2(Mg, Fe) SiO_3 (clinopyroxene)

$\rightarrow$ 2 (MgO (periclase), 2 FeO (wüstite))

$+ SiO_2$ (stishovite) (3)

Our calculations were carried out assuming that we are dealing with only a two-phase system, and thus the reaction products are assumed to behave as a single phase, with thermochemical and equation-of-state properties equal to the appropriate molar average. Ideality in the solid solution is also assumed. This assumption has been shown to be approximately valid in the case of the olivine-spinel transformations [*Akimoto*, 1970] and in the case of reaction 2, as demonstrated by the present calculational results.

In order to calculate the reaction pressures at various temperatures for the Mg-Fe end members of reactions listed above, it is convenient to employ standard enthalpies and entropies under standard temperature and pressure conditions for these compounds. For $MgSiO_3$ (clinopyroxene), and for the oxides FeO, MgO and SiO_2 (stishovite), these data as well as the appropriate molar volumes are listed in *Robie and Waldbaum's* [1968] recent compilation of thermochemical data. Thermochemical data for the spinels, Fe_2SiO_4 and Mg_2SiO_4, (γ phase) have been calculated by *Mao* [1967]. For $FeSiO_3$ (ferrosilite) the *P-T* phase diagram for the reactions

$FeSiO_3$ (orthopyroxene)

$\rightarrow FeSiO_3$ (clinopyroxene) (4)

and the calculated phase line

2 $FeSiO_3$ (clinopyroxene)

$\rightarrow Fe_2SiO_4$ (spinel) $+ SiO_2$ (coesite) (5)

which have been studied by *Akimoto et al.* [1965], were used to calculate values for the standard entropy and enthalpy of clinoferrosilite. The resulting values were: 0.022 kcal/mole °K and $-$ 2.63 kcal/mole, respectively.

At a temperature T, the transformation pressure p_i^T for a given end member may be calculated from

$$\Delta G_i^{T,p} = \Delta H_i^T - T\Delta S_i^T = -\int_0^{p_i^T} (V_i^2 - V_i^1)\, dp \qquad (6)$$

Here i indicates the end member component (1 or 2) of a solid-solution series, the superscripts 1 and 2 refer to the high-pressure and low-pressure phase, respectively, and ΔH_i^T and ΔS_i^T are the differences in enthalpy and entropy at zero-pressure and at temperature T. The integral in (6) is along the isotherm at temperature T. Equation 6 must be solved for p_i^T for each component $i = 1, 2$ for each temperature. For a two-component, ideal mixing solid-solution system, the mole fractions of component 1, in the low-pressure phase X_{11}, in equilibrium with the high-pressure phase of composition X_{21}, are given by

$$X_{11} = \frac{\exp(\Delta G_1^{T,p}/nRT)[\exp(\Delta G_2^{T,p}/nRT) - 1]}{\exp(\Delta G_2^{T,p}/nRT) - \exp(\Delta G_1^{T,p}/nRT)} \qquad (7)$$

$$X_{21} = \frac{\exp(\Delta G_2^{T,p}/nRT) - 1}{\exp(\Delta G_2^{T,p}/nRT) - \exp(\Delta G_1^{T,p}/nRT)}$$

Here n is the number of atoms in each molecule that can enter the solid solution. In the present calculation, n is assumed to be 2; its actual value will depend on the degree of Mg^{++}–Fe^{++} ordering in the solid solution. Solution of equation 6, which determines the phase lines of the end members in p, T space, depends on knowledge of the enthalpies and entropies as a function of temperature. p_i^T in (6) and (8) depends on knowledge of the p-V isotherms at various temperatures. A calculational method that has been used to determine these quantities is outlined below.

At each temperature it is assumed that the pressure-volume isotherms are given by the Birch-Murnaghan form of the isothermal equation of state. It is also assumed that the thermodynamic quantity

$$(\partial p/\partial e)_v = \gamma/V \qquad (8)$$

is constant for each material and has the value observed, or calculated, at standard temperature and pressure [*Walsh and Christian*, 1955]. Here γ is the Grüneisen parameter and e is the internal energy. This assumption and another (discussed below) concerning the variation of $(\partial K_T/\partial p)_T$ for different materials are made because a complete knowledge of the pertinent equations of state is, in general, lacking.

The temperature dependence of C_v, the specific heat at constant volume, was assumed to be given by a Debye theory. The Debye temperature at each phase is estimated from its standard enthalpy or from specific heat data. To obtain an estimate of the variations in bulk modulus with temperature, we have applied an empirical observation of *Anderson* [1967*a*]. In the case of oxides and silicates Anderson observed that the variation of the bulk modulus with volume is similar when the volume change is produced by either compression or changes in temperature. Specifically, data for ten minerals listed by Anderson suggests the relation

$$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_p \cong \left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_T + 0.85 \qquad (9)$$

Taking (12) as an equality, it follows that

$$\left(\frac{\partial K_T}{\partial T}\right)_p = -\alpha K_T\left[\left(\frac{\partial K_T}{\partial p}\right)_T + 0.85\right] \qquad (10)$$

The properties of the various phases can be calculated numerically at a series of finite temperature increments as a function of temperature in the order given below. The change in volume is calculated from the coefficient of expansion α. At each successive temperature the value of α is revised by using the Grüneisan relation

$$\alpha = (\gamma/V)(C_p/K_s) \qquad (11)$$

where K_s is the adiabatic bulk modulus and C_p is the specific heat at constant pressure. The change in the Debye temperature θ_D with changing volume is calculated from

$$\theta_D = \theta_0 \exp[\gamma(V_0 - V)/V_0] \qquad (12)$$

which follows from the Debye model and the assumption regarding equation 8. A new value of C_p is calculated from the thermodynamic identity

$$C_p = C_v + \alpha^2 VTK_T \qquad (13)$$

and the change in enthalpy and entropy due to the incremental temperature increase is then calculated for both end members, in their high-pressure and low-pressure phases.

Using the above procedure, the theoretical phase diagrams calculated for reactions 2 to 3 are shown in Figures 2 and 3.

The calculation for reaction 3, summarized in Figure 3, indicates that it takes a greater shock pressure, at least 180 kb at room temperature, than the 135 kb observed to produce the direct transformation of clinoenstatite to mixed oxide-type phase for a stoichiometry corresponding to Bamle enstatite. (The temperature rise due to shock compression and the small density and enthalpy differences between

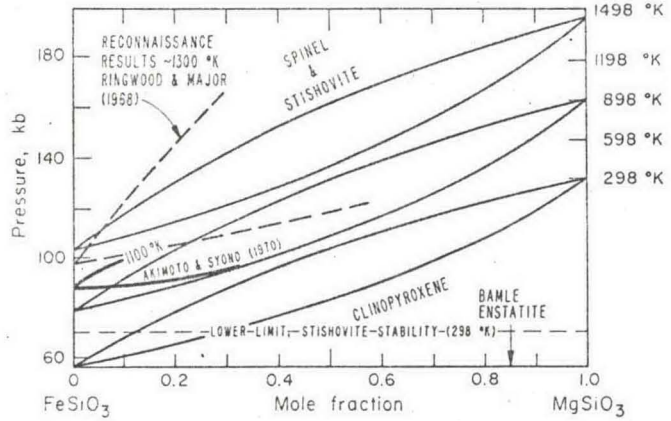

Fig. 2. Theoretical phase diagram for breakdown of (Mg, Fe) pyroxene to (Mg, Fe)$_2SiO_4$ (ringwoodite) + SiO_2 (stishovite). Comparison of theoretical diagram with experimental data of *Akimoto and Syono* [1970] indicates the approximate validity of ideal mixing assumption.