Chapter 5

THERMOCHEMISTRY OF HETEROGENEOUS MIXTURES

The technology of shock chemistry in solids is said to be "an exercise in old-fashioned chemistry with an unfamiliar and poorly characterized process" (Duvall, 1984). Since then there have been better characterized experiments and improvements in our understanding of the process, but it is still correct to say that the technology remains "a science of end states where substances are mixed and processed, and the reaction products are collected and analyzed", and that we are still in a jungle and finding our way by trial and error. There are some who even doubt the occurrence of strong chemical reactions in the shock front. Nevertheless, we are beginning to see not only accumulating evidence that very fast reactions do take place in heterogeneous powder mixtures, but also data that give some insight into the mechanisms of the process and the final products (Graham, 1992 and Thadhani, 1992).

At the present time, there is no generally accepted theory of shock chemistry of materials. So far, any theoretical effort to analyze the problem has been mostly conceptual and based on ideas and approaches that are used in the description of analogous processes such as combustion phenomena of various kinds, including detonation, mechanical alloying, reaction sintering at high pressures, and geochemical reactions. Also, there has been the mention of unique features of shock chemistry that may result from a combination of high-speed deformation and high pressures (Duvall, 1984). But to date, no model exists that delineates these features in a quantitative form. We do not know yet how "unique" is unique except the speed.

Since there is not yet a body of systematized theoretical knowledge concerning shock compression chemistry in solid materials, we discuss in this chapter selected conventional ideas that we believe may form the theoretical background of shock chemistry of materials with special focus on the thermodynamics of powder mixtures.

From a theoretical point of view, almost all topics in chemical thermodynamics are relevant to the shock chemistry of materials. But in this chapter, we shall limit our attention mostly to those topics that form a central background to the
continuum modeling of shock chemistry and numerical process simulation that will be discussed in the next chapter. Also, our discussion will be heuristic. For more thorough expositions, the readers are referred to the many excellent texts on chemical thermodynamics (e.g., Lupis, 1983; Prigogine and Defay, 1954; and Denbigh, 1966).

5.1 Thermodynamic Functions of Heterogeneous Mixtures

Figure 5-1(a) shows an idealized picture of a powder mixture consisting of two different materials, A and B. Such an assembly of particles may appear to be well mixed on a macroscopic level, but it is not a mixture in the sense used in classical thermodynamics. It is a composite material system. To highlight the difference, a comparable system can be constructed of gases using internal partitions as shown in Fig. 5-1(b). The powder mixture may be in a state of mechanical equilibrium, but thermodynamically it is in a metastable (or non-equilibrium) state. It remains in a high energy state because of high barriers against mass diffusion of constituent atoms. If these barriers were removed by,
say, raising temperature or mixing mechanically, then the composite system will transform to, given sufficient time for mass transfer, a mixture on the atomic level and undergo a chemical reaction (or reactions) appropriate to given conditions of temperature, pressure, composition, etc.

In this section, we shall investigate equilibrium thermodynamic functions of powder mixtures. However, to simplify the task we assume
(a) a closed mixture system,
(b) local equilibrium of constituent particles,
(c) extensivity of certain variables, such as volume and internal energy, and
(d) negligible surface energy.

Recovery experiments are indeed closed systems. Assumptions (b) and (c) are part of the basis for thermodynamic analysis. The reasonableness of the last assumption may be seen from Table 5-1 where relative magnitudes of various energies are evaluated in decreasing order of particle size using copper as a representative case. The effects of surface energy appear to become significant only for particles or radius less than 100 nm.

We begin with postulates (b) and (c) and specify the volume and internal energy of a mixture based on the mass of each constituent. That is,

\[ E = \sum_i m_i e_i \]  

(1)

\[ V = \sum_i m_i v_i \]  

(2)

\[ M = \sum_i m_i \]  

(3)

where \( e_i \) and \( v_i \) are the specific internal energy and volume of \( i \)-component, respectively, and \( m_i \) mass of \( i \)-component. In what follows, the term "component" (or "constituent") will include both chemical species and phases.*

The enthalpy of the mixture may also be defined as the sum of the enthalpy of each component.

\[ H = \sum_i m_i h_i = \sum_i m_i (e_i + p_i v_i) = E + \sum_i p_i (m_i v_i) \]  

(4)

This equation shows that for \( H \) to be extensive in standard form, the pressure must

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*A phase is typically defined as a restricted part of a system with distinct, homogeneous physical and chemical properties. A choice of chemical species can be made in a number of different ways and depends on the type of thermodynamic problems (Kern and Weisbrod, 1967).
Table 5-1. Energy composition of a single copper particle.*

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</thead>
<tbody>
<tr>
<td>10 Å</td>
<td>$1.36 \times 10^{22}$</td>
<td>$4.68 \times 10^{-21}$</td>
<td>$4.27 \times 10^9$</td>
<td>$1.53 \times 10^4$</td>
<td>$7.59 \times 10^4$</td>
<td>$6.12 \times 10^4$</td>
<td>$1.24 \times 10^4$</td>
<td>\text{Not applicable}</td>
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<tr>
<td>100 Å</td>
<td>$10^9$</td>
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</table>


Mole Weight = 63.54,  
Density = 8.93 g/cm³,  
Surface Energy = 1,500 erg/cm²,  
Cohesive Energy = 8.12 kcal/mol,  
Kinetic energy (mv²/2) at 1 mm/s,  
Thermal Energy (kT/2) at 0 °C.
be uniform in the mixture: \( p_i = p \) for all \( i \). Then

\[
H = E + p \sum_i m_i v_i = E + pV
\]  

(5)

Similarly, if we introduce the Gibbs function of the mixture by

\[
G = \sum_i m_i g_i = \sum_i m_i \left( h_i - T_i s_i \right)
\]  

(6)

we find that for \( G \) to be extensive in the classical sense, the pressure and the temperature must be uniform throughout the mixture. That is,

\[
G = H - TS
\]  

(7)

\[
S = \sum_i m_i s_i
\]  

(8)

provided that \( p_i = p \) and \( T = T_i \) for all \( i \).

Let us now consider the question of extensivity using incremental equations (Silver, 1971). Since each component is said to be in thermodynamic equilibrium,

\[
T_i ds_i = de_i + p_i dv_i
\]  

(9)

Then, multiplying with \( m_i \) and summing, one obtains

\[
\sum_i T_i m_i ds_i = \sum_i m_i de_i + \sum_i p_i m_i dv_i
\]

If the temperature and the pressure were uniform, then

\[
dE = TdS + pdV
\]  

(10)

Similarly, with Eqs. (5) and (7), one obtains incremental equations for \( H \) and \( G \).

\[
dH = TdS + pdV
\]  

(11)

\[
dG = -SdT + Vdp
\]  

(12)

Thus, the assumption of homogeneous pressure and temperature is an essential step in the development of the thermodynamic functions of the mixture.
In deriving Eqs. (10) through (12), we have implicitly avoided the question of changing \( m_i \). So, we shall now consider the effects of their variation explicitly. However, we still assume a system closed to mass transfer from outside so that

\[
M = \sum_i m_i = \text{constant} \tag{13}
\]

Let \( \bar{Q}_i \) denote total \( Q \) of \( i \)-component. Then,

\[
d \bar{E}_i = d(m_i e_i) = m_i de_i + e_i dm_i \tag{14}
\]

\[
d \bar{S}_i = d(m_i s_i) = m_i ds_i + s_i dm_i \tag{15}
\]

\[
d \bar{V}_i = d(m_i v_i) = m_i dv_i + v_i dm_i \tag{16}
\]

If the pressure and temperature were uniform, then

\[
de_i = T d s_i - p d v_i \tag{17}
\]

A more general approach without this assumption is found in texts on chemical thermodynamics (e.g., Lupis, 1983).

Substituting Eqs. (15) through (17) into Eq. (14), we obtain

\[
d \bar{E}_i = T d \bar{S}_i - p d \bar{V}_i + (e_i + p v_i - T s_i) dm_i
\]

or

\[
\sum_i d \bar{E}_i = T \sum_i d \bar{S}_i - p \sum_i d \bar{V}_i + \sum_i g_i dm_i \tag{18}
\]

If the energy, entropy, and volume of the total mixture were equal to the sums of those of the individual components, then

\[
dE = T dS - pdV + \sum_i g_i dm_i \tag{19}
\]

where

\[
E = \sum_i \bar{E}_i, \quad S = \sum_i \bar{S}_i \text{ and } V = \sum_i \bar{V}_i
\]
Using Eqs. (5) and (7), the following equations may also be derived.

\[ dH = TdS - Vdp + \sum_i g_i dm_i \]  \hspace{1cm} (20)

\[ dG = -SdT + Vdp + \sum_i g_i dm_i \]  \hspace{1cm} (21)

In the derivation of Eq. (19), it is postulated that the entropy change of the mixture \((ds)\) is equal to the sum of the changes of its constituents \((\sum d\bar{s}_i)\). If we relax this condition, while retaining the extensivity of \(E\) and \(V\) (Silver, 1971), one obtains

\[ T\sum d\bar{s}_i - TdS = -\sum g_i dm_i \]

Since the entropy of an isolated system can only increase in a natural process,

\[Td\bar{s}_i - TdS \leq 0\]

where the equality indicates equilibrium processes. With Eq. (21), the above inequality relation becomes

\[(dG)_{p,T} \leq 0\]

This implies that the Gibbs free energy decreases at a constant pressure and temperature, and reaches a minimum at equilibrium. Hence, the criterion of equilibrium is

\[dG \geq 0\]

while the stability of equilibrium (minimum condition) is

\[d^2G > 0\]

Thus, the Gibbs function plays a role of "chemical potential" in the purview of equilibrium thermodynamics. It is analogous to gravitational potential in classical mechanics and addresses such questions of the tendency of material to react as

a) stable equilibrium states of a substance (or a collection of substances) under given conditions,
(b) stability of substances (or a system thereof) at given conditions,

(c) necessary conditions for a system to change from one state into another, and

(d) interactions with the environment due to a change in a system.

However, we need to emphasize limitations also:

(a) a negative $dG$ is not a sufficient condition for the initiation and propagation of reactions;

(b) reactions can occur even when $dG>0$, and

(c) irreversible processes are outside of the purview of equilibrium thermodynamics.

We shall return to these questions in later sections where we consider phase transitions and chemical reactions. For now, we turn our attention to the calculation of other useful thermodynamic functions of powder mixtures with constant compositions. There are three quantities of particular interest to shock wave calculations (Thompson 1979):

$$C_v = \left( \frac{\partial e}{\partial T} \right)_v, \left( \frac{\partial p}{\partial T} \right)_v, \text{ and } \left( \frac{\partial p}{\partial T} \right)_T$$

where $e=E/M$

Since the evaluation of these functions involve differentiations with respect to temperature $T$ and specific volume $v$, it will be assumed that the following functions are known:

$$e_i = e_i(v_i, T) \quad (22)$$

$$p_i = p_i(v_i, T) \quad (23)$$

A representative example of $e_i$ and $p_i$ will be discussed in the next section.

Consider first the specific heat of the mixture, $C_{vm}$. 
\[ \frac{\partial e_i}{\partial v_i}_T = \sum_i \frac{m_i}{M} \frac{\partial e_i}{\partial T}_v = \sum_i \frac{m_i}{M} \left[ C_{v_i} + \left( \frac{\partial e_i}{\partial v_i} \right)_T \frac{\partial v_i}{\partial T}_v \right] \quad (24) \]

The quantity \( \frac{\partial e_i}{\partial v_i}_T \) in Eq. (24) is determined by use of a thermodynamic identity relation

\[ \left( \frac{\partial e_i}{\partial v_i} \right)_T = -p + T \left( \frac{\partial p}{\partial T} \right)_v \quad (25) \]

The last term in Eq. (24) is a thermal expansion coefficient of \( i \)-component, but its derivation is made difficult because of its imposed condition of constant total specific volume. To determine the coefficient, we form a system of \( n \) equations involving Eq. (23) and the kinematic condition, Eq. (2). They are

\[ p_i(v_i, T) = p_n(v_n, T), \quad i = 1, \ldots, n-1 \quad (26) \]

\[ Mv = \sum_i m_i v_i \quad (27) \]

We now evaluate the partial derivatives of the above system of equations with respect to \( T \) while keeping \( v \) constant. Then,

\[ \left( \frac{\partial p_i}{\partial T} \right)_v + \left( \frac{\partial p_i}{\partial v_i} \right)_T \left( \frac{\partial v_i}{\partial T} \right)_v = \left( \frac{\partial p_m}{\partial T} \right)_v + \left( \frac{\partial p_n}{\partial v_n} \right)_T \left( \frac{\partial v_n}{\partial T} \right)_v, \quad i = 1, \ldots, n \quad (28) \]

\[ \sum \lambda_i \left( \frac{\partial v_i}{\partial T} \right)_v = 0 \quad (29) \]

where \( \lambda_i = m_i / M \).

Since \( \frac{\partial p_i}{\partial v_i}_T \) and \( \frac{\partial p_i}{\partial T}_v \) are known quantities, Eqs. (28) and (29) are a system of \( n \)-linear equations for \( \frac{\partial v_i}{\partial T}_v \). Denoting \( \frac{\partial p_i}{\partial v_i}_T \) and \( \frac{\partial p_i}{\partial T}_v \) as \( b_i \) and \( p_i^* \), respectively, and rearranging terms, Eqs. (28) and (29) become
\[
\begin{pmatrix}
  b_1, 0, \ldots, 0, -b_n \\
  0, b_2, \ldots, 0, -b_n \\
  \vdots \\
  0, 0, \ldots, b_{n-1}, -b_n \\
  \lambda_1, \lambda_2, \ldots, \lambda_{n-1} \alpha_n
\end{pmatrix}
\begin{pmatrix}
  (\partial v_1 / \partial T) \nu \\
  (\partial v_2 / \partial T) \nu \\
  \vdots \\
  (\partial v_{n-1} / \partial T) \nu \\
  (\partial v_n / \partial T) \nu
\end{pmatrix}
= 
\begin{pmatrix}
  p'_n - p'_1 \\
  p'_n - p'_2 \\
  \vdots \\
  p'_n - p'_{n-1} \\
  0
\end{pmatrix}
\]  
(30)

The determinant needed to solve for \( (\partial v / \partial T) \nu \) is

\[
D = b_1 \ldots b_n 
\begin{vmatrix}
  1 & 0 & \ldots & 0 & -1 \\
  0 & 1 & \ldots & 0 & -1 \\
  0 & 0 & \ldots & 1 & -1 \\
  \frac{\lambda_1}{b_1} & \frac{\lambda_2}{b_2} & \ldots & \frac{\lambda_{n-1}}{b_{n-1}} & \frac{\lambda_n}{b_n}
\end{vmatrix}
\]

By adding the first to (n-1)th columns to the n-th column, and expanding the matrix along the n-th column, one obtains

\[
D = b_1 \ldots b_n \left( \frac{\lambda_1}{b_1} + \frac{\lambda_2}{b_2} + \ldots + \frac{\lambda_n}{b_n} \right)
\]  
(31)

We shall now solve Eq. (30) for \( (\partial v / \partial T) \nu \) as a representative example

\[
\begin{pmatrix}
  \frac{\partial v_1}{\partial T} \nu \\
  \frac{\partial v_2}{\partial T} \nu \\
  \vdots \\
  \frac{\partial v_{n-1}}{\partial T} \nu \\
  \frac{\partial v_n}{\partial T} \nu
\end{pmatrix} = \frac{1}{D}
\begin{pmatrix}
  p'_n - p'_1 & 0 & \ldots & 0 & -b_n \\
  p'_n - p'_2 & b_2 & \ldots & 0 & -b_n \\
  \vdots \\
  p'_n - p'_{n-1} & 0 & \ldots & b_{n-1} & -b_n \\
  0 & \frac{\lambda_2}{b_2} & \ldots & \frac{\lambda_{n-1}}{b_{n-1}} & \frac{\lambda_n}{b_n}
\end{pmatrix}
\]  
(32)
\[
\begin{vmatrix}
    \hat{p}_n - \hat{p}_1 & 0 & \ldots & 0 & -1 \\
    \hat{p}_n - \hat{p}_2 & b_2 & \ldots & 0 & -1 \\
    \vdots & \vdots & \ddots & \vdots & \vdots \\
    \hat{p}_n - \hat{p}_{n-1} & 0 & \ldots & 1 & -1 \\
    0 & \frac{\lambda_2}{b_2} & \ldots & \frac{\lambda_{n-1}}{b_{n-1}} & \frac{\lambda_n}{b_n}
\end{vmatrix}
\]

\[= \frac{b_2 \ldots b_n}{D} \]  

Subtracting the first row from the other rows, Eq. (33) becomes

\[
\begin{vmatrix}
    \hat{p}_n - \hat{p}_1 & 0 & \ldots & 0 & -1 \\
    -\left( \hat{p}_n - \hat{p}_2 \right) & 1 & \ldots & 0 & 0 \\
    \vdots & \vdots & \ddots & \vdots & \vdots \\
    -\left( \hat{p}_{n-1} - \hat{p}_n \right) & 0 & \ldots & 1 & 0 \\
    0 & \frac{\lambda_2}{b_2} & \ldots & \frac{\lambda_{n-1}}{b_{n-1}} & \frac{\lambda_n}{b_n}
\end{vmatrix}
\]

\[= \frac{b_2 \ldots b_n}{D} \]  

Now expanding the matrix along the first column,

\[
\left( \frac{\partial v_1}{\partial T} \right)_v = \frac{b_2 \ldots b_n}{D} \left[ \left( \hat{p}_n - \hat{p}_1 \right) \frac{\lambda_n}{b_n} + \left( \hat{p}_2 - \hat{p}_1 \right) \frac{\lambda_2}{b_2} + \ldots + \left( \hat{p}_{n-1} - \hat{p}_1 \right) \frac{\lambda_{n-1}}{b_{n-1}} \right]
\]

\[
= \frac{\sum_k \left( \hat{p}_n - \hat{p}_1 \right) \frac{\lambda_k}{b_k}}{b_1 \left( \sum_k \frac{\lambda_k}{b_k} \right)}
\]

Finally, generalizing the above result to the \( i \)th-component,
\[
\left( \frac{\partial v_i}{\partial T} \right)_v = \sum_k \left[ \left( \frac{\partial p_k}{\partial T} \right)_{v_k} - \left( \frac{\partial p_i}{\partial T} \right)_{v_i} \right] \frac{\lambda_k}{b_k} \sum_i \left( \frac{\lambda_k}{b_k} \right)
\]

(35)

When any of \( b_i \) vanishes (e.g., due to melting) special formulas must be developed. In our calculations, however, the problem has been avoided by introducing a separate chemical species for the new phase.

Once \((\partial v_i/\partial T)_v\) is known, other quantities are easier to calculate. For instance,

\[
\left( \frac{\partial p}{\partial T} \right)_v = \left( \frac{\partial p_i}{\partial T} \right)_v = \left( \frac{\partial p_i}{\partial v_i} \right)_{v_i} + \left( \frac{\partial p_i}{\partial v_i} \right)_T \left( \frac{\partial v_i}{\partial T} \right)_v
\]

(36)

Also,

\[
\left( \frac{\partial p}{\partial v} \right)_v = \left( \frac{\partial p_i}{\partial v_i} \right)_T = \left( \frac{\partial p_i}{\partial v_i} \right)_T \left( \frac{\partial v_i}{\partial v} \right)_T
\]

(37)

\[
\sum_i \lambda_i \left( \frac{\partial v_i}{\partial v} \right) = 1
\]

(38)

Hence, substituting Eq. (37) into Eq. (38) yields

\[
\left( \frac{\partial p}{\partial T} \right)_T = \frac{1}{\sum_i \left( \frac{\lambda_i}{b_i} \right)}
\]

(39)

With Eq. (37), one obtains

\[
\left( \frac{\partial v_i}{\partial v} \right)_v = \frac{1}{b_i \sum_k \left( \frac{\lambda_k}{b_k} \right)}
\]

(40)

The results are summarized in Table 5-2 for purpose of reference. Specific
Table 5-2. Thermodynamic functions for ideal mixtures.

1. \[ C_m = \sum_i \zeta_i \left[ C_{vi} + \left( \frac{\partial \varepsilon_i}{\partial v_i} \right)_{T_m} \left( \frac{\partial v_i}{\partial T_m} \right)_{v_i} \right] \]

where

\[ \left( \frac{\partial v_i}{\partial u_i} \right)_{T_m} = -p + T_m \left( \frac{\partial p}{\partial T_m} \right)_{v_i} \]

\[ \left( \frac{\partial v_i}{\partial T_m} \right)_{T_m} = \sum_k \left[ \left( \frac{\partial p_k}{\partial T_m} \right)_{v_k} - \left( \frac{\partial p}{\partial T_m} \right)_{v_i} \right] \left( \frac{\zeta_k}{b_k} \right) \left/ \left[ \sum_k \left( \zeta_k / b_k \right) \right] \right. \]

\[ b_i = \left( \frac{\partial v_i}{\partial T_m} \right)_{T_m} = -\beta_i v_i, \]

\[ \left( \frac{\partial p}{\partial T_m} \right) = \gamma_i C_{vi} / v_i \]

Therefore,

\[ C_m = \sum_i \zeta_i C_{vi} + \sum_i \zeta_i \left[ -p + T_m \gamma_i C_{vi} / v_i \right] \]

\[ \left\{ \sum_k \left[ \gamma_k C_{vk} / v_k - \gamma_i C_{vi} / v_i \right] \left( \frac{\zeta_k}{b_k} \right) \left/ \left[ \sum_k \left( \zeta_k / b_k \right) \right] \right. \right. \]

2. \[ \gamma_m = \left( \frac{v_m}{C_m} \right) \left( \frac{\partial R}{\partial T_m} \right)_{v_m} \]

\[ = \left( \frac{v_m}{C_m} \right) \left[ \left( \frac{\partial p_i}{\partial T_m} \right)_{v_i} + \left( \frac{\partial p}{\partial T_m} \right)_{v_i} \left( \frac{\partial v_i}{\partial T_m} \right)_{v_i} \right] \]

\[ \gamma_i C_{vi} / v_i + \sum_k \left[ \gamma_k C_{vk} / v_k - \gamma_i C_{vi} / v_i \right] \left( \frac{\zeta_k}{b_k} \right) \left/ \left[ \sum_k \left( \zeta_k / b_k \right) \right] \right. \]

3. \[ \beta_{T_m} = -v_m \left( \frac{\partial p}{\partial v_m} \right)_{T_m} = -v_m \left/ \sum_k \left( \zeta_k / b_k \right) \right. \]

where

\[ \beta_{T} = \beta_{T} + C_n \gamma^2 T / v \]

applications of the formulas are discussed in the next chapter.

Using thermodynamics to calculate the properties of composite materials is not unique. The determination of composite properties from those of the components is a subject of long standing in fields such as mechanics (Christensen,
1979) and earth science (Watt et al., 1976). So, for comparison, we shall study one of the techniques which has yielded average properties of isotropic composite materials that are most frequently used in practical applications. For illustration purpose, we consider a composite of two isotropic elements (Hill, 1963). Average values will be denoted by a bar placed above and defined by

$$
\bar{A}_i = \frac{1}{\bar{V}_i} \int_{\bar{V}_i} A_i dV
$$

where $\bar{V}_i$ is the volume of the region occupied by component $i$. Then, the overall average stress and strain are

$$
\bar{\sigma} = \alpha_1 \bar{\sigma}_1 + \alpha_2 \bar{\sigma}_2, \quad \bar{\varepsilon} = \alpha_1 \bar{\varepsilon}_1 + \alpha_2 \bar{\varepsilon}_2
$$

(41)

where $\alpha_i$ is the volume fraction of component $i$.

Since at any point in the constituents there exists tensorial elastic stress-strain relationships,

$$
\sigma_1 = M_1 \varepsilon_1, \quad \sigma_2 = M_2 \varepsilon_2
$$

$$
\varepsilon_1 = S_1 \sigma_1, \quad \varepsilon_2 = S_2 \sigma_2
$$

(42)

On putting these in Eq. (41),

$$
\bar{\sigma} = \alpha_1 M_1 \bar{\varepsilon}_1 + \alpha_2 M_2 \bar{\varepsilon}_2
$$

$$
\bar{\varepsilon} = \alpha_1 S_1 \bar{\sigma}_1 + \alpha_2 S_2 \bar{\sigma}_2
$$

(43)

If a volume under consideration is large enough so that the whole mixture on average is macroscopically uniform and surface effects are negligible, then the average strain of each constituent can be related to the average overall strain of the mixture. That is,

$$
\bar{\varepsilon}_1 = A_1 \bar{\varepsilon}, \quad \bar{\varepsilon}_2 = A_2 \bar{\varepsilon}
$$

(44)

Thus, from Eqs. (41) and (44),

$$
\alpha_1 A_1 + \alpha_2 A_2 = I
$$

(45)

where $I$ is the unit tensor.
Let us define the effective modulus by

$$\bar{\sigma} = M^* \bar{\epsilon}$$  \hspace{1cm} (46)

With Eqs. (43) and (45), the above equation yields

$$M^* = \alpha_1 M_1 A_1 + \alpha_2 M_2 A_2$$  \hspace{1cm} (47)

Similarly, the effective compliance may be given by

$$S^* = \alpha_1 S_1 B_1 + \alpha_2 S_2 B_2$$  \hspace{1cm} (48)

where $\bar{\sigma}_i = B_i \bar{\sigma}$ and $\alpha_1 B_1 + \alpha_2 B_2 = 1$.

Thus, the calculation of the elastic properties is reduced to that of the average stress and strain in constituent materials. But the task is known to be "hopelessly complex" (Hill, 1963). There are two commonly used approximations known as the Voigt and Reuss averages. The former assumes homogeneous strain ($A_1 = A_2$), and the latter, homogeneous stress ($B_1 = B_2$) in the mixture. They are equivalent to parallel and series arrangements of a two spring system. On substituting these assumptions into Eqs. (47) and (48), one obtains

$$M_v^* = \alpha_1 M_1 + \alpha_2 M_2$$  \hspace{1cm} (49)

$$S_R^* = \alpha_1 S_1 + \alpha_2 S_2$$  \hspace{1cm} (50)

Since compliance $S_i$ of an isotropic material is the inverse of stiffness,

$$\left( M_R^* \right)^{-1} = \alpha_1 \left( M_1 \right)^{-1} + \alpha_2 \left( M_2 \right)^{-1}$$  \hspace{1cm} (51)

Hill (1963) showed that the Voigt and Reuss averages are the upper and lower bounds of the actual modulus of the composite. That is, with $n$ components,

$$M_R^* = \left( \sum_i \alpha_i M_i \right)^{-1} \leq M^* \leq \sum_i \alpha_i M_i \leq M_v^*$$  \hspace{1cm} (52)

Also, Hill suggested that either the arithmetic mean or the geometric mean might be a useful approximation to the actual moduli. Figure 5-2 shows a case study with the mixture of MgO and AgCl. It also includes the Hashin-Shtrikman
estimates that are known to provide tighter bounds than the Voigt and Reuss averages.

Similar analyses on theoretical bounds for thermal expansion coefficients and specific heats of composite materials are available in Walsh (1973) and Rosen and Hashin (1970). But they are beyond the scope of this book.

It is apparent that since \( \alpha = m \nu / m v \), the isothermal bulk modulus of the mixture, Eq. (37) derived by thermodynamic means, is identical to the Reuss average given by Eq. (51). It is also easy to show that Eq. (37) holds for the adiabatic modulus of the mixture. Then, the modulus based on Eq. (37) describes the lower bound for wave propagation. The corresponding upper bound may be calculated from the Voigt average of adiabatic moduli. But Barker (1971) proposed an upper bound of a different kind based on a mechanistic model. The idea is very much similar to that used in Section 4.1 to determine wave propagation in beads on a string.

In the Barker model, the composite is composed of alternating flat layers of two (for the sake of illustration) different materials (see Fig. 5-3). Then, he defines the fastest wave speed by

\[
\frac{1}{C_I} = \frac{\alpha_A}{C_A} + \frac{\alpha_B}{C_B}
\]

where \( \alpha_A \) and \( \alpha_B \) as the volume fractions of A and B, respectively. The subscript I signifies the "instantaneous" speed. In terms of mass fractions, this becomes
\[ \frac{v}{C_I} = \frac{\lambda_A v_A}{C_A} + \frac{\lambda_B v_B}{C_B} \] (54)

where \( v = 1/\rho \) and

\[ \frac{1}{v} = \frac{\alpha_A}{v_A} + \frac{\alpha_B}{v_B} \] (55)

Thus, the corresponding upper bound modulus is defined by

\[ K_I = \rho C_I^2 \] (56)

Application of the idea is described in Section 5.3.

5.2 Analytical Equations of State

In the previous section, a formal procedure is developed to determine equilibrium thermodynamic properties of heterogeneous mixtures. It is also indicated that because of the homogeneous pressure and temperature assumption, these properties represent lower bounds of the mixture properties. We shall now develop a particular form of Eqs. (22) and (23) required in the evaluation of mixture properties.

Complex equations of state are required to cover a wide range of thermodynamic parameters (e.g., Eliezer et al., 1986). But often a simple function such as the ideal equation of state is found to be useful in capturing essential features (or their model analogue) of mixture properties. The following equations of state are considered with this thought in mind. These equations are found to be useful not only in the study of shock-induced phase transitions (Johnson et al., 1974; Hayes,
1974), but also in a model study of unsteady detonations resulting from phase transitions (Rabie, 1977).

The construction of the model function involves three assumptions.

Assumption I:  \( C_v = \text{constant} \)

Assumption II \( \gamma/v = \text{constant} \)

Assumption III the isothermal bulk modulus is given by the Murnaghan relation,

\[
-v \left( \frac{\partial p}{\partial v} \right)_T = K_T = K_{T0} (v_0/v)^n
\]  

(57)

Assumption III is equivalent to

\[
K_T = K_{T0} + n \left( p - p_0 \right)
\]

(58)

For a more general model involving only the first two assumptions, see Cowperthwaite (1966) and Johnson et al. (1974).

We begin with the construction of the entropy function whose differential is given by

\[
ds = \left( \frac{\partial s}{\partial v} \right)_T dv + \left( \frac{\partial s}{\partial T} \right)_v dT
\]

(59)

where \( s = S/M \).

We need several identity equations to relate the first two assumptions to Eq. (59).

\[
\left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial p}{\partial T} \right)_v = \left( \frac{\partial p}{\partial e} \right)_v \left( \frac{\partial e}{\partial T} \right)_v
\]

(60)

where by definition

\[
\left( \frac{\partial p}{\partial e} \right)_v = \frac{\gamma}{v}
\]

(61)
\[
\left( \frac{\partial e}{\partial T} \right)_v = T \left( \frac{\partial s}{\partial T} \right)_v = C_v
\] (62)

Substituting Eqs. (60) through (62) into Eq. (59),

\[
ds = \frac{\gamma}{v} C_v dv + \frac{C_v}{T} dT
\] (63)

Integrating from an initial state \((v_0, T_0)\) to a general state \((v, T)\),

\[
s = s_0 + \frac{\gamma}{v} C_v (v - v_0) + C_v \ell n \left( \frac{T}{T_0} \right)
\] (64)

Next, we develop the specific Helmholtz energy function \(f\) by integrating

\[
df = \left( \frac{\partial f}{\partial v} \right)_T dv + \left( \frac{\partial f}{\partial T} \right)_v dT
\]

\[
= -pdv - sdT
\] (65)

where \(p\) is the isothermal function given in Eq. (58). The integration yields

\[
f = f_0 + p_0 (v_0 - v) + \frac{K_{T_0} v_0}{n(n-1)} \left[ \left( \frac{v_0}{v} \right)^{n-1} + (n-1) \frac{v}{v_0} - n \right] - s_0 (T - T_0)
\]

\[
+ C_v \left\{ (T - T_0) \left[ 1 + \left( \frac{\gamma}{v} \right)_0 (v_0 - v) \right] + T \ell n \left( \frac{T_0}{T} \right) \right\}
\] (66)

It is easy to show that

\[
p = \left( \frac{\partial f}{\partial v} \right)_T = p_0 + \frac{K_{T_0} v_0}{n} \left[ \left( \frac{v_0}{v} \right)^n - 1 \right] + C_v \left( \frac{\gamma}{v} \right)_0 (T - T_0)
\] (67)

Thus, the specific internal and Gibbs energies are given by
\[ e = f + Ts = e_0 + \frac{K_{T0}v_0}{n(n-1)} \left[ \left( \frac{v_0}{v} \right)^{n-1} + (n-1) \frac{v}{v_0} - n \right] + C_v \left[ T - T_0 \left( 1 + \left( \frac{\gamma}{\nu} \right)_0 (v_0 - v) \right) \right] \]  \hspace{1cm} (68)

\[ g = f + pv = g_0 - S_0(T - T_0) + \frac{K_{T0}v_0}{(n-1)} \left[ \left( \frac{v_0}{v} \right)^{n-1} - 1 \right] + C_v \left[ (T - T_0) \left( 1 + \left( \frac{\gamma}{\nu} \right)_0 v_0 \right) + T(n-1) \frac{T_0}{T} \right] \]  \hspace{1cm} (69)

Rabie (1977) finds that in theoretical model studies even \((\gamma/\nu)_0\) can be assumed to be zero without losing essential features of thermodynamic interrelationships. Such functions may not correspond to any specific material, but they serve as a model representing a reasonably complete description of the interrelationship of the actual physical situation.

Lastly, let us consider the adiabatic bulk modulus in the simple form. Assuming \(p=p(T, \nu)\) in Eq. (67),

\[ dp = \left( \frac{\partial p}{\partial T} \right)_\nu dT + \left( \frac{\partial p}{\partial \nu} \right)_T d\nu \]

Hence,

\[ \left( \frac{\partial p}{\partial \nu} \right)_s = \left( \frac{\partial p}{\partial T} \right)_\nu \left( \frac{\partial T}{\partial \nu} \right)_s + \left( \frac{\partial p}{\partial \nu} \right)_T \]  \hspace{1cm} (70)

Using the identity relations,

\[ \left( \frac{\partial p}{\partial T} \right)_\nu = \left( \frac{\gamma}{\nu} \right) C_v \]  \hspace{1cm} (71)

\[ \left( \frac{\partial T}{\partial \nu} \right)_s = -\left( \frac{\gamma}{\nu} \right) T \]  \hspace{1cm} (72)
\[ K_s = -\nu \left( \frac{\partial p}{\partial \gamma} \right)_s = K_f + \nu \left( \frac{\gamma}{\nu} \right)^2 C_v T = K_{T0} \left( \frac{\nu_0}{\nu} \right)^n + \nu \left( \frac{\gamma}{\nu} \right)^2 C_v T \]  

(73)

The calculation of the temperature in Eq. (73) can be developed as we have done in Chapter 2 for Hugoniot calculations. That is,

\[ dT = \left( \frac{\partial T}{\partial p} \right)_v dp + \left( \frac{\partial T}{\partial \gamma} \right)_p d\gamma \]

\[ = \left( \frac{\nu}{\gamma} \right) \frac{1}{C_v} \left[ dp + \frac{K_T}{\nu} d\gamma \right] \]

(74)

5.3 Hugoniots of Inert Mixtures

There are several models that can be used to determine Hugoniots of inert mixtures. The central question is the treatment of heterogeneity inherent in such media. If the mixture were porous initially, the problem of heterogeneity and energy distribution would be further accentuated. In highly porous mixtures, thermal energies become comparable to, if not larger than, energies associated with compression. Then, depending on geometry, particle size and thermal properties, the question of thermal energy relaxation will present an additional difficulty.

Garg and Kirsh (1971) identified five types of composite models based on assumptions imposed on the question of mechanical and thermal equilibrium among constituents. They vary from complete thermal equilibrium to no equilibrium. Tsou (1972) conducted a comparative study of four of these models using a composite consisting of aluminum (fiber) and epoxy (matrix) and claimed that the model he and Chou (1971) developed gave the best fit to the experimental values of shock speed over the range of 1.8 to 2.3 mm/µs. To the authors’ knowledge, there are no such comparative studies of models with powder mixtures.

In this chapter, representative hydrodynamic models of mixture Hugoniot will be presented.

5.3.1 Thermodynamically equilibrium models

In this model, the end point of shock compression is that of a thermodynamically equilibrium state having uniform pressure and temperature. Then, the differential Hugoniot equation is identical to that of a single component,
\[
\left( \frac{dp}{dv} \right)_H = \frac{\left( \frac{\partial p}{\partial v} \right)_s + \frac{\gamma}{2v} (p - p_0)}{1 - \frac{\gamma}{2v} (v_{00} - v)}
\] (75)

provided that the terminal state has no pores. \(v_{00}\) is the specific volume of the powder mixture. If isothermal properties of the constituents are known, then the procedure discussed in the previous section may be used to determine \(\left( \frac{\partial p}{\partial v} \right)_s\) and \(\left( \frac{\gamma}{v} \right)\) for the mixture.

Figure 5-4 shows the Hugoniot\s of non-porous mixtures of quartz and polyethylene (Duvall and Taylor, 1971). They thought that the calculations were not particularly noteworthy, except the result that although \(\left( \frac{\gamma}{v} \right)\) for each component is assumed to be constant, the value for the mixture was strongly volume dependent.

If temperatures are not too high, solutions of the above equilibrium model for porous mixtures can be obtained without intensive computational effort as follows. The Hugoniot equation in terms of specific enthalpy is given by

![Graph showing Hugoniot curves for different pressures and specific volumes.](image)

Fig. 5-4. Calculated Hugoniot\s of dense mixtures of quartz and polyethylene (after Duvall and Taylor, 1971).
\[ h = \frac{1}{2} p (v_0 + v) \] (76)

Since the shocked state is assumed to be homogeneous,

\[ v = \sum \lambda_i v_i (p, T) \] (77)

\[ h = \sum \lambda_i h_i (p, T) \] (78)

The equation of state of each species be described by the Murnaghan equation

\[ p = p_0 + \frac{K_{T0}}{n} \left[ \left( \frac{v_0}{v} \right)^n - 1 \right] + c_v \left( \frac{v}{v_0} \right)_0 (T - T_0) \] (79)

Then the species enthalpy function in Eq. (73) can be determined as before by integrating

\[ dh = c_p dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp \] (80)

Since thermal expansion coefficients of solids are on the order of \(10^{-5}\), the above expression can be approximated by

\[ dh = c_p dT + vd\] (81)

This expression is valid for temperatures less than \(2,000 \sim 3,000\) K. Then, choosing a convenient path for integration from \((T_0, p_0)\) to \((T, p)\),

\[ h = h_0 + \int_{T_0}^{T} c_p (T, p) dT + \int_{p_0}^{p} v(T_0, p) dp \] (82)

Assuming \(h_0 = 0\), \(c_p(T, p) = \text{constant}\), and \(p_0 = 0\), one obtains

\[ h \cong c_p (T - T_0) + \frac{1}{2} (v_0 + v) p \] (83)

The significance of errors involved in the volume integral will be discussed.
shortly.

Now, substituting Eqs. (76) and (82) into Eq. (78) yields

\[
\frac{1}{2} p \left( v_{00} + \sum_i \lambda_i v_i \right) = \sum_i \lambda_i \left[ c_{pi} (T - T_0) + \frac{1}{2} (v_{io} + v_i) p \right] \tag{84}
\]

Rearranging terms, one finds

\[
T - T_0 = \frac{P}{2} \left[ \frac{v_{00} - \sum_i \lambda_i v_{i0}}{\sum_i \lambda_i c_{pi}} \right] = \frac{1}{2} \frac{p (v_{00} - v_{s0})}{c_{pm}} \tag{85}
\]

where \(v_{s0}\) is the initial average specific volume of solid components and \(c_{pm}\) is the heat capacity of the mixture at constant pressure. At given shock conditions, the specific volume of each component is calculated through the equation of state, Eq. (79). It may be seen now that the approximation used in the volume integral is within typical experimental errors in shock experiments so long as \(v_{00}\) is not too close to \(v_{s0}\).

Figures 5-5 and 5-6 show a sample calculation of the Hugoniots of elemental Ni/Al powder mixtures at three different initial densities. Shock velocity is based on

\[
U = v_{00} \left[ \frac{P}{(v_{00} - v)} \right]^{1/2} \tag{86}
\]

Krieger and Vreeland (1991) considered a mixture model in which pressures are homogeneous, but internal energies can assume different metastable values. They also assumed that the internal energies can be separated into elastic (isentropic) and thermal components. The equation of state is the usual Grüneisen equation with constant \((\gamma/\nu)\).

Mathematically, it is assumed that

\[
e = e_E + e_T
\]

\[
p = p_E + \left( \frac{\gamma}{\nu} \right)_0 e_T = - \frac{de_E}{d\nu} + \left( \frac{\gamma}{\nu} \right)_0 e_T
\]
Fig. 5-5. Calculated Hugoniot of porous Ni-Al mixtures. The volume ratio of solid Ni and Al is 50/50. Percentages indicate initial porosities.

Fig. 5-6. Calculated shock speed-pressure (Us-p) relationships for the Hugoniot shown in Fig. 5-5.
\[ p_E = \frac{K_{s0}}{n} \left[ \left( \frac{v_0}{\nu} \right)^n - 1 \right] \]

where \( n = K_{s0}' = dK_{s0}/dp \).

Integrating \( p_E \) with respect to \( \nu \), we find as before

\[ e_E = \frac{K_{s0}}{n} \left[ \frac{v_0}{(1-n)} \left( \frac{v_0}{\nu} \right)^{1-n} + \nu + \frac{n v_0}{(1-n)} \right] \]

Thus, for a single component system, the Hugoniot equation, \( e = p(v_0 - \nu)/2 \), yields

\[ p \left[ \frac{1}{2} (v_0 - \nu) - \left( \frac{\nu}{\gamma} \right)_{0} \right] = e_E - \left( \frac{\nu}{\gamma} \right)_{0} p_E \quad (87) \]

This equation determines a curve in the \( p-\nu \) plane.

For a porous mixture of two constituents, Eq. (87) becomes

\[ p \left[ \frac{1}{2} \left( v_{00} + \sum_i \lambda_i v_i \right) - \sum_i \lambda_i \left( \frac{\nu}{\gamma} \right)_{i0} \right] = \sum_i \lambda_i e_{Ei} - \sum_i \lambda_i \left( \frac{\nu}{\gamma} \right)_{i0} p_{Ei} \quad (88) \]

where \( \lambda_i \) is the mass fraction of \( i \)-component. Although \( e_{Ei} \) and \( p_{Ei} \) are functions of the specific volumes \( \nu_i \), the above equation does not specify a unique curve in the \( p-\nu \) plane.

Krueger and Vreeland (1991) resolved the indeterminacy by partitioning the thermal energies in an ad hoc fashion by specifying \( \xi \) given by

\[ \xi = \frac{e_{T2}}{e_{T1}} = \frac{(p - p_{E1})(\nu/\gamma)_{i0}}{(p - p_{E2})(\nu/\gamma)_{20}} \quad (89) \]

For any specified partitioning, Eqs. (82) and (83) determine a unique Hugoniot curve.

Figure 5-7 shows calculated and experimental results for W infiltrated with 24% wt Cu. The former assumed two extreme cases: \( \xi = 0 \) or \( \infty \). They show better fits than that calculated using mass averaged properties, but the results are said to be very insensitive to \( \xi \) over the range of particle velocity considered. This may be explained by their choice of elastic energy along isentropic compression. That
Fig. 5.7. Calculated and experimental Hugoniots of Sintered W infiltrated with 24% wt Cu. The calculated distention from the exp. data is 1.014 (after Krueger and Vreeland, 1991).

is, at low pressures, \( (p-p_{Ei})/p_{Ei} \) is a relatively small quantity, so \( \xi \) has little effect on the mixture Hugoniot.

5.3.2 Mechanical models

The models considered so far incorporated thermodynamics explicitly. But calculations of Hugoniots involved both lengthy algebra and material properties that may not be always available. So we shall consider next a simple mechanical model based on wave propagation in laminated media (Munson and Schuler, 1975). Results for model beryllium-polyethylene composite are found to show good fits to those of Tsou and Chou.

Since the analysis for wave propagation normal to laminates is found to be identical to that for propagation parallel to the laminates, we shall consider the former alone. As described earlier in Fig. 5.3, consider a laminate of two layers repeated regularly. Let initial layer thicknesses be \( d_n^0 \) and initial volume fractions \( \alpha_n^0 = d_n^0/d^0 \) where \( d^0 = \sum_n d_n^0 \). A steady shock is assumed to propagate at speed \( U \) in the direction normal to the laminate. Far behind the shock front, the material moves with velocity \( u \).

A balance of mass and linear momentum between the initial and terminal states may be developed for the repetition unit as follows. Since the wave propagation is steady, the continuity of mass requires

\[
\frac{U}{d_0} = \frac{U-u}{d} \quad \text{(per unit time)} \tag{90}
\]
Then, using the conservation of mass for the repetition unit, $d_n\rho_n = d^0_n\rho^0_n$, one obtains

$$U\left(\sum_n d_n\right) = U\left(\sum_n \frac{d^0_n\rho^0_n}{\rho_n}\right) = (U - u)d_0 \quad (91)$$

or

$$U - u = U\left[\sum_n \left(\frac{d^0_n}{d_0}\right)\frac{\rho^0_n}{\rho_n}\right] = U\sum_n \alpha^0_n\left(\frac{\rho^0_n}{\rho_n}\right) \quad (92)$$

Thus,

$$u = U\left[1 - \sum_n \left(\frac{\alpha^0_n\rho^0_n}{\rho_n}\right)\right] \quad (93)$$

Momentum conservation follows in a straightforward fashion.

$$p = \left(\frac{U}{d_0}\right) u \left(\sum_n d^0_n\rho^0_n\right) = uU\sum_n \alpha^0_n\rho^0_n \quad (94)$$

With Eq. (93), this can be solved for $U$.

$$U^2 = \frac{p}{\left[\sum_n \alpha^0_n\rho^0_n\left(1 - \sum_n \left(\frac{\alpha^0_n\rho^0_n}{\rho_n}\right)\right)\right]} \quad (95)$$

Finally, it is assumed that the Hugoniot of each component be taken as the equation of state of the component

$$\rho_n = f(p) \quad (96)$$

Figure 5-8 shows predicted and experimental results for a 70% wt quartz-phenolic composite. The deviation of experimental data at low stresses is noticable, but this deviation is thought to be caused by material strength effects that are not accounted for in this model.
Fig. 5-8. Calculated Hugoniot of a quartz-phenolic mixture based on a mechanical model of Munson and Schuler (1971). References for the experimental data are listed in their paper.

The application of Eq. (95) to porous heterogeneous mixtures is straightforward, provided that the pores can be assigned to each component initially in a meaningful manner. It will be interesting to see whether Eq. (95) can be used to test the partition of energy associated with pore collapse among mixture constituents. In some mixtures, Eq. (95) may be used to scope out the sensitivity of hydrostats to various schemes of heterogeneous energy deposition.

5.4 First-Order Phase Transitions

As exemplified by the synthesis of diamond powder from graphite, the subject of phase transitions is one of several central themes of the shock chemistry of materials. Hence, there exists a vast amount of literature, dating back to the 1920s and the study of phase transformation by itself can fill a space of many volumes. So, in this section we shall be concerned only with selected features of a simple thermodynamic theory of phase transitions in a single substance. Discussions of more complicated topics, such as multi-component phase transitions, are referred to in standard texts (e.g., Gordon, 1968).

The second law of thermodynamics states that for a closed system

\[ de - Tds + pdv \leq 0 \]  

(97)
where the equality holds for equilibrium processes. With Eq. (19), the above condition becomes

$$\sum g_i dm_i \leq 0$$  \hspace{1cm} (98)

For a single component system, we have

$$\left(g_\alpha - g_\beta\right) dm_\alpha \leq 0$$

This shows that any spontaneous transition between two phases $\alpha$ and $\beta$ must be in the direction of lowering the free energy. That is, if $dm_\alpha > 0$, then $g_\alpha < g_\beta$. At equilibrium

$$g_\alpha = g_\beta$$  \hspace{1cm} (99)

Thus, the most stable phase of a material under a given set of conditions is the one for which the free energy is the minimum. Figure 5-9 illustrates a typical equilibrium phase diagram of a one component system.

Substituting the definition of $g$ into Eq. (99), one finds

$$\left(e_\alpha - e_\beta\right) - T\left(s_\alpha - s_\beta\right) + p\left(v_\alpha - v_\beta\right) = 0$$  \hspace{1cm} (100)

or

$$\Delta e - T\Delta s + p\Delta v = 0$$  \hspace{1cm} (101)

where $\Delta$ signifies the difference in phase quantities. Therefore, under equilibrium conditions a phase transition at constant pressure and temperature is described by

$$\Delta g = 0$$  \hspace{1cm} (102)

The calculation of the free energy difference can be carried out using a model equation such as Eq. (69), or by integrating $\Delta g$ from $(T_0, p_0=0)$ to $(T, p)$. The latter yields (Kern and Weisbrod 1967)

$$(\Delta g)_T^p = (\Delta h)_T^0 - T(\Delta s)_T^0 + \int_0^p (\Delta v)_T dp$$
\[ (\Delta h)^0_{T_0} - T(\Delta s)^0_{T_0} + \int_{T_0}^{T} \frac{(\Delta c_p)^0}{T} \, dT - T \int_{T_0}^{T} \frac{(\Delta c_p)^0}{T} \, dT + \int_{T_0}^{T} (\Delta v) \, dp \] (103)

where the superscript “0” denotes \( p_0 \) and \( h = e + pv \). A very simple case will emerge if we assume that \( \Delta c_p = 0 \) and \( (\Delta v)_T = (\Delta v)^0_T \). They are not unreasonable assumptions for solids to obtain first order estimates. The result is

\[ (\Delta g)^p_T = (\Delta h)^0_{T_0} - T(\Delta s)^0_{T_0} + p(\Delta v)^0_{T_0} \] (104)

A line defined by \( (\Delta g)^p_T = 0 \) describes a phase boundary in the \( p-T \) plane.

For illustration, material constants for diamond and graphite are given in Table 5-3. Substitution of these constants in Eq. (104) with \( (\Delta g)^p_T = 0 \) yields

\[ p(kb) = \frac{T(\degree C)}{56.7} + 14.9 \] (105)
Table 5-3. Material constants for graphite and diamond (after Yoshida, 1988).

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<tr>
<th></th>
<th>Graphite</th>
<th>Diamond</th>
</tr>
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<tr>
<td>$\rho_0$ (g/cm$^3$)</td>
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<td>3.515</td>
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<td>$a$ (km/s)</td>
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<td>$b$</td>
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<td>$S_0$ (J/g K)</td>
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<td>0.209</td>
</tr>
</tbody>
</table>

$a$, $b$: Constants in $U_s = a + b \cdot u$

where $(\Delta h)_t^0$ is equated to $(\Delta e)_t^0$.

The experimental data that are thought to be most accurate are described by (Kennedy and Kennedy 1976) the equation

$$ p(kb) = \frac{T(\degree C)}{40} + 19.4 $$  \hspace{1cm} (106)

More accurate calculations involving variable $\Delta c_p$ and $\Delta v$ are found in Kern and Weisbrod (1967). They show an increasing curvature in $p$ but the above linear approximation, Eq. (105), is a reasonable approximation for temperatures less than 1,500 °C.

The slope of a phase boundary in a $p$–$T$ plane can be related to the latent heat of the transition. Consider two neighboring states on a phase boundary as shown in Fig. 5-10. The changes in the free energy of each phase from $(p, T)$ to $(p+dp, T+dT)$ are given by

$$ dg_\alpha = -s_\alpha dT + v_\alpha dp $$  \hspace{1cm} (107)

$$ dg_\beta = -s_\beta dT + v_\beta dp $$  \hspace{1cm} (108)

Since the two phases are in equilibrium,

$$ dg_\alpha = dg_\beta $$
Thus,

$$\frac{dp}{dT} = \frac{s_{\beta} - s_{\alpha}}{v_{\beta} - v_{\alpha}} = \frac{\Delta s}{\Delta v} \quad (109)$$

Consider now the change in enthalpy

$$\Delta h = T\Delta s + v\Delta p$$

For a phase change, pressure and temperature are constant. So the enthalpy change at constant pressure, called the latent heat, is expressible as

$$(\Delta h)_p = L = T\Delta s \quad (110)$$

Substituting $L$ into Eq. (109),

$$\frac{dp}{dT} = \frac{L}{T\Delta v} \quad (111)$$

This is the Clapeyron-Clausius equation.

When a Hugoniot curve intersects a phase boundary, the effect of an equilibrium transition can be classified into several types using the signs of quantities such as $dp/dT$, $\Delta v$, and $L$ (Duvall and Horie, 1965; Fortov, 1972). Table
5-4 shows a system of classification by Al’tshuler (1979). We shall consider two normal cases. The first case is a normal polymorphic transition, such as the graphite-diamond transition. It has \( dp/dT > 0 \), \( \Delta v < 0 \), and \( L < 0 \). The second is normal melting and is associated with \( dp/dT > 0 \), \( \Delta v > 0 \), and \( L > 0 \).

Table 5-4. Classification of phase transitions.

<table>
<thead>
<tr>
<th>Type of Transition</th>
<th>( \frac{dT}{dp} )</th>
<th>( \frac{dS}{dp} )</th>
<th>( \Delta v )</th>
<th>( Q )</th>
<th>( \frac{d\dot{v}_1}{dp} )</th>
<th>( \Delta )</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
<td>&gt; 0</td>
<td>( \frac{\partial v}{\partial p} ) ( \tau_i )</td>
<td>&lt; 0</td>
<td>Polymorphic transition; anomalous melting</td>
</tr>
<tr>
<td>2</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
<td>( \frac{\partial v}{\partial p} ) ( \tau_i )</td>
<td>&lt; 0</td>
<td>Polymorphic transition; solidification</td>
</tr>
<tr>
<td>3</td>
<td>&gt; 0</td>
<td>&lt; 0</td>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>( \frac{\partial v}{\partial p} ) ( \tau_i )</td>
<td>&lt; 0</td>
<td>Melting</td>
</tr>
</tbody>
</table>

“1” denotes the first phase.

Figure 5-11 shows Hugoniot curves loaded through a transition of the first kind in \( p-T, p-v \), and \( U-u \) planes. Relative positions of isotherms and isentropes are also indicated in the figure. The cusp in the Hugoniot curve in the \( p-v \) plane may be traced to the discontinuity in slope of isentropes at the mixed phase boundary which is given by

\[
\frac{\partial v_{s1}}{\partial p} - \frac{\partial v_{sm}}{\partial p} = \frac{T}{c_p} \left( \frac{ds}{dp} \right)^2 > 0
\]

where subscripts \( s1 \) and \( sm \) refer to the incident and mixed phase isentropes (Duvall and Horie 1965). The sign of the discontinuity assures that the incident isentrope is steeper than that in the mixed phase. An example of the cusp is shown in Fig. 5-12. This implies that under some circumstances the condition of shock stability will be violated. That is

\[
\left( \frac{dp}{dv} \right)_H < \frac{p - p_0}{v - v_0}
\]

(112)
Therefore, the appearance of a double shock like that caused by an elastic-plastic transition discussed in Chapter 2 provides a simple means of identifying polymorphic transformations. For some materials, such as Fe, iron alloys, Bi, and KCl, there is excellent agreement of transition pressures between static and dynamic data. There are, however, notable exceptions, such as Si and CdS (Duvall and Graham, 1977). Such discrepancies must be strongly related to the question of transformation rates and mechanisms.

Figure 5-13 shows a graphical illustration of Hugoniot curves loaded
through a transition of the second type: \( dp/dT > 0, \Delta v > 0, \) and \( L > 0. \) A representative example of this type is melting.

In contrast to the first type, normal melting does not create a double shock at its phase boundary (Carter, 1973). Hence, in spite of many attempts, experimental detection of equilibrium melting has been circuitous.

Heterogeneous melting, the kind that occurs in the shock compression of powders, may be studied using the approach proposed by Grady (1977), but it remains an open field of inquiry. A promising new experimental approach is the use of thin films to control thermal loading after melting (Nellis et al. 1986).

5.5 Chemical Equilibria

The thermodynamic basis of chemical reactions in a closed system is identical to that of phase transitions of a single component system. The system as a whole is closed, but now a redistribution of mass occurs within the system. Thus, from Eqs. (19)-(21),

\[
\begin{align*}
    dE &= TdS - pdV + \sum \mu_i dn_i \\
    dH &= TdS - Vdp + \sum \mu_i dn_i \\
    dG &= Vdp - SdT + \sum \mu_i dn_i
\end{align*}
\]  

(113)  

(114)  

(115)

where we have replaced \( g_i \) and \( m_i \) by more commonly used variables \( \mu_i \) and \( n_i \), \( n_i = m_i/M_i \) (Molar weight). Similar changes of unit hold for other variables. Then, from Eq. (115), it may be easily seen that
\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j \neq n_i} \]  

(116)

Also, it follows that Helmholtz energy is given by

\[ dF = -SdT - pdV + \sum \mu_i dn_i \]  

(117)

If the condition of extensivity were assumed as before for \( E, V, S, \) and \( n_i \), then

\[ E(\lambda S, \lambda V, \lambda n_i) = \lambda E(S, V, n_i), \text{ etc.} \]  

(118)

Differentiating \( E \) with respect to \( \lambda \), one obtains

\[ E = \frac{\partial E}{\partial (\lambda S)} \frac{d(\lambda S)}{d\lambda} + \frac{\partial E}{\partial (\lambda V)} \frac{d(\lambda V)}{d\lambda} + \frac{\partial E}{\partial (\lambda n_i)} \frac{d(\lambda n_i)}{d\lambda} \]

\[ = \frac{\partial E}{\partial (\lambda S)} S + \frac{\partial E}{\partial (\lambda V)} V + \frac{\partial E}{\partial (\lambda n_i)} n_i \]  

(119)

Letting \( \lambda = 1 \), and using the partial derivatives based on Eqs. (107)-(109), one obtains

\[ \left( \frac{\partial E}{\partial S} \right) = T, \quad \left( \frac{\partial E}{\partial V} \right) = -p, \quad \left( \frac{\partial E}{\partial n_i} \right) = \mu_i \]

So it may be seen that

\[ E = TS - pV + \Sigma \mu_i n_i \]  

(120)

Now, from the relationships of \( E \) to \( H, F, \) and \( G \), one may find integral forms of other potential functions:

\[ H = E + pV = TS + \Sigma \mu_i n_i \]  

(121)

\[ F = E - TS = -pV + \Sigma \mu_i n_i \]  

(122)

\[ G = E + pV - TS = \Sigma \mu_i n_i \]  

(123)
Taking the derivative of Eq. (123) and substituting it into Eq. (115), we have the Gibbs-Duhem equation:

\[ SdT - VdT + \Sigma n_i d\mu_i = 0 \quad (124) \]

To illustrate a general treatment of chemical equilibria, let us consider a heterogeneous system consisting of reactants (A, B, C,...) and products (X, Y, Z,...) that react according to a single equation

\[ \nu_A A + \nu_B B + \ldots + \nu_C C \leftrightarrow \nu_X X + \nu_Y Y + \ldots + \nu_Z Z \]

where \( \nu_i \) are stoichiometric coefficients. Or, disregarding separate notation for reactants and products,

\[ \Sigma \nu_i \Delta_i = 0 \quad (125) \]

where it is assumed that \( \nu_i \) for reactants is negative. Then, at a constant temperature and pressure, the condition of equilibrium is

\[ (\delta G)_{P,T} = 0 \quad (126) \]

where \( \delta \) signifies an infinitesimal mass redistribution \( \delta n_i \) based on Eq. (125). To evaluate this displacement, we introduce the following quantities:

\[ m_i^0 = \text{mass of } i\text{-component at initial time } (t=0) \]

\[ m_i(t) = \text{mass of } i\text{-component at time } t \]

\[ M_i = \text{molar weight of } i\text{-component} \]

\[ \xi = \text{progress variable of the reaction defined by} \]

\[ m_i(t) - m_i^0 = \nu_i M_i \xi \quad (127) \]

where \( \nu_i \) for reactants is negative. If \( \nu_i M_i \) is understood to represent initial masses, then it may be seen from Eq. (127) that

\[ \xi = 0, \text{ no reaction at } t=0 \]

\[ \xi = 1, \text{ complete reaction at } t=\infty \]
Hence, for an infinitesimal virtual displacement, Eq. (127) yields

$$\delta m_i(t) = \nu_i M_i \delta \xi$$

$$\delta n_i(t) = \delta \left( \frac{m_i}{M_i} \right) = \nu_i \delta \xi$$

(128)

On substitution of Eq. (128) into Eq. (126),

$$(\delta G)_{p,T} = \sum \left( \frac{\delta G}{\delta n_i} \right)_{p,T} \delta n_i = \left[ \sum \left( \frac{\delta G}{\delta n_i} \right) \nu_i \right] \delta \xi = 0$$

So,

$$\sum \left( \frac{\delta G}{\delta n_i} \right)_{p,T} \nu_i = \sum \mu_i \nu_i = 0$$

(129)

Hence, the quantity, $\sum \mu_i \nu_i$, may be perceived as a thermodynamic driving force. At equilibrium this force vanishes. However, the evaluation of $\mu_i \nu_i$ for a system with variable composition is cumbersome, and requisite thermodynamic data are not readily available (e.g. Leitner et al., 1989; Lupis, 1983). An exception is an ideal system in which the chemical potential is given by

$$\mu_i = G_i^\circ(T, p) + RT \ln x_i$$

(130)

where $x_i = n_i / \sum n_i$, $G_i^\circ(T, p)$, is the molar free energy of pure $i$-component, and $R$ the universal gas constant. Then, substituting Eq. (130) into Eq. (129), one obtains

$$\Delta G^\circ = \left( \nu_X G_X^\circ + \nu_Y G_Y^\circ + \ldots \right) - \left( \nu_A G_A^\circ + \nu_B G_B^\circ + \ldots \right)$$

$$= -RT \ln \frac{x_X^{\nu_X} x_Y^{\nu_Y}}{x_A^{\nu_A} x_B^{\nu_B}}$$

$$= -RT \ln K(T, p)$$

(131)

where $K$ is called the equilibrium constant. Equation (131) shows that for an ideal
system, the chemical potentials of pure components determine equilibrium compositions.

Since,

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]  \hspace{1cm} (132)

\( \Delta G^\circ \) is always negative if \( \Delta H^\circ < 0 \) and \( \Delta S^\circ > 0 \). In fact, with many of the solid-state reactions of the type

\[ A(S) + B(S) = AB(S) \]

the reactions have a small positive entropy change, but a large heat of formation. Thus, these reactions rarely reach chemical equilibrium at practical laboratory conditions. For instance, using a crude estimate of \( \Delta G^\circ \) given by Eq. (104), and ignoring the pressure term, equilibrium temperatures (\( \Delta G^\circ = 0 \)) were calculated for three representative examples using the thermodynamic data of Kubaschewski and Evans (1979). In any of these systems, once the reaction is initiated, at appropriate conditions of pressure and temperature, it will not stop until some components are exhausted.

\[ \text{Si} + \text{C} = \text{SiC} : \quad 1.91T - 16\times10^3 = 0, \quad T_e = 8.4\times10^3 \text{ K} \]

\[ \text{Ti} + \text{C} = \text{TiC} : \quad 2.89T - 28.8\times10^3 = 0, \quad T_e = 10^4 \text{ K} \]

\[ \text{Ni} + \text{Al} = \text{NiAl} : \quad 0.98T - 28.3\times10^3 = 0, \quad T_e = 2.9\times10^4 \text{ K} \]

\[ \quad \text{Ideal mixture} \]

\[ \quad \text{Product} \]

\[ \text{Gibbs Energy, } G \]

\[ \text{A} \quad \text{AB} \quad \text{B} \]

**Fig. 5-14.** Schematic illustration of the Gibbs free energy of an ideal two-component mixture and its product AB.
Many other examples of this type are shown in Table 5-5. As shown in Fig. 5-14 schematically, the free energies of the mixture A+B for these systems are much higher than those of the product AB. The products do not dissociate back to the reactants unless temperatures become extremely high. Thus, in shock loading of reactive powder mixtures, there no longer exists a thermodynamic boundary as that of a phase transition. Initiation and subsequent propagation of reaction is

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Reaction (cal/g)</th>
<th>Adiabatic Reaction Temperature (°C)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiSn</td>
<td>-134</td>
<td>1000 (1)</td>
</tr>
<tr>
<td>LiSb</td>
<td>-170</td>
<td>1060 (1)</td>
</tr>
<tr>
<td>Al₂C₃</td>
<td>-560</td>
<td>1440 (1)</td>
</tr>
<tr>
<td>UMg</td>
<td>-157</td>
<td>1940 (1)</td>
</tr>
<tr>
<td>UC₃</td>
<td>-111</td>
<td>500 (s)</td>
</tr>
<tr>
<td>SnCa₂</td>
<td>-379</td>
<td>1484 (1)</td>
</tr>
<tr>
<td>TiB₂</td>
<td>-1155</td>
<td>3770 (1)</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>-690</td>
<td>3400 (1)</td>
</tr>
<tr>
<td>HiB₂</td>
<td>-394</td>
<td>3380 (1)</td>
</tr>
<tr>
<td>VB</td>
<td>-528</td>
<td>2400 (s)</td>
</tr>
<tr>
<td>NbB₂</td>
<td>-511</td>
<td>2900 (s)</td>
</tr>
<tr>
<td>TaB₄</td>
<td>-216</td>
<td>2400 (s)</td>
</tr>
<tr>
<td>TiAl₂</td>
<td>-314</td>
<td>1370 (1)</td>
</tr>
<tr>
<td>ZrAl₂</td>
<td>-281</td>
<td>1650 (1)</td>
</tr>
<tr>
<td>VA₉</td>
<td>-198</td>
<td>750 (s)</td>
</tr>
<tr>
<td>NiAl</td>
<td>-329</td>
<td>1639 (1)</td>
</tr>
<tr>
<td>PdAl</td>
<td>-327</td>
<td>2380 (1)</td>
</tr>
<tr>
<td>PtAl</td>
<td>-216</td>
<td>2800 (1)</td>
</tr>
<tr>
<td>UB₄</td>
<td>-214</td>
<td>1770 (s)</td>
</tr>
<tr>
<td>SiC</td>
<td>-394</td>
<td>1680 (s)</td>
</tr>
<tr>
<td>TiC</td>
<td>-737</td>
<td>3600 (1)</td>
</tr>
<tr>
<td>ZrC</td>
<td>-461</td>
<td>3800 (1)</td>
</tr>
<tr>
<td>HiC</td>
<td>-268</td>
<td>4200 (s)</td>
</tr>
<tr>
<td>VC</td>
<td>-412</td>
<td>2030 (s)</td>
</tr>
<tr>
<td>NbC</td>
<td>-321</td>
<td>2730 (s)</td>
</tr>
<tr>
<td>TaC</td>
<td>-184</td>
<td>2800 (s)</td>
</tr>
<tr>
<td>VSi₂</td>
<td>-700</td>
<td>3280 (1)</td>
</tr>
<tr>
<td>NbSi₂</td>
<td>-480</td>
<td>3300 (1)</td>
</tr>
<tr>
<td>TaSi₂</td>
<td>-117</td>
<td>1570 (s)</td>
</tr>
<tr>
<td>CePb</td>
<td>-81</td>
<td>1380 (1)</td>
</tr>
</tbody>
</table>

b The notation (1) or (s) denotes whether the reaction product is liquid or solid at the adiabatic reaction temperature, based on a reference temperature of 298 °K. The reaction product should be liquid at the reaction temperature to assure a self-propagating reaction.
strictly controlled by kinetic conditions as well as mass transport.

The effect of shock pressure will not significantly alter $\Delta G^\circ$. Figure 5-15 shows a model calculation of $\Delta G^\circ$ for the system $(C+2S=CS_2)$ using the equation of state described in section 5.2 (Sheffield 1978).

![Gibbs free energies of CS$_2$ and its products C+2S in terms of principal Hugoniot pressures (after Sheffield, 1979).](image)

**Fig. 5-15.** Gibbs free energies of CS$_2$ and its products C+2S in terms of principal Hugoniot pressures (after Sheffield, 1979).

### 5.6 Reaction Kinetics

From the purview of thermodynamics, the Gibbs potential function is the measure of chemical driving forces. It determines the propensity of reactions. But in reality a large chemical force does not necessarily result in an observable reaction. In fact kinetic factors such as defect structure, interfacial energy, and mass transport are the ones that mostly control the observability of a reaction. In this section, we shall peruse a few selected concepts and models that have been used or proposed for organizing and understanding theoretically the kinetics of shock-induced phase transitions and chemical reactions.

#### 5.6.1 Rate equations

Kinetics of solid state processes are often represented by the Arrhenius rate equations

$$\ln K^* = -\Delta Q/RT + \text{constant},$$

where $Q$ is a constant with dimension of energy, $R$ the gas constant, and $K^*$ the rate constant for the forward reaction in the formalized equation, Eq. (125). $K^*$ is related to the kinetics equation as follows:
\[- \frac{d}{dt} \text{(reactants)} = AK^* \text{(reactants)}^n, \tag{134}\]

where \(A\) is a constant and \(n\) is the so-called order of reaction.

A similarity of Eq. (133) to Eq. (131) is obvious. Explicit importation of thermodynamics into reaction kinetics can be accomplished by the transition state theory. This theory views that during any chemical reaction that involves the breaking and remaking of bonds, there is a transition state (or activated state) which is of a high energy content and intrinsically unstable (see Fig. 5-16 where the energy peak corresponds to the transition state). It is further assumed that during the reaction, equilibrium is maintained between the activated and non-activated species according to a Boltzmann distribution. Then the theory leads to a rate equation

\[K^* = f \exp(-\Delta G^*/RT) \tag{135}\]

where \(f\) has the dimension of time\(^{-1}\) and is proportional to \(kT/h\) for gases, \(k\) Boltzmann’s constant, and \(h\) Planck’s constant.

As \(\Delta G^o\) determines an equilibrium state, \(\Delta G^*\) determines all the “thermodynamic” quantities in kinetic relationships. For instance, it can be easily seen from Eq. (135) that

\[
\left( \frac{\partial \ln K^*}{\partial p} \right)_T = -\frac{1}{RT} \left( \frac{\partial \Delta G^*}{\partial p} \right)_T = -\frac{\Delta V^*}{RT}, \tag{136}
\]

![Diagram](image-url)

**Fig. 5-16.** Schematic illustration of the concept of transition or activated state.
where $\Delta V^*$ is the difference in volume between the initial material and the transition state. Since chemical bonds are thought to be elongated at the transition state, the above equation shows that the effect of increasing pressure is to decrease the rate of forward reaction. In some chemical systems, it is known that $\Delta V^*$ is linearly proportional to $\Delta V$.

Another insight into the activated state is obtained from the relationship

$$\Delta G^* = \Delta H^* - T\Delta S^*. \quad (137)$$

Then, the rate equation becomes

$$K^* = f \exp(\Delta S^*/R) \exp(-\Delta H^*/RT). \quad (138)$$

Upon comparison of Eq. (138) with Eq. (133) one finds that the experimentally observed activation energy can be compared with the enthalpy of the transition state. What is significant is that chemical reactivity can be quantitatively reviewed in terms of the free energy of the system under the purview of thermodynamics.

A simple means of evaluating $f$ and $\Delta G^*$ is to obtain relaxation time defined by

$$\tau = \frac{1}{K^*} = \frac{\exp(\Delta G^*/RT)}{f} \quad (139)$$

The plot of $\ln \tau$ vs. $(1/T)$ yields an estimate of $\Delta G^*$ and $f$. Presently there are no data on the rate of shock-induced reactions in this form. Sheffield’s attempt (1978) on the dissociation of $CS_2$ is a rare exception.

5.6.2 Nucleation

Many reactions occur discontinuously forming embryonic products. Homogeneous nucleations are those that occur without the benefit of preferential sites in parent phases. If they occur on preferential high energy sites such as defects and grain boundaries, they are called heterogeneous nucleation.

Typical free energy functions for nucleation are

$$\Delta G = -A\Delta G_v + B\gamma + C \in \quad (140)$$

and

$$\Delta G = -A\Delta G_v + B\gamma + C \in -\Delta G_D \quad (141)$$

where $\Delta G_v$ is the volume free energy change, $\gamma$ the interfacial energy, $\varepsilon$ the strain
energy, $\Delta G_D$ the energy of the defect destroyed, and $A$, $B$, and $C$ are shape factors. Most examples listed in Table 2-2 fall in the second category. Therefore, heterogeneous nucleation phenomena are expected in various stages of the chemical process under shock loading. For instance in solids, it could be a precipitation of a second phase. In powder, it could be a solidification process from melt, a solid-state transformation, or a solid-solid and a solid-liquid reaction.

Although realistic evaluation of the free energy functions, Eqs. (140)-(141) is difficult, Fig. 5-17 shows a schematic illustration of $\Delta G$ in terms of nucleus radius. Since $\Delta G$, and $\varepsilon$ are cubic functions, whereas $\gamma$ is a quadratic function, $\Delta G$ will normally have a maximum at some radius $r_c$. This implies that since a natural process occurs in the direction of minimizing the free energy, embryos cannot grow unless its radius is greater than $r_c$. However, as shown in the figure, defects such as dislocation may even completely eliminate the barriers. Then the progression of reaction is totally controlled by mass transport.

Fig. 5-17. Illustration of Gibbs free energy of embryonic nucleation and effects of defects such as dislocation (after Chadwick, 1972).

A simple kinetic model of nucleation (Christian 1965) can be developed using $\Delta G$, as the activation energy of the transition state described in Fig. 5-15 and Eq. (135) as the rate equation:

$$I = A \frac{ND}{a^2} \exp\left(-\frac{\Delta G_c}{kT}\right)$$  \hspace{1cm} (142)

where $I$ is the rate of nucleation, $A$ a constant, $a$ an interatomic distance, $N$ the number
of atoms per unit volume, and $D$ the mass transport coefficient given by

$$D = a^2 v \exp\left(-\Delta G_m/kT\right)$$  \hspace{1cm} (143)

where $v$ is a frequency factor and $\Delta G_m$ the activation energy for mass transport.

Since $\Delta G_c$ is temperature dependent, the nucleation rate has a local minimum at a certain temperature $T_m$ and approaches zero both at 0 and at $T_c (T_m)$. Above $T_c$ the rate increases rapidly for the reverse reaction.

5.6.3 Growth

Once the nuclei achieves the critical size, they will grow and eventually transform the reactant into the product.

Models of growth rate can be classified into two types: interface controlled model or diffusion controlled model. The first model makes use of an idea similar to the activated transfer of atoms in nucleation reactions discussed earlier. The net transfer of atoms is considered to obtain the advance of an interface. The result is

$$\dot{G} = a_0 v \exp(-\Delta G^*)_\left[1 - \exp\left(-\Delta G_c/RT\right)\right],$$  \hspace{1cm} (144)

where $\dot{G}$ is the rate of growth, $a_0$ is the jump distance, $v$ the frequency factor, and $\Delta G^*$ the activation energy. Using the form of Eq. (143), one finds an alternative expression,

$$\dot{G} = \frac{D}{a_0} \left[1 - \exp\left(-\Delta G_c/RT\right)\right]$$  \hspace{1cm} (145)

For diffusion controlled types, the diffusion equation may be solved for a particular mechanism considered. But normally, simplified analytical solutions are found to be sufficient. One example is given by

$$\dot{G} = \alpha(D/t)^{1/2}$$  \hspace{1cm} (146)

where $\alpha$ is a function of concentrations. Others may be found in Sharp et al. (1966) for various geometries and boundary conditions.

The calculation of overall kinetics in terms of nucleation and growth mechanisms involves many assumptions. Typically, it assumes random nucleation, isotropic growth, and no interaction among particles. An example is given by
\ln(1 - f) = S_0^t \int_0^t G(t - \tau) d\tau \tag{147}

where $f$ is the volume fraction of the new product, $S$ a shape factor, and $t$ an induction period for initial nucleation. The discussions regarding the questions of impingement, nucleation sites, shape factors, and special growth laws are considered in Christian (1965).

Johnson (1972) considered a model of shock-induced phase transformation in solids using a kinetic equation similar to Eq. (147). In this model he addresses not only the question of heterogeneous nucleation of second phase along a dislocation line and at a grain boundary, but also the construction of a thermodynamically consistent equation of state as discussed in section 5.2. However, to our knowledge it has not been used to interpret actual shock data. It may be that, in general, available shock data are too limited to justify analysis by a mechanistic model such as Johnson's.* Typically, kinetic equations are simply assumed as a function of $\Delta G$ and/or other differentials such as $\Delta p$ (Horie and Duvall, 1968; Kamegai, 1975).

In the case of chemical reactions, phenomenological rate equations have also been developed to describe the kinetics of overall reaction (a catch all model) involving drastically idealized reaction processes. These equations are typically expressed in terms of a single reaction coordinate or the fractional amount of products. For instance,

\[ A \rightarrow B; \quad \frac{d\lambda}{dt} = K(1 - \lambda) \]

\[ A + A \rightarrow B; \quad \frac{d\lambda}{dt} = K(1 - \lambda)^2 \]

where $K$ is often assumed to be constant.

5.6.4 Pressure effects

While both temperature and pressure are important factors in studying chemical reactions, in the present discussion we call attention to the importance and fruitfulness of investigating the effect of pressure. Our comments, however, will be limited to the subject of kinetics.

Pressure affects both the nucleation and growth rates through several parameters: concentration of defects, diffusion coefficient, and the chemical and surface energies. Concentrations are known to vary according to

* Iron is an exception where some success has been obtained using a mechanistic model analysis (Forbes, 1976).
\[ \frac{c_p}{c_0} = \exp(-p\Delta V / RT) \]

where \(c_p\) is the concentration at pressure \(p\) and \(\Delta V\) is the change in partial molar volume involved in the creation of a defect. The order of magnitude calculation shows that if \(\Delta V = 5\) cm\(^3\) per mole, \(T = 500^\circ\text{K}, p = 10\) GPa, then \(c_p/c_0\) is \(4 \times 10^{-6}\). This is a significant change.

The influence of pressure on diffusion is generally studied through the activation volume \(\Delta V\) given by

\[ \Delta V = \left( \frac{\partial \Delta G}{\partial p} \right)_T \]

where \(\Delta G\) is the activation energy for diffusion. It is known that a pressure of several GPa is equivalent to a lowering of temperature of several hundred degrees (Lazarus and Nachtrieb 1963).

The evaluation of the chemical and surface energies involves a variety of assumptions. For a single component system, the pressure derivatives may be approximated by Hanneman (1969)

\[
\left( \frac{\partial \Delta G}{\partial p} \right)_T \approx -\frac{2A\gamma}{\Delta p^3} \left( \frac{V}{\Delta V} \right)^2
\]

\[
\left( \frac{\partial \gamma}{\partial p} \right)_T = -\Gamma V
\]

where \(A\) is a shape factor, \(\Delta p\) the excess pressure beyond the equilibrium point, \(\Gamma\) the surface excess mass. If \(\Delta V\) is about 5%, then the free energy change is about 600 cal/mole at 5 GPa and is not insignificant when compared even with that of a chemical reaction.

5.7 Shock-Induced Reactions in Powder Mixtures

We have seen in Section 5.5 that there is no chemical equilibria for many powder mixtures of interest at high temperatures and high pressures. Once reactions are initiated, they go to completion unless there are kinetically unfavorable conditions. Therefore, shock-induced chemical reactions are fundamentally different from those of high-pressure phase transitions. If there exists a threshold state on the “frozen” mixture Hugoniot, as shown in Fig. 5-17a, it only marks kinetic initiation conditions. It does not imply the condition of equality of Gibbs free energies among constituents. This means that we cannot expect a priori that at higher pressures the reactions will initiate from an extended frozen state, say,
Reactive powder mixtures are more like high explosives. Also, their upstream metastable equilibrium conditions are similar to those of a relaxing gas flow through a Laval nozzel (Becker and Bohme, 1969). In the latter, a drastic reduction of relaxation times takes place due to a sudden change of state.

Boslough (1990) introduced the term “heat detonations” to describe shock-induced strongly exothermic reactions such as intermetallics (see Table 5-5), thermites and other energetic mixtures. He showed that if the reaction proceeds rapidly and an equilibrium state is established behind the shock wave, then many of the exothermic systems have melt products whose densities are less than those of initial solid components. Then, the Rayleigh line intersects the product Hugoniot before the “frozen” Hugoniot (see Fig. 5-18a). According to Fickett and Davis (1979), the reaction of this type is a “strong” or “overdriven” detonation. If the reaction initiates on the reactant Hugoniot as the ZND model of detonation, then the corresponding pressure profile is shown in Fig. 5-18b.

If an equilibrium (or metastable equilibrium state) is assumed behind the shock wave, the determination of both the reactant and product Hugoniots can be carried out using any of the techniques discussed in Section 5.1. Boslough’s calculations for initially 50% thermite reaction,

\[ Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe, \]

are shown in Fig. 5-19. They involve the Mie-Gruneisen approximation (Eq. (31) in Chapter 2) and

\[
p_H(v) = \left( -Q - \int_{v_0}^{v} p_S dv - \left[ \frac{v}{\gamma} \right] p_S \right) \left/ \left( \frac{1}{2} (v_{00} - v) - \frac{v}{\gamma} \right) \right.,
\]

where \( v_0 \) and \( v_{00} \) are the initial specific volumes of the dense and porous mixtures respectively. The isentropic pressure \( p_S \) is calculated using the Bridgman quadratic equation

\[
\frac{v}{v_0} = 1 - \left( \frac{p_S}{K_{0S}} \right) + \frac{1}{2} \left( 1 + \frac{K'_{0S}}{K_{0S}} \right) \left( \frac{p_S}{K_{0S}} \right)^2,
\]

and the Reuss average (Eq. (51)) for \( K_{0S} \) and \( K'_{0S} \). The particle velocity is related to the pressure by

\[
u = \sqrt{p_H(v_{00} - v)},
\]
Fig. 5-18. Schematic illustration of Hugoniots with condensed-phase chemical reactions. Accompanying pressure profiles assume the initiation of reactions from a frozen state pf.

The temperature calculation is based on the Mie Grüneisen approximation and the isentropic temperature change given by Eq. (63) in Chapter 2. That is,

\[
T_H = \frac{1}{C_V} \frac{v_0}{\gamma_0} \left( P_H - P_S \right) + T_0 \exp \left[ \frac{\gamma_0}{v_0} (v_0 - v) \right].
\]

where \(C_V\) and \(\gamma/v\) are both assumed to be constant. The residual temperature is based on isentropic unloading.
Fig. 5-19. Calculated Hugoniots and shock temperatures of initially 50% porous thermite reactant and its product (after Boslough, 1990).

\[ T_F = T_H \exp \left[ \frac{\gamma_0}{\nu_0} (\nu - \nu_F) \right] \]

where "F" signifies residual values at zero pressure.

Steady state assumption in Boslough's analysis requires that the Rayleigh line in Fig. 5-18 must satisfy the conservation equations of continuity and momentum along its cord. Thus, using the coordinates fixed to the shock front, these requirements become (see Eqs. (5) and (6) of Chapt. 2)

\[ \rho u = \rho_0 u_0 = \rho_1 u_1 \]  \hspace{1cm} (148)

\[ p + \rho u^2 = p_0 + \rho_0 u_0^2 = p_1 + \rho_1 u_1^2 \]  \hspace{1cm} (149)

where the subscripts "0" and "1" signify the initial and final states. Then, using notation \( m_0 = \rho_0 u_0 \), \( q_0 = p_0 + \rho_0 u_0^2 \), they become

\[ \rho u = m_0 \]  \hspace{1cm} (150)

\[ p = q_0 - m_0 u \]  \hspace{1cm} (151)

To simplify the accompanying energy equation, we introduce a single equation of state and an internal parameter to describe the extent of chemical reactions (Horie and Kipp, 1988). The latter can be generalized to any number of parameters (e.g., Becker and Bohme, 1969; Hermann, 1982) if necessary. But the number of internal variables is not germane to the following analysis. Then, the
energy equation, Eq. (7) of Chapter 2, may be transformed to

\[ \bar{h}(p_0, \rho_0, \lambda) + \frac{1}{2} u_0^2 = h(p_1, \rho_1) + \frac{1}{2} u_1^2 \]  

(152)

Let

\[ Q = \bar{h}(p_0, \rho_0, \lambda) - h(p_0, \rho_0) \]

Then, Eq. (152) becomes

\[ h(p_0, \rho_0) + \frac{1}{2} u_0^2 + Q = h(p_1, \rho_1) + \frac{1}{2} u_1^2 \]  

(153)

In order to gain some insight into the enthalpy change along a Rayleigh line, we define the total enthalpy or adiabatic stagnation enthalpy, \( h_t \), in the usual way:

\[ h_t = h(p, \rho) + \frac{1}{2} u^2 \]  

(154)

Differentiating Eq. (154), one obtains

\[ dh_t = \left( \frac{\partial h}{\partial p} \right)_\rho dp + \left( \frac{\partial h}{\partial \rho} \right)_p d\rho + u du \]  

(155)

On substitution of Eqs. (148) and (149) into Eq. (155)

\[ \frac{dh_t}{du} = -m_0 \left( \frac{\partial h}{\partial \rho} \right)_p \left( \frac{1}{u^2} - \frac{1}{C^2} \right) \]  

(156)

where \( C \) is the equilibrium sound speed given by

\[ C^2 = \left( \frac{\partial h}{\partial \rho} \right)_p \sqrt{\left( \frac{\partial h}{\partial \rho} \right)_p - \frac{1}{\rho}} \]

Hence, \( h_t \) has an extreme when \( u = C \).
Fig. 5-20. Schematic illustration of Rayleigh line in the $h_t-u$ plane (after Becker and Bohme, 1969).

Fig. 5-21. Schematic illustration of Rayleigh line in the $h_t-u$ plane when the reaction starts from a shocked frozen state.
The testing of the second derivative is lengthy, so we shall quote the result of Becker and Bohme.

\[ \frac{d^2 h_i}{du^2} = \frac{m_0 (u + C)}{2 \rho^3 u^2 C^4} \left( \frac{\partial^2 p}{\partial y^2} \right)_{s, \lambda = \lambda_{eq}} \]

Consequently, for normal materials, the extreme of \( h_i \) is a maximum. A schematic illustration of \( h_i \) is shown in Fig. 5-20. It may be seen from the diagram that a Rayleigh line in the \((h_i-u)\) plane is a cord between an initial state where \( u_0 < C_0 \) and a final state where \( u_f < C_1 \). There are two distinct possibilities depending on the signs of \( Q \). However, if the reaction (or relaxation) is assumed to take place from some frozen state such as \( p_f \) (see Fig. 5-17), then there are four possible solutions because \( u_f \) can now be smaller than \( C_f \). These four cases are illustrated in Fig. 5-21.

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