) with a projected region of liquid/liquid immiscibility or 'sail' superimposed (Fig. 15). The region of liquid/liquid immiscibility intersects the eutectic projection along the $GL\alpha$ line at a temperature between T_{QA} and T_{QB} . The superposition re-

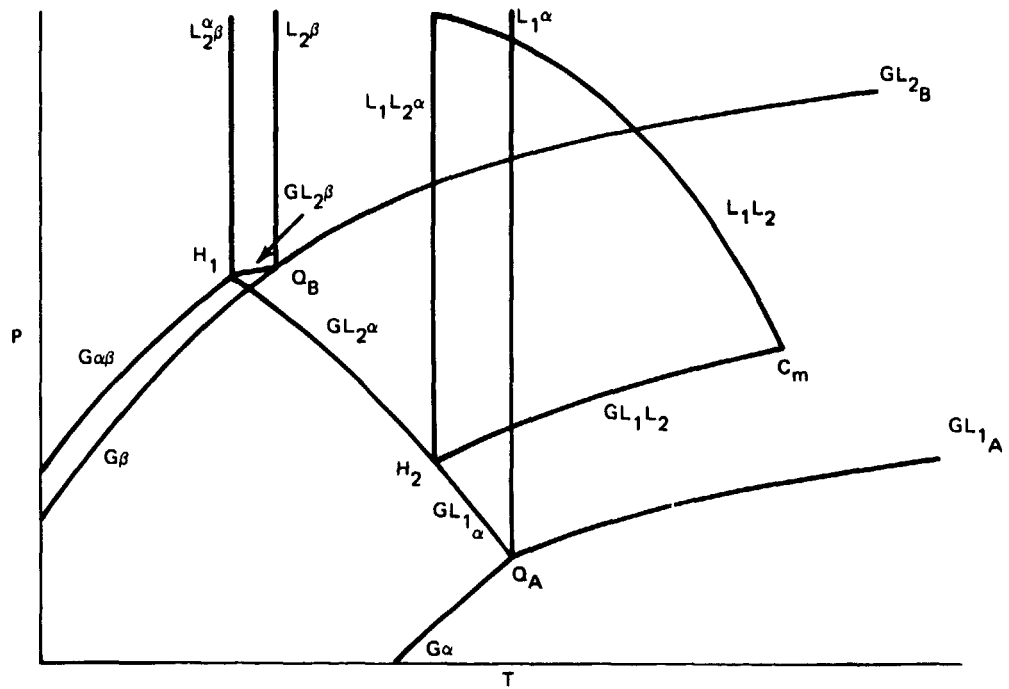


Fig. 15. - Monotectic Pressure - Temperature Projection For Binary Systems A-B.

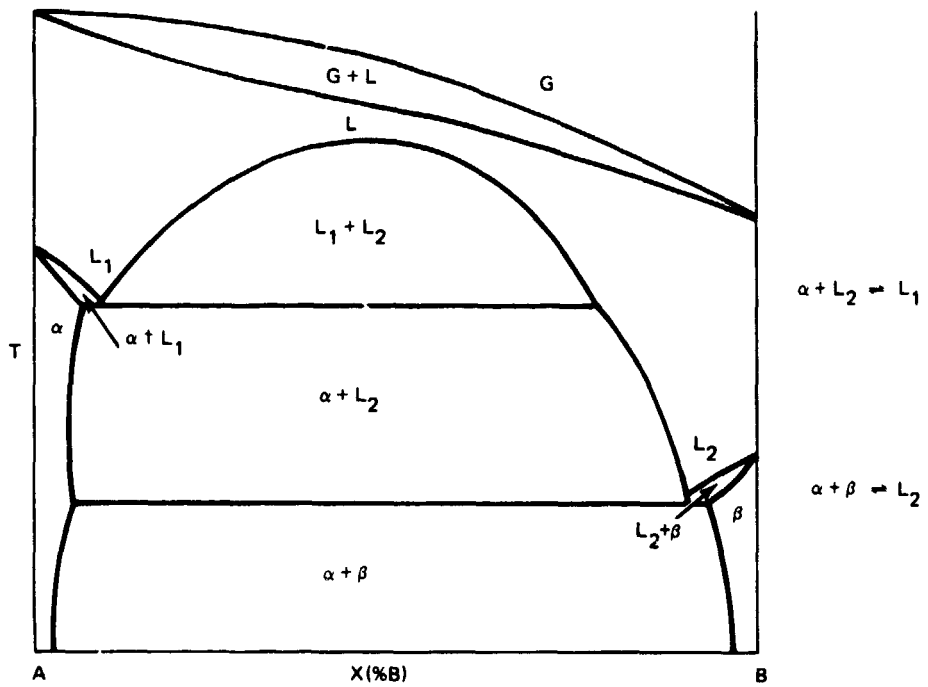


Fig. 16. - Monotectic Temperature - Composition Diagram For The System A-B.

TABLE 5 PRESSURE-TEMPERATURE PROJECTION VARIATIONS FOR BINARY MONOTECTIC SYSTEMS.

-
1. $T_{QA} > T_{H2} > T_{QB} > T_{HI}$; $P_{QB} > P_{QA}$
 - a. $P_{QB} > P_{QA} > P_{H2} > P_{HI}$
 - b. $P_{QB} > P_{HI} > P_{H2} > P_{QA}$
 - c. $P_{HI} > P_{QB} > P_{H2} > P_{QA}$
 - d. $P_{HI} > P_{H2} > P_{QB} > P_{QA}$

 2. $T_{QA} > T_{H2} > T_{QB} > T_{HI}$; $P_{QA} > P_{QB}$
 - a. $P_{QA} > P_{H2} > P_{QB} > P_{HI}$
 - b. $P_{QA} > P_{H2} > P_{HI} > P_{QB}$ $P_{H2} > P_{GLB}$ at T_{H2}
 - c. $P_{QA} > P_{H2} > P_{HI} > P_{QB}$ $P_{H2} < P_{GLB}$ at T_{H2}
 - d. $P_{HI} > P_{H2} > P_{QA} > P_{QB}$ $P_{H2} > P_{GLB}$ at T_{H2}
 - e. $P_{HI} > P_{H2} > P_{QA} > P_{QB}$ $P_{H2} > P_{GLB}$ at T_{H2}
 - f. $P_{QA} > P_{QB} > P_{H2} > P_{HI}$

 3. $T_{QA} > T_{H2} > T_{QB} > T_{HI}$; $P_{QA} > P_{GLB}$ at $T_{QA} > P_{QB}$
 - a. $P_{QA} > P_{H2} > P_{QB} > P_{HI}$
 - b. $P_{QA} > P_{H2} > P_{HI} > P_{QB}$
 - c. $P_{HI} > P_{H2} > P_{QA} > P_{QB}$
 - d. $P_{QA} > P_{QB} > P_{H2} > P_{HI}$
-

sults in a second quadruple point (H_2) with G, L_1 , L_2 , and α in equilibrium, as shown in Fig. 15. The variations within monotectic projections are tabulated in Table 5 and involve perturbations of both quadruple points. This tabulation considers only the relative location of H_2 and does not detail the extent, in the pressure or temperature directions, of the 'sail'. The latter is an important consideration, and may actually be the determining factor in defining the T-X behavior in any given system and pressure regime. As the extent of this region can only be defined experimentally, the P-T projections shown are somewhat arbitrary, however, all perturbations have been considered analytically.

All possible reactions within monotectic systems, throughout P-T space, are listed in Table 6. While it would appear that four possible reactions are missing, the thermodynamic rule of progression (Ref. 5) prohibits them. Three of the four excluded reactions are of the

TABLE 6 REACTIONS OCCURRING IN BINARY MONOTECTIC SYSTEMS, THROUGHOUT PRESSURE-TEMPERATURE SPACE.

| | |
|---|--|
| $\alpha + \beta \rightleftharpoons L$ | (eutectic) |
| $\alpha + \beta \rightleftharpoons L_2$ | |
| $G + \beta \rightleftharpoons L_2$ | |
| $G + \alpha \rightleftharpoons L_2$ | |
| $\alpha + \beta \rightleftharpoons G$ | |
| $L_2 + \beta \rightleftharpoons G$ | |
| $L_1 + L_2 \rightleftharpoons G$ | |
| $\alpha + L_2 \rightleftharpoons G$ | |
| $\alpha + L_2 \rightleftharpoons L_1$ | (monotectic) |
| $\alpha + G \rightleftharpoons L_1$ | |
| $L_2 + G \rightleftharpoons L_1$ | |
| $L_2 \rightleftharpoons L_1 + G$ | |
| $L_2 \rightleftharpoons \alpha + G$ | |
| $L_1 \rightleftharpoons \alpha + G$ | |
| $\left. \begin{array}{l} L_1 \rightleftharpoons L_2 + G \\ L_1 \rightleftharpoons L_2 + \alpha \\ L_2 \rightleftharpoons L_1 + \alpha \\ L_2 + G \rightleftharpoons L_1 \end{array} \right\}$ | Perturbations Excluded Thermodynamically |

peritectic type. The other excluded reaction is a eutectic involving the GL_1L_2 line. The most direct evolution of this reaction sequence would be on crossing the L_1L_2 line before the GL_1L_2 line. This is clearly impossible so we conclude that these four reactions cannot occur.

A close look at Table 6 demonstrates manifestation of eutectic behavior in monotectic systems. Previously presented eutectic reactions (Figs. 5, 6, 7 and 9) demonstrate all of the reactions in Table 6 with the exception of those involving liquid/liquid immiscibility. These latter are illustrated in Figs. 16-18. While all of the behavioral characteristics representative of the eutectics are applicable to monotectic systems, we also must consider the ramifications of the immiscibility in low-g.

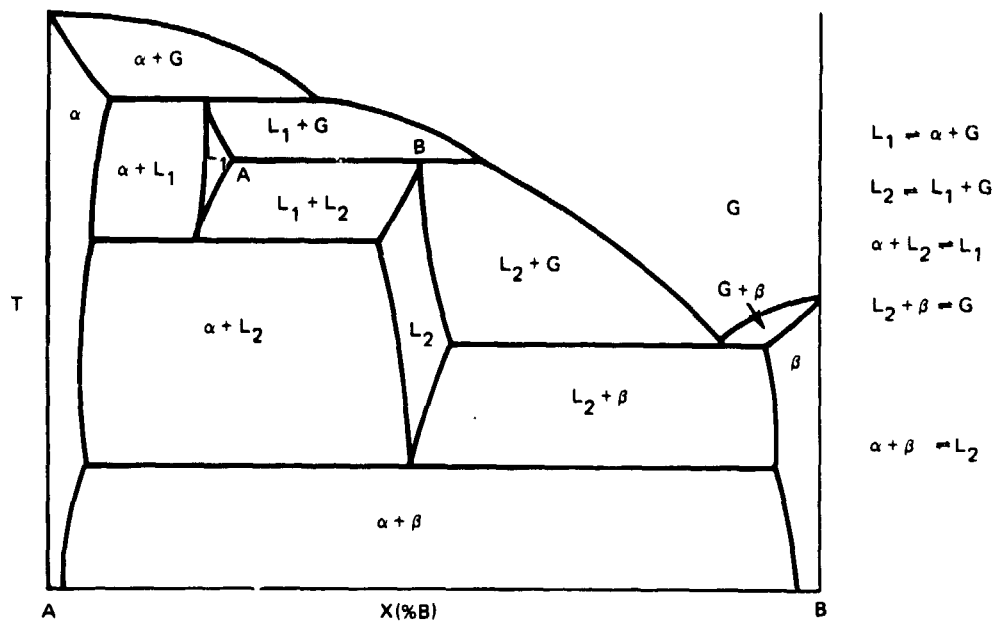


Fig. 17. - T-X Diagram Showing $\alpha\beta L_2$, $L_2\beta G$, $\alpha L_2 L_1$, $L_2 L_1 G$, and $L_1 \alpha G$ Reactions.

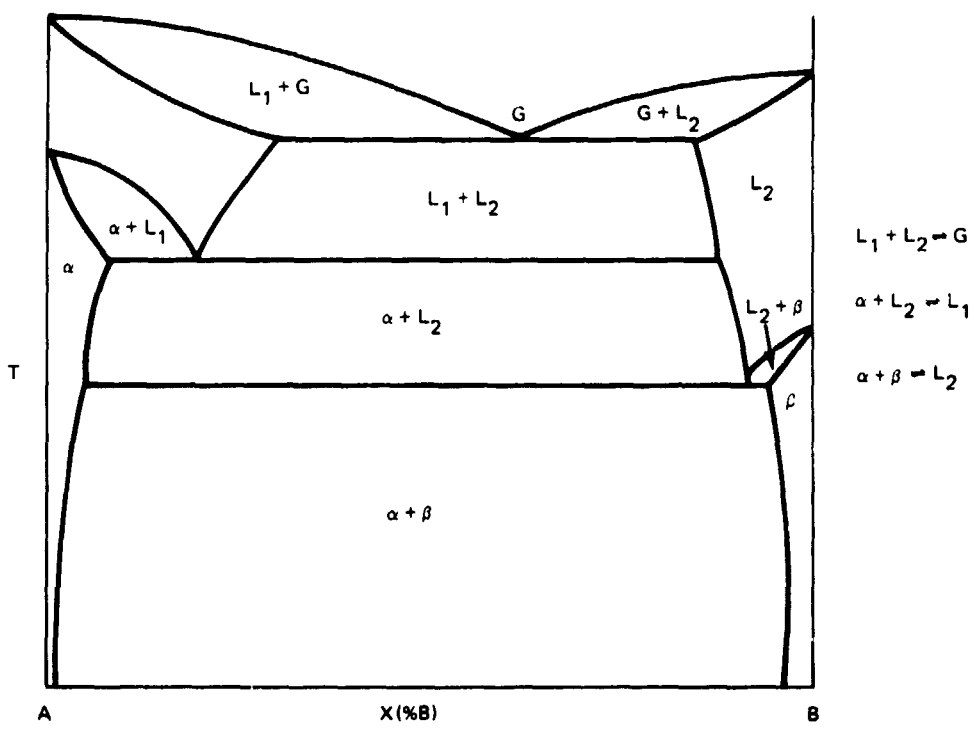


Fig. 18. - T-X Diagram Showing $\alpha\beta L_2$, $\alpha L_2 L_1$, and $L_1 L_2 G$ Reactions.

Figure 16 illustrates a normal monotectic T-X diagram. Gravitationally dependent pressure effects would not be expected to alter these relations appreciably unless the pressure reduction was such that the gas envelope intersected the $L_1 L_2$ region, resulting in an invariant $GL_1 L_2$ reaction. The onset temperature of this reaction would vary appreciably with changes in internal pressure. Even if reaction modification did not take place, the near absence of gravitational convection and sedimentation should result in atypical dispersions of the L_1 , L_2 phases and/or the α , L_2 phases. This is significant in controlling the solidification morphology of immiscible materials.

Figures 17 and 18 illustrate the balance of reactions that are possible within monotectic systems. Perhaps the most significant feature occurs between points A and B in Fig. 17. Upon crossing AB $L_1 + L_2 \rightleftharpoons L_1 + G$. The significance of this is that cavitation could be induced at prescribed locations (the site of discrete L_2 particles). This might result in a uniform array of pores within the fluid (L_1) body which might be retained during solidification. Applications of such forms are considered in Section 3. We may then conclude that both controlled reaction modification and controlled morphological modification are feasible within monotectic systems in the low-g environment but impractical terrestrially.

2.4.4 Syntectic

In a syntectic system the 'sail', which is the projection of the region of liquid/liquid immiscibility, meets the extended peritectic GL projection at a quadruple point. The quadruple point is located, in P-T space, such that $T_H > T_{QA} > T_{QB}$ and marks the four phase equilibria between G, L_I , L_{II} and α . All of the thermodynamically acceptable mathematical perturbations of the triple and quadruple points are listed in Table 7 and possible phase reactions in Table 8. The mathematical possibilities must be tested thermodynamically utilizing the rule of progression previously described. Because of the extension of the peritectic $GL\alpha$ line to temperatures in excess of T_{QA} , note that location of the quadruple point below both of the GL projections, at T_H , is prohibited and within any isobaric section it is impossible for a three phase invariant reaction to exist at higher temperatures than all of its binary constituents.

Reference to Table 8 indicates that the region of liquid/liquid immiscibility adds some reaction possibilities to those documented within the peritectic parent projection (Table 4). The differences shown are limited to those imposed by the immiscibility and those imposed by the secondary peritectic have been omitted. We have utilized a peritectic reaction as the

TABLE 7 QUADRUPLE AND TRIPLE POINT PERMUTATIONS WITHIN BINARY
 SYNTECTIC PRESSURE-TEMPERATURE PROJECTIONS WITH A PERITECTIC
 SECONDARY REACTION.

-
1. $T_{H2} > T_{QA} > T_{HI} > T_{QB}; P_{QB} > P_{QA}$
 - a. $P_{QB} > P_{H2} > P_{HI} > P_{QA}$
 - b. $P_{QB} > P_{HI} > P_{H2} > P_{QA}$
 - c. $P_{H2} > P_{QB} > P_{HI} > P_{QA}$
 - d. $P_{H2} > P_{QB} > P_{QA} > P_{HI}$
 - e. $P_{QB} > P_{H2} > P_{QA} > P_{HI}$

 2. $T_{H2} > T_{QA} > T_{HI} > T_{QB}; P_{QA} > P_{GLB} | QA > P_{QB}$
 - a. $P_{H2} > P_{GLA} | H2 > P_{QA} > P_{QB} > P_{HI}$
 - b. $P_{GLA} | H2 > P_{H2} > P_{QA} > P_{QB} > P_{HI}$
 - c. $P_{QA} > P_{H2} > P_{GLB} | H2 > P_{QB} > P_{HI}$
 - d. $P_{H2} > P_{GLA} | H2 > P_{QA} > P_{HI} > P_{QB}$
 - e. $P_{GLA} | H2 > P_{H2} > P_{QA} > P_{HI} > P_{QB}$
 - f. $P_{QA} > P_{H2} > P_{GLB} | H2 > P_{HI} > P_{QB}$
 - g. $P_{H2} > P_{GLA} | H2 > P_{QA}$

 3. $T_{H2} > T_{QA} > T_{HI} > T_{QB}; P_{QA} > P_{QB}$
 - a. $P_{H2} > P_{GLB} | H2 > P_{GLA} | H2 > P_{QA} > P_{QB} > P_{HI}$
 - b. $P_{GLB} | H2 > P_{H2} > P_{GLA} | H2 > P_{QA} > P_{QB} > P_{HI}$
 - c. $P_{H2} > P_{GLB} | H2 > P_{GLA} | H2 > P_{QA} > P_{HI} > P_{QB}$
 - d. $P_{GLB} | H2 > P_{H2} > P_{GLA} | H2 > P_{QA} > P_{HI} > P_{QB}$
 - e. $P_{H2} > P_{GLB} | H2 > P_{HI} > P_{QA} > P_{QB}$
 - f. $P_{H2} > P_{HI} > P_{GLB} | H2 > P_{QA} > P_{QB}$

 4. $T_{H2} > T_{QA} > T_{HI} > T_{QB}; P_{QA} > P_{QB}$
 - a. $P_{QA} > P_{H2} > P_{HI} > P_{QB}$
 - b. $P_{H2} > P_{QA} > P_{HI} > P_{QB}$
 - c. $P_{H2} > P_{GLA} | H2 > P_{QA} > P_{HI} > P_{QB}$
 - d. $P_{QA} > P_{H2} > P_{HI} > P_{QB}$
 - e. $P_{H2} > P_{QA} > P_{HI} > P_{QB}$
 - f. $P_{H2} > P_{GLA} | H2 > P_{QA} > P_{HI} > P_{QB}$
-

TABLE 7 QUADRUPLE AND TRIPLE POINT PERMUTATIONS WITHIN BINARY
 SYNTECTIC PRESSURE-TEMPERATURE PROJECTIONS WITH A PERITECTIC
 SECONDARY REACTION (Continued)

-
- g. $P_{H2} > P_{HI} > P_{GL_A} \mid H2 > P_{QA} > P_{QB}$
 - h. $P_{H2} > P_{GL_A} \mid H2 > P_{HI} > P_{QA} > P_{QB}$
 - i. $P_{HI} > P_{H2} > P_{GL_A} \mid H2 > P_{QA} > P_{QB}$
 - j. $P_{HI} > P_{GL_A} \mid H2 > P_{H2} > P_{QA} > P_{QB}$
-

TABLE 8 THREE PHASE REACTIONS POSSIBLE WITHIN THE FOUR-PHASE G, L₁, L₂,
 AND α SYNTECTIC PRESSURE-TEMPERATURE PROJECTIONS.

-
- $\alpha \rightleftharpoons L_1 + L_2$
 - $\alpha \rightleftharpoons L_1 + G$
 - $\alpha \rightleftharpoons L_2 + G$
 - $L_2 \rightleftharpoons \alpha + G$
 - $L_2 \rightleftharpoons L_1 + G$
 - $L_1 \rightleftharpoons L_2 + G$
 - $L_1 \rightleftharpoons \alpha + G$
 - $G + \alpha \rightleftharpoons L_2$
 - $G + \alpha \rightleftharpoons L_1$
 - $L_2 + \alpha \rightleftharpoons L_1$
 - $L_2 + \alpha \rightleftharpoons G$
 - $L_1 + \alpha \rightleftharpoons G$
 - $L_1 + L_2 \rightleftharpoons G$
 - $L_1 + \alpha \rightleftharpoons L_2$
 - $L_2 \rightleftharpoons \alpha + L_1$
 - $L_1 \rightleftharpoons \alpha + L_2$
 - $G + L_1 \rightleftharpoons L_2$
 - $G + L_2 \rightleftharpoons L_1$
- } Perturbations Excluded Thermodynamically
-

secondary reaction throughout and peritectic reactions have been omitted as they do not affect the syntectic projection directly. That is, reaction variations, resulting from the syntectic ($GL_1 L_2 \alpha$) are shown in Table 8. Additional reactions occur, in P-T space, on cooling and these may be eutectic or peritectic in nature. The reader is referred to those sections in order to consider all possible three phase reactions resulting from the four phase equilibria involving G, α , β , and L_2 , which follows the G, L_1 , L_2 , α syntectic.

As was the case with the monotectic systems, the low gravity environment is of particular interest because macroscopic sedimentation will not occur in the liquid.

In those systems where the internal pressure reduction is sufficiently large, the $L_1 L_2$ critical behavior will be superseded by a $GL_1 L_2$ reaction. This is important for two reasons. First the $GL_1 L_2$ projection is highly sensitive to pressure in P-T space, and a relatively small pressure reduction can result in appreciable reduction in the onset temperature of the $GL_1 L_2$ reaction. This results in a gaseous phase being formed in a temperature regime where stable liquids exist in one-g. Secondly, this consideration may also be beneficial, as discussed in the monotectic section, in that seeded cavitation can be envisioned.

A syntectic reaction with a secondary peritectic reaction is shown in Fig. 19. This can result in reactions consistent with $GL_1 \alpha$, $GL_2 \alpha$, $\alpha L_1 L_2$, and $GL_1 L_2$ peritectic-class behavior shown in Figs. 20 and 21. All perturbations within these systems cannot be shown because of their inordinate variety and complexity. The increased number of perturbations is obvious when Table 7 is considered.

We may conclude that syntectic systems are excellent candidate systems with which to demonstrate both reaction and morphological control that cannot be exercised terrestrially because of the omnipresent gravitationally dependent forces.

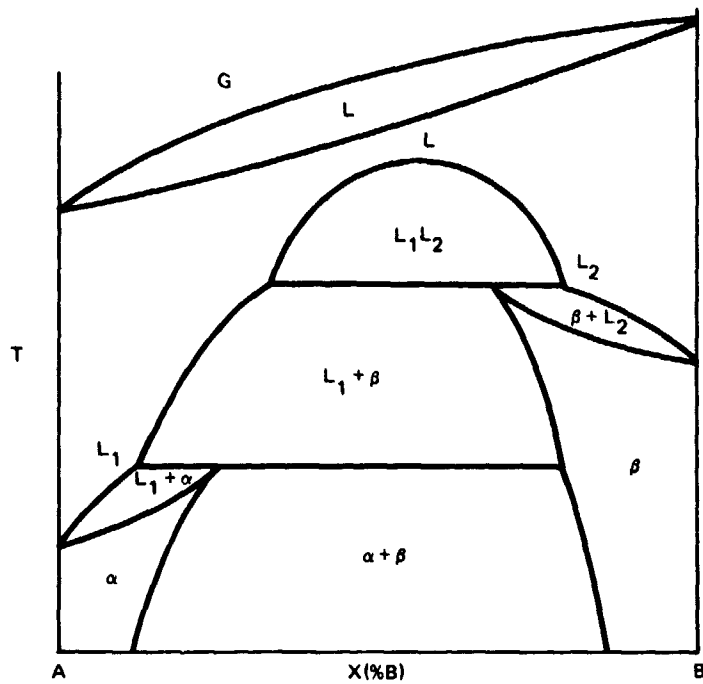


Fig. 19. – T-X Diagram Showing a Syntectic Reaction With a Secondary Peritectic Reaction.

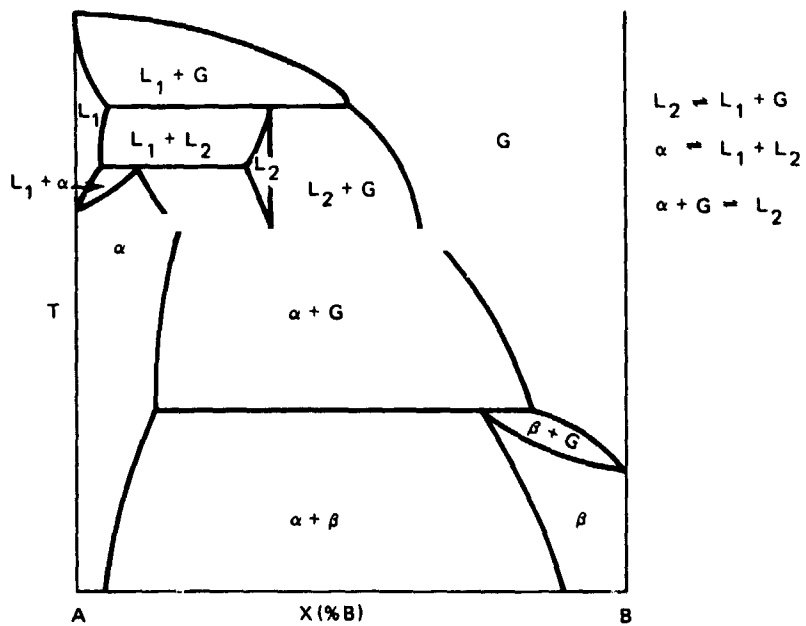


Fig. 20. – T-X Diagram Showing αGL_2 , $\alpha L_1 L_2$, and $L_2 L_1 G$ Invariant Reactions

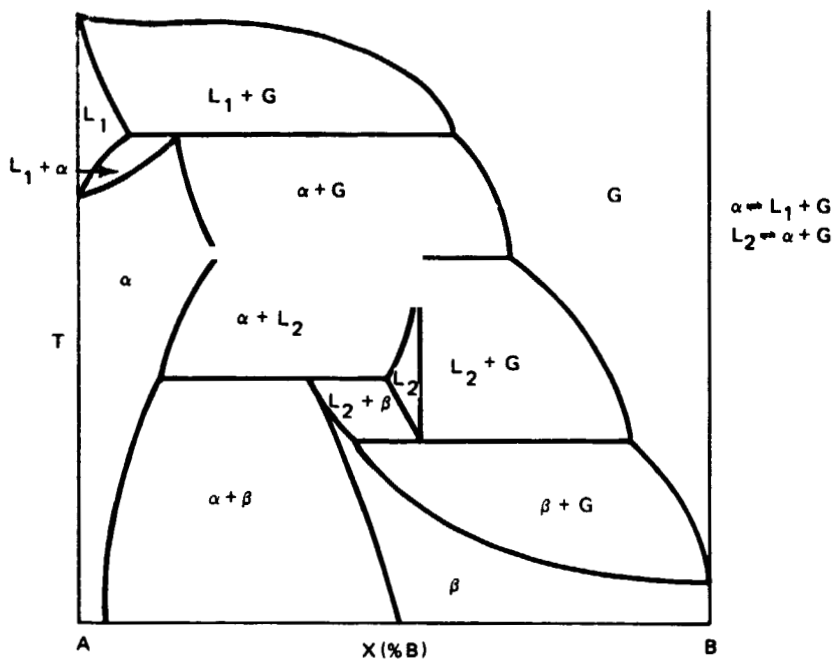


Fig. 21.— T-X Diagram Showing αL_1G , and $L_2\alpha G$ Invariant Reactions

3. POTENTIAL APPLICATIONS

New, two phase arrays of liquid/solid, liquid/liquid, and liquid/vapor are achievable in low-g in metal/metal, metal/semimetal, or metal/ceramic systems. In this section we explore the potential of these reactions to the development of new products.

3.1 Use of Solid/Liquid Reactions

Nucleation of a solid within a liquid at constant temperature and uniform internal pressure should produce a homogeneous structure. If convection can be controlled and particularly if it can be reduced to a minimal level, then uniform solid arrays will form in the liquid which can then be frozen in. This will be true whether the second phase is naturally occurring (a precipitate) or is introduced by inoculation. This makes homogeneous two-phase arrays possible for the first time through liquid state processing. Random arrays can be fabricated for second phase (dispersion) strengthening or controlled thermal or field effects can be used to create aligned alloys. Obvious applications for the former are improved high temperature alloys for turbines and for the latter would be the alignment of high strength non-continuous magnetic particles in a lower melting point matrix, or dispersion of a controlled amount of particulate insulation in a superconducting matrix resulting in a composite which could carry higher critical currents because of an increase in magnetic flux pinning (Ref. 4).

3.2 Use of Liquid/Liquid Reactions

Consideration of the possibility of controlling liquid/liquid arrays in the low-g environment is a fascinating one. In the near absence of convection, agglomeration would seemingly be addressable as a time dependent random walk problem since buoyancy and sedimentation forces would be eliminated. Liquid/liquid mixtures could be solidified with controlled arrays for application in the magnetic and electronic areas (Ref. 4). These arrays can be intermeshed continuous networks or size controlled independent particles within a continuous matrix. Thermal and compositional parameters could seemingly control the resultant array. The electrical properties of solidified immiscible components can be divided into four classes: insulators, semiconductors, conductors, and superconductors (Ref. 4). A few materials in each class may assume the properties of the adjacent class depending on temperature, pressure, and composition. The properties of a material usually fall into one class only. Liquid/liquid controlled dispersion of disparate electronic materials and subsequent controlled solidification offers the possibility of obtaining entirely new electronic materials with crossbred properties from all of the above classes and perturbations.

If the magnetic properties are similarly grouped, the possible perturbations are equally exciting. A unique example of a controlled magnetic dispersion is a low retentivity ferromagnetic material dispersed within a magnetoresistive matrix, for example Fe-Bi (Ref. 4). The resulting composite array should have greatly enhanced magnetoresistive properties for such applications as sonar, magnetic switches, or solid-state relays with fast switching times. Once again, entirely new magnetic materials with crossbred properties can be envisioned.

Intelligent consideration of both the electronics and magnetic properties should prove to be an even more fertile field, and although they may not be planned, synergistic effects are almost certain to occur.

3.3 Use of Liquid/Vapor Reactions

Controlled cavitation of metals, on heating in low-g, could result in metallic foams of high specific properties, for use as surgical implants. Pores lined with a selected second phase could be fabricated to reradiate laser radiation for military application. The most direct means of generating this array would be to superheat an immiscible dispersion such that one of the liquid phases cavitates. Allowing for free expansion, the expanded volume of fluid could then be solidified. The immiscible dispersion would thus 'seed' the uniform occurrence of the cavitative reaction.

3.4 Use of Liquid/Solid/Vapor Reactions

Second phase bubble arrays can be formed in a controllable fashion on solidification, within systems of a catatectic* type. This is readily accomplished in the solidification of water with dissolved air; the air bubbles forming a prescribed array during solidification. Similar arrays could be formed in metallic systems for the first time in low-g. Second phase potassium bubbles dispersed in a controlled array in tungsten light bulb filaments provide substantially higher creep resistance than solid particles (e.g., thoria) (Ref. 3). This can only be accomplished in a small number of solid/vapor systems terrestrially but could be conducted in a diversity of systems from the liquid state in the low-g environment. Turbine vanes, blades, rotors, or stators are possible applications but what is really implied here are new creep resistant materials resulting from bubble dispersion effects best achieved in low-g.

*Reactions following the sequence: Phase 1 ^{cooling} Phase 2 + Phase 3 are termed catatectic (Ref. 5) _{heating}

4. SUMMARY AND CONCLUSIONS

We may draw many conclusions if we attempt to deal with specific reaction types or a specific variation within each reaction type. It is more important to draw the broad or general conclusions and then allow the experimenter to apply them to singular systems.

From previous work (Ref. 1) we concluded that vacuum processing metallic fluids in the orbital environment would result in a pressure reduction within the fluid that was sufficient to cause an appreciable decrease in the onset temperature of cavitation on heating in a large number of metallic systems. This work further elaborated upon the reactions that could be anticipated within metallic systems if the gravitationally dependent pressure drop was sufficient. The work contained herein is then hypothetical, however, when paired with the Part 1 Report (Ref. 1) and its quantitative conclusions it is readily apparent that these reactions will be encountered in a large number of metallic systems.

The consideration of the Clausius-Clapeyron equation pointed to the fact that melting or solidification reactions involving strictly solid/liquid or liquid/liquid phase equilibria will be insignificantly affected by the gravitationally dependent pressure drop. This does not mean, however, that gravity dependent phenomena play no role. In fact, gravity plays a great role in the final morphology of solidified specimens. Buoyancy and gravitationally driven convection determine morphologies and frequently the end result is a macroscopically inhomogeneous material. In low-g, there is little or no tendency toward sedimentation, the processes of agglomeration and ripening should be appreciably slowed, and morphological control should be a realizable goal. Thus, controlled arrays of disparate or immiscible phases should be attainable in the low-g orbital environment whereas the balance of forces in the one-g environment is uncontrollable from a process standpoint.

If the pressure reduction or thermal regime is sufficient to induce a reaction involving the vapor phase, then the Clausius-Clapeyron equation demonstrates that the onset temperature of the reaction is a sensitive function of pressure. The gravitationally dependent pressure reduction in a low-g environment may then alter the phase reaction, and also alter the thermal regime in which these reactions would take place. One exciting prospect is that of inducing vapor reactions in low-g that are unattainable in one-g. Of equal importance, however, is the aspect of control of these reactions, reactions that are uncontrollable terrestri-

ally. The question of limiting agglomeration throughout the large volume increases associated with vaporization of a component may, in fact, limit the control of liquid/vapor reactions in orbit. However, there seems little doubt that such control may be exerted in liquid/liquid/vapor and solid/liquid/vapor reactions and these occur more frequently in the orbital environment.

From the applications presented we may conclude that space processing will generate a multitude of new products in the commercial, scientific, and military sectors of the economy.

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