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Thermodynamics and Equations of State

> *The art of narrative consists in concealing from your audience everything it wants to know until after you expose your favorite opinions on topics foreign to the subject. I will now begin, if you please, with a horoscope located in the Cherokee Nation; and end with a moral tune on the phonograph.*
>
> —O. HENRY, "CABBAGES AND KINGS"

THERMODYNAMICS

The total energy contained in a system, such as a mineral, is called the *internal energy, U,* and includes the kinematic and potential energy of all the atoms. It depends on temperature, pressure and position in the field of gravity. For an infinitesimal change of the system, the law of conservation of energy, or the *first law of thermodynamics,* is

$$dU = dQ - d\mathcal{W}$$

where Q is the heat flow and $\mathcal{W}$ is the mechanical work, for example the change of volume acting against a hydrostatic pressure

$$d\mathcal{W} = P\,dV$$

The *enthalpy* or heat content of a system is

$$H = U + PV$$

$$dH = dU + P\,dV + V\,dP$$

The energy contents cannot be determined in absolute terms; they are only known as differences. The usual, but arbitrary, zero point is known as the *standard state* and is denoted ΔH°.

The *heat capacity* or *specific heat* is the heat required to raise a unit mass of the material by one degree. This can be done at constant volume or at constant pressure and the corresponding symbols are C_V and C_P,

$$dU = C_V\,dT$$

$$dH = C_P\,dT$$

For minerals,

$$C_V \approx C_P \approx 0.3\ \text{cal/°C g}$$

A certain fraction of the heat entering a system, dQ/T, is not available for mechanical work. The integral of this is the entropy, S, defined from

$$dS = dQ/T$$

giving the *second law of thermodynamics,*

$$T\,dS = dU + d\mathcal{W}$$

which applies to reversible processes, processes that do not lose energy to the environment. In irreversible processes,

$$T\,dS > dU + d\mathcal{W}$$

Entropy is a measure of the energy associated with the random arrangement and thermal motion of the atoms and that is therefore unavailable for external work. At absolute zero temperature a perfectly ordered crystal has zero entropy; with increasing temperature a certain disorder or randomness is introduced. The entropy at temperature T is

$$S = \int_0^T (C/T)\,dT$$

At high temperature,

$$S \approx C \ln T$$

When a mineral undergoes a change of phase at temperature T involving a change in enthalpy or latent heat of transformation ΔH, there is a discontinuous change of entropy:

$$\Delta S = \Delta H/T$$

The mechanical part of the free energy U is the Helmholtz free energy F:

$$\begin{aligned} F &= U - TS \\ \mathrm{d}F &= \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T \\ &= -P\,\mathrm{d}V - S\,\mathrm{d}T \end{aligned}$$

giving

$$P = -(\partial F/\partial V)_{\mathrm{T}}$$

$$S = -(\partial F/\partial T)_{\mathrm{V}}$$

When using P and T as independent variables, instead of V and T, it is convenient to use the *Gibbs free energy, G:*

$$G = H - TS = U + PV - TS = F + PV$$

For a reversible process,

$$\mathrm{d}G = V\,\mathrm{d}P - S\,\mathrm{d}T$$

$$V = (\partial G/\partial P)_{\mathrm{T}}$$

$$S = (\partial G/\partial T)_{\mathrm{P}}$$

If W is any thermodynamic function, the volume and pressure derivatives at constant temperature may be related by writing

$$(\partial W/\partial V)_{\mathrm{T}} = (\partial W/\partial P)_{\mathrm{T}}\,(\partial P/\partial V)_{\mathrm{T}}$$

or

$$(\partial W/\partial V)_{\mathrm{T}} = -(K_{\mathrm{T}}/V)\,(\partial W/\partial P)_{\mathrm{T}}$$

We can also write

$$(\partial W/\partial T)_{\mathrm{V}} = (\partial W/\partial T)_{\mathrm{P}} + \alpha K_{\mathrm{T}}(\partial W/\partial P)_{\mathrm{T}}$$

where α is the volume expansion coefficient.

Thermodynamic Identities

There are a variety of relations between the partial differentials of the standard thermodynamic parameters. Some of the standard forms are:

TABLE 5-1
Differentials of Thermodynamic Parameters

Differential	**Constant**			
element	***T***	***P***	***V***	***S***
∂T	—	1	1	γT
∂P	$-K_{\mathrm{T}}/V$	—	$\alpha K_{\mathrm{T}}=\gamma\rho C_{\mathrm{v}}$	K_{s}
∂V	1	αV	—	$-V$
∂S	$\alpha K_{\mathrm{T}}=\gamma\rho C_{\mathrm{v}}$	mC_{p}/T	mC_{v}/T	—
∂U	$\alpha K_{\mathrm{T}}T-P=\gamma\rho C_{\mathrm{v}}T-P$	$mC_{\mathrm{p}}-\alpha VP$	mC_{v}	PV
∂H	$-K_{\mathrm{T}}(1-\alpha T)$	mC_{p}	$mC_{\mathrm{v}}(1+\gamma)$	$K_{\mathrm{s}}V$
∂F	$-P$	$-S-\alpha VP$	$-S$	$PV-\gamma TS$
∂G	$-K_{\mathrm{T}}$	$-S$	$-S+\alpha K_{\mathrm{T}}V=-S+\gamma mC_{\mathrm{v}}$	$K_{\mathrm{s}}V-\gamma TS$
	U	***H***	***F***	***G***
∂T	$P-\alpha TK_{\mathrm{T}}=P-\gamma\rho C_{\mathrm{v}}T$	$1-\alpha T$	P	1
∂P	$-\rho C_{\mathrm{v}}(K_{\mathrm{s}}-\gamma P)$	$-\rho C_{\mathrm{p}}$	$K_{\mathrm{T}}(S/V+\alpha P)$	S/V
∂V	mC_{v}	$\alpha V(1+1/\gamma)$	$-S$	$\alpha V-S/K_{\mathrm{T}}=(1/K_{\mathrm{T}})(\gamma mC_{\mathrm{v}}-S)$
∂S	$mC_{\mathrm{v}}P/T$	mC_{p}/T	$mC_{\mathrm{v}}(P/T-\gamma S/V)$	$mC_{\mathrm{p}}/T-\alpha S$
∂U	—	$mC_{\mathrm{p}}-PV\alpha(1+1/\gamma)$ $=\alpha V[K_{\mathrm{s}}/\gamma-P(1+1/\gamma)]$	$mC_{\mathrm{v}}P-S\gamma\rho C_{\mathrm{v}}T+SP$	$mC_{\mathrm{p}}-\alpha TS-P\alpha V+PS/K_{\mathrm{T}}$
∂H	$mC_{\mathrm{v}}[P(1+\gamma)-K_{\mathrm{s}}]$	—	$SK_{\mathrm{T}}(1-\alpha T)+mC_{\mathrm{v}}P(1+\gamma)$	$mC_{\mathrm{p}}+S(1-\alpha T)$
∂F	$\rho C_{\mathrm{v}}(\gamma TS-PV)-PS$	$-S(1-\alpha T)-PV\alpha(1+1/\gamma)$	—	$-S(1-P/K_{\mathrm{T}})-P\alpha V$
∂G	$mC_{\mathrm{v}}[\gamma TS/V+\alpha P-K_{\mathrm{s}}]-PS$	$-S(1-\alpha T)-mC_{\mathrm{p}}$	$S(K_{\mathrm{T}}-P)+PV\alpha K_{\mathrm{T}}$	—

Stacey (1977).

U	Internal energy*	V	Volume*
H	Enthalpy*	γ	Gruneisen parameter
F	Helmholtz free energy*	α	Volume expansion coefficient
G	Gibbs free energy*	ρ	Density
S	Entropy*	m	Mass of material*
T	Absolute temperature	K	Bulk modulus = incompressibility
P	Pressure	C	Specific heat

Subscripts signify parameters held constant.

*Parameters proportional to mass.

$$dU = (\partial U/\partial S)_V\, dS + (\partial U/\partial V)_S\, dV = T\, dS - P\, dV$$

$$dH = T\, dS + V\, dP$$

$$dF = -S\, dT - P\, dV$$

$$dG = -S\, dT + V\, dP$$

The Maxwell relations are:

$$(\partial T/\partial V)_S = -(\partial P/\partial S)_V = -\gamma T/V$$

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V = \gamma\rho C_V = \alpha K_T$$

$$(\partial T/\partial P)_S = (\partial V/\partial S)_P = \gamma T/K_S$$

$$-(\partial S/\partial P)_T = (\partial V/\partial T)_P = \alpha V$$

Table 5-1 represents all possible partial differentials of the standard parameters. The individual entries are to be taken in pairs. Thus $(\partial T/\partial P)_S$ is ∂T at constant S (that is, γT) divided by ∂P at constant S (that is, K_S) giving

$$(\partial T/\partial P)_S = \gamma T/K_S$$

The following partial differentials are of particular interest:

$$(\partial P/\partial T)_V = \gamma\rho C_V$$

is the differential form of the Mie-Grüneisen equation and gives the variation in pressure in heating at constant volume.

$$(\partial\alpha/\partial P)_T = (1/K_T^2)(\partial K_T/\partial T)_P$$

connects the pressure dependence of the coefficient of thermal expansion with the temperature dependence of the bulk modulus. The relation

$$T(\partial\alpha/\partial T)_V = -\rho(\partial C_V/\partial P)_T$$

is useful in the high-temperature limit where $C_V \approx 3R$ (R being the gas constant) and α is independent of T at constant V and nearly independent of T at constant P.

Table 5-2 gives thermodynamic data for a few minerals.

The combination αK_T occurs in many thermodynamic relationships. The following second derivative thermodynamic identities are therefore useful:

$$\left[\frac{\partial(\alpha K_T)}{\partial V}\right]_T = -\frac{1}{V}\left(\frac{\partial K_T}{\partial T}\right)_V$$

$$\left[\frac{\partial(\alpha K_T)}{\partial P}\right]_T = \frac{1}{K_T}\left(\frac{\partial K_T}{\partial T}\right)_V$$

$$\left[\frac{\partial(\alpha K_T)}{\partial T}\right]_V = \frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T = -\frac{\rho K_T}{T}\left(\frac{\partial C_V}{\partial P}\right)_T$$

$$\left[\frac{\partial(\alpha K_T)}{\partial T}\right]_P = K_T\left(\frac{\partial\alpha}{\partial T}\right)_V$$

Chemical Equilibria

The fact that a mineral assemblage changes into a different assemblage means that the new association has a lower free energy than the old. At equilibrium both assemblages have the same free energy. The stable phase has the lowest free energy, at the given pressure and temperature and mineral association, of all alternative phases. In general, the denser phases are favored at high pressure and low temperature.

The *partial molal free energy* or *chemical potential* per mole of species i is F_i,

$$F_i = RT \ln a_i + F_i^\circ$$

where a_i is the *activity* of a chemical species, and F_i° is the free energy in a standard state. The total energy is

$$G = \sum n_i F_i$$

where G is Gibbs free energy and n_i is the number of moles of species i. At constant temperature and pressure,

$$dG = \sum F_i\, dn_i$$

$$F_i = M_i \mu_i$$

TABLE 5-2
Thermodynamic Properties of Minerals

Mineral	C_P	C_V	α	K_s	γ	θ
	erg/g/K (10^6)		($K^{-1}\times 10^{-6}$)	(kbar)		(K)
MgO	9.25	9.11	31.5	942	1.55	940
CaO	7.50	7.42	29.0	675	1.31	680
Al_2O_3	7.79	7.74	16.4	1035	1.33	1040
Mg_2SiO_4	8.38	8.31	24.7	760	1.18	760
$MgSiO_3$	7.8	7.60	47.7	706	1.89	710
$MgAl_2O_4$	8.15	8.07	20.8	863	1.41	860
SiO_2	7.41	7.35	36.6	572	0.7	570
Garnet	7.61	7.55	21.6	745	1.21	750
Garnet	7.0	6.96	18.3	739	1.09	740

and M_i is the molecular weight and μ_i is the *chemical potential per gram*. The change of activity with pressure is

$$\left(\frac{\partial \ln a}{\partial P}\right)_T = \frac{V}{RT}$$

The total Gibbs free energy of a system of C components and p phases is

$$G = \sum_{i=1}^{C} \sum_{j=1}^{p} \mu_i^j n_i^j$$

where n_i^j is the number of moles of the component i in phase j and μ_i^j is its chemical potential in phase j. The equilibrium assemblage, at a given pressure and temperature, is found by minimizing G. Taking the standard state of i to be pure i in phase j at the pressure and temperature of interest,

$$\mu_i^j = \mu^0 + RT \ln a_i^j$$

$$\mu^0 = H_{0,T}^j - TS_{0,T}^j + \int_0^P V_T^j \, dP$$

where $H_{0,T}^j$, $S_{0,T}^j$ and V_T^j are the enthalpy and entropy of pure i in phase j at $P = 0$ and T and volume at T. With the chosen standard state for the activity, a_i^j in phase j containing pure i is one. The activity of pure liquids or pure solids is unity. In an ideal solution a_i is equal to the mole fraction of component i.

At equilibrium the standard-state free-energy change at the pressure and temperature of interest is

$$\Delta G_{P,T}^0 = -RT \ln K$$

where K is the equilibrium constant. Consider the hypothetical reaction

$$2A \rightleftarrows C + D$$

where two molecules of A react to form one molecule each of C and D. The rate of reaction is proportional to the collisional probability between any two molecules, which is related to the product of the concentrations. For equilibrium the rates of the two reversible reactions are the same, and

$$K = \frac{(C) \times (D)}{(A)^2}$$

where (A), (C) and (D) are the concentrations or activities. For the general reaction,

$$nA + mB = qC + rD$$

then

$$K = \frac{(C)^q \times (D)^r}{(A)^n \times (B)^m}$$

The equation for equilibrium

$$d(\Delta G) = \Delta V \, dP - \Delta S \, dT = 0$$

yields

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

which is the Clausius-Clapeyron equation.

For a system in equilibrium the following relation holds between the number of coexisting phases p, components c, and degrees of freedom f:

$$p = c + 2 - f$$

This is the phase rule of J. Willard Gibbs. The *phases* are the parts of the system that can be mechanically separated, for example, the minerals and any coexisting liquid and gas. The *components* are the smallest number of chemical species necessary to make up all the phases. The *degrees of freedom* are generally the temperature, pressure and composition.

The components distribute themselves over all the phases of the system. No phase can be without some contribution from all components since the chemical potential or activity of each component must be the same in all phases of the system. The phase rule places a limitation on the number of minerals that can occur in equilibrium in a given rock. The maximum number of phases can be attained only in an invariant system, one with P and T fixed. If both P and T vary during the process of formation of a rock, then

$$p \leq c$$

which is the *mineralogical phase rule* of Goldschmidt. Because of the phenomenon of solid solution, the number of different minerals in a rock is less than the number of components.

Table 5-3 is a compilation of the terms and relations introduced in this section.

THEORETICAL EQUATIONS OF STATE

The equation of state of a substance gives the pressure P as a function of volume V and temperature T:

$$P = P(V,T)$$

The general expression for the free energy of a crystal can be written in terms of three functions

$$F(X,T) = U(X) + f_1(\theta/T) + f_2(X,T)$$

where $X = V_o/V = \rho/\rho_o$ is the dimensionless volume relative to the volume at normal conditions and θ is a characteristic temperature, such as the Debye or Einstein temperature. $U(X)$ is the potential part of the free energy, which depends only on the volume. The second term is the phonon term and is usually calculated from the Debye or Einstein theory. The third term represents high-temperature corrections to the equation of state. This term, which is generally

TABLE 5-3
Notation and Basic Relationships

V = Specific volume
$V_o = V$ at $P = 0$
ρ = Density = $\bar{M}/V$
$\rho_o = \rho$ at $P = 0$
T = Absolute temperature
P = Pressure
S = Entropy
$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$ = Volume thermal expansion
$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \rho\left(\frac{\partial P}{\partial \rho}\right)_T$ = Isothermal bulk modulus
$K_S = -V\left(\frac{\partial P}{\partial V}\right)_S = \rho\left(\frac{\partial P}{\partial \rho}\right)_S$ = Adiabatic bulk modulus
$\Phi_S = K_S/\rho = V_p^2 - \frac{4}{3}V_s^2 = \left(\frac{\partial P}{\partial \rho}\right)_S$ = elastic ratio
$\gamma = \alpha K_T/\rho C_V = \alpha K_S/\rho C_P$ = Grüneisen ratio
C_V = Specific heat at constant volume
C_P = Specific heat at constant pressure
V_p, V_s = Velocity of compressional and shear waves
$K_S = K_T(1+\alpha\gamma T)$
$\left(\frac{\partial P}{\partial T}\right)_V = K_T\alpha$
$\left(\frac{1}{K_T}\right)\left(\frac{\partial K_T}{\partial T}\right)_P = -V\left(\frac{\partial \alpha}{\partial V}\right)_T$
$\left(\frac{1}{K_T}\right)\left(\frac{\partial K_T}{\partial T}\right)_P = K_T\left(\frac{\partial \alpha}{\partial P}\right)_T$
θ = Characteristic temperature
$\bar{M}$ = Mean atomic weight
Bulk modulus = Incompressibility = 1/Compressibility.
$\delta = [\partial \ln K/\partial \ln \rho]_P$ = Second Grüneisen ratio

small, is due to anharmonic lattice oscillations, formation of point defects and thermal excitation of conduction electrons in metals. For most geophysical problems $U(X)$ is the dominant term.

The potential energy of a crystal can be written as the sum of an attractive potential, which holds the atoms together, and a repulsive potential, which keeps the crystal from collapsing:

$$U = -\frac{A}{r^m} + \frac{B}{r^n} = -\frac{A}{V^{m/3}} + \frac{B}{V^{n/3}}$$

where r is the interatomic spacing and A, B, m and n are constants, different from those in the last section. The functional form of the repulsive potential is uncertain, and an exponential form is also often used.

The pressure is obtained by differentiation:

$$P = \left(\frac{\partial U}{\partial V}\right)_T$$

The isothermal bulk modulus, K_T, is

$$K_T = -V(\partial P/\partial V)_T$$

The bulk modulus is also called the incompressibility. At $P = 0$, $V = V_o$ and $K_T = K_T(0)$. The PV equation of state can therefore be written as

$$P = \frac{3K_T(0)}{(m-n)}\left[\left(\frac{V_o}{V}\right)^{(m+3)/3} - \left(\frac{V_o}{V}\right)^{(n+3)/3}\right]$$

and the bulk modulus as

$$K_T = \frac{K_T(0)}{(m-n)} \times \left[(m+3)\left(\frac{V_o}{V}\right)^{(m+3)/3} - (n+3)\left(\frac{V_o}{V}\right)^{(n+3)/3}\right]$$

The pressure derivative of K_T at $P = 0$ is

$$K_T'(0) = (m + n + 6)/3$$

$K_T'(0)$ is approximately 4 for many substances. Since the repulsive potential is a stronger function of r than the attractive potential, $n > m$ and $3 < n < 6$ for $K_T'(0) = 4$.

THE GRÜNEISEN RELATIONS

Grüneisen (1912) introduced the concept of a "thermal pressure" derived from the pressure of a collection of atoms vibrating under the excitation of the energy associated with nonzero temperature. A crystalline solid composed of N atoms has $3N$ degrees of freedom, and the solid can be viewed as a collection of harmonic oscillators. The energy levels of a harmonic oscillator are $nh\nu$, where n are successive integers and h is Planck's constant. In thermal equilibrium a given energy level is populated with the probability $\exp(-nh\nu/kT)$, where k is Boltzmann's constant. The individual oscillators have a frequency ν_i, and these are considered to be independent of temperature but dependent on the volume, V.

The quantity

$$\gamma_i = -\frac{\mathrm{d}\log \nu_i}{\mathrm{d}\log V}$$

is involved in calculations of the thermal pressure and is known as the Grüneisen ratio. If it is assumed that all the γ_i are the same, then

$$\nu_i \approx V^{-\gamma}$$

The Grüneisen equation of state is

$$P = P_o + \frac{\gamma U_D}{V}$$

where P_0 is the pressure at absolute zero and U_D is the internal energy of the oscillators in a volume V due to the elevated temperature:

$$U_D = \frac{h\nu_i}{\exp(h\nu_i/kT) - 1}$$

Differentiating P with respect to temperature gives

$$\left(\frac{dP}{dT}\right)_V = \frac{\gamma C_V}{V}$$

where C_V is the specific heat at constant V. From the thermodynamic relations

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{K_T}\left(\frac{\partial P}{\partial T}\right)_V$$

where α is the volume coefficient of thermal expansion, the following relation can be derived:

$$\gamma = \frac{VK_T\alpha}{C_V}$$

which is called the Grüneisen relation.

The thermal energy of a crystal is equal to the sum over all oscillators and, therefore, over all pertinent frequencies. In the Debye theory the sum is replaced by an integral, and it is assumed that all frequencies of vibration are bounded by some maximum value $\nu_i < \nu_m$.

In an elastic solid three modes of wave motion are permitted, one compressional mode and two shear modes having orthogonal particle motions. The total thermal energy is therefore

$$U_D = \frac{9N_0}{\nu_m^3}\int_0^{\nu_m} \frac{h\nu^3\, d\nu}{\exp(h\nu/kT) - 1}$$

where N_0 is the number of atoms per unit volume.

The maximum oscillation frequency is related to the volume available to the oscillator and the velocity of elastic waves. In the Debye theory a mean sound velocity is implied, and thus

$$\nu_m^3 = \frac{9N_A\rho}{4\pi\overline{M}}\left(\frac{1}{V_p^3} + \frac{2}{V_s^3}\right)^{-1}$$

where N_A is Avogadro's number, ρ is the density, and $\overline{M}$ is the mean atomic weight (molecular weight divided by the number of atoms in the molecule). In the Debye theory it is assumed that velocity is isotropic and nondispersive, that is, independent of direction and frequency.

The Debye temperature is defined as

$$\theta = h\nu_m/k$$

and therefore

$$\theta = \frac{h}{k}\left(\frac{3N_A\rho}{4\pi\overline{M}}\right)^{1/3} V_m$$

where V_m is mean velocity:

$$V_m = \left[\frac{1}{3}\left(\frac{2}{V_s^3} + \frac{1}{V_p^3}\right)\right]^{-1/3}$$

The Debye temperature can be estimated from the velocities of elastic waves and, therefore, can be estimated for the mantle from seismic data. In principle, the velocities should be measured at frequencies near ν_m ($\sim 10^{13}$ Hz) since there is some dispersion. Ignoring dispersion, however, is consistent with Debye's original assumption. There are also optical modes, as well as acoustic modes, and these are ignored in the simple theories. By differentiation of U we obtain for the thermal pressure

$$P^* = \frac{U_D}{V}\frac{d\log\theta}{d\log V}$$

and, therefore,

$$\gamma = \frac{-d\log\theta}{d\log V} = \frac{-d\log\nu_m}{d\log V}$$

At high temperature, $\theta/T \ll 1$,

$$P^* = \frac{3NkT\gamma\rho}{\overline{M}} = P^*(\mathrm{HT})$$

At very low temperature,

$$P^* = \frac{3}{5}\pi^4\left(\frac{T}{\theta}\right)^3\frac{NkT\gamma\rho}{\overline{M}}$$

At intermediate temperature,

$$P^* = 3P^*(\mathrm{HT})\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{\xi^3\, d\xi}{e^{\xi} - 1}$$

where $\xi = h\nu/kT$.

The thermal pressure in the mantle is estimated to be between 10 and 200 kilobars, increasing with depth. The Debye temperature increases by about a factor of 2 through the mantle, and the Grüneisen parameter probably remains close to 1.

The specific heat can be written

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 9N_0k\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{\xi^4 e^{\xi}\, d\xi}{(e^{\xi} - 1)^2}$$

At $T \gg \theta$ we have the classic high-temperature limit,

$$C_V = 3kN_0$$

Silicates show a close approach to the "classical" values at temperatures greater than about 1000°C. Under these conditions C_V approaches 6 cal/°C g atom for each particle of the chemical formula. The mean atomic weight for most rock-forming minerals is close to 20, so the specific heat at high temperatures is close to 0.3 cal/°C g. The variation of specific heat with pressure is

$$\frac{1}{C_P}\left(\frac{\partial C_P}{\partial P}\right)_T = -\frac{T\alpha\gamma}{K_S}\left[1 + \frac{1}{\alpha^2}\left(\frac{\partial\alpha}{\partial T}\right)_P\right]$$

The specific heat probably only decreases about 10 percent at the highest mantle pressures, and its variation is therefore small relative to the changes expected for bulk modulus and thermal expansion.

Most of the interior of the Earth is hot, well above the Debye temperature. This means that the Earth's interior probably can be treated with classical solid-state physics concepts. I say "probably" because the interior of the Earth is at simultaneous high temperature and high pressure and these are competing effects. The quantization of lattice vibrations and the departures from classical behavior that are of interest to quantum and low-temperature physicists are not relevant except, in some cases, when extrapolating from laboratory measurements to the high temperatures in the interior. The close relationship between γ and the elastic constants and their pressure derivatives means that γ can be estimated from seismology.

The thermal pressure, P^*, can be viewed as the radiation pressure exerted on the solid by completely diffuse elastic waves, that is,

$$P^* = \frac{U_p}{V}\left(\frac{1}{3} - \frac{V}{V_p}\frac{\partial V_p}{\partial V}\right) + 2\frac{U_s}{V}\left(\frac{1}{3} - \frac{V}{V_p}\frac{\partial V_s}{\partial V}\right)$$

$$= \frac{-U_p}{\theta_p}\frac{\partial \theta_p}{\partial V} - 2\frac{U_s}{\theta_s}\frac{\partial \theta_s}{\partial V}$$

where the U_m, V_m and θ_m are the thermal energies, elastic wave velocities and characteristic temperatures associated with the longitudinal (P) and transverse (S) waves. At high temperature we have

$$P^* = \frac{RT}{V}\gamma_P + 2\frac{RT}{V}\gamma_s$$

or, for $\gamma_P = \gamma_s$,

$$P^* = \frac{3RT\gamma\rho}{M}$$

The thermal pressure can be written in a form analogous to the perfect gas equation:

$$P^* = \frac{Q}{V}RT, \quad Q = \gamma_p + 2\gamma_s$$

where Q is of the order of 5 or 6 for many elements and is near 4 for MgO and Al_2O_3.

EFFECT OF TEMPERATURE ON BULK MODULI

The pressure and the isothermal bulk modulus are volume derivatives, at constant temperature, of the free energy $F(V,T)$. The corresponding adiabatic quantities are volume derivatives of the internal energy U (V,S) at constant entropy. The equation of state of simple solids subjected to hydrostatic pressure can be written in two alternative forms. The *vibrational* formulation splits the free energy of the solid into the *lattice* energy, $U_L(V)$, which is the energy of a static solid of volume V in its electronic ground state, and a *vibrational* energy $U^*(V,T)$. The *thermal* formulation splits the free energy into a nonthermal *cohesive* energy $U_c(V)$ of the solid of volume V at 0 K and a *thermal* energy $U^*(V,T)$. Note that the lattice and cohesive energies depend only on volume and the terms with asterisks depend, in general, on both volume and temperature; in the Hildebrand approximation the thermal and vibrational energies are taken to be a function of temperature alone, this being a good approximation at high temperatures where the heat capacity at constant volume has attained its classical value. The cohesive energy is the free energy required to assemble the atoms from infinity to form the rigid lattice; it includes both static lattice and zero-point energy contributions. The total vibrational energy of the solid is the sum over all the modes of lattice vibration of all the particles. The vibrational energy $U^*(V,T)$ consists of the zero-point vibrational energy, $U^*(V,0)$, of the normal modes at $T = 0$ K plus the energy required to heat the lattice at constant volume, V, from 0 K, to T K; that is,

$$U^*(V,T) = U^*(V,0) + \int_0^T C_V \, dT$$

The Helmholtz free energy, in the Hildebrand approximation, can be written, for example,

$$F(V,T) = U_c(V) + U^*T - TS(V,T)$$

Since

$$P = -(\partial F/\partial V)_T$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T$$

we have

$$P(V,T) = -\frac{\partial U_c(V)}{\partial V} + \alpha K_T T = P(V) + P^*(V,T)$$

and

$$K_T(V,T) = V\left(\frac{\partial^2 U_c(V)}{\partial V^2}\right)_T - VT\left(\frac{\partial \alpha K_T}{\partial V}\right)_T$$

$$= K_T(V) + K_T^*(V,T)$$

or

$$K_T(V,T) = K_T(V,0) + T\alpha K_T(V,T)\left[\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T\right]$$

or

$$K_T(V,T) = K_T(V,T_o) + (T - T_o)\alpha K_T \times \left[\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T\right]$$

The quantity

$$\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T$$

is of the order of -1. The quantity αK_T is of the order of 10 to 100 bar/K for elements and is between about 30 and 70 for compounds of interest in the deeper mantle. The quantity

$$\alpha K_T \left[\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T\right]$$

is of the order of -50 bar/K, and a temperature rise of some 2000 K changes the bulk modulus by about 100 kbar, which is about 10 percent of estimated values for the bulk modulus in the mantle.

The following relations are useful and serve to define the second Grüneisen parameter, δ:

$$\left(\frac{\partial \ln K_T/\partial T}{\partial \ln \rho/\partial T}\right)_P = \left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P = \left(\frac{\rho}{K_T}\frac{\partial K_T}{\partial \rho}\right)_P$$

$$= (K_T\alpha)^{-1}\left(\frac{\partial K_T}{\partial T}\right)_P = \delta_T \qquad (1)$$

$$\left[\frac{\partial \ln K_S/\partial T}{\partial \ln \rho/\partial T}\right]_P = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P = \left(\frac{\rho}{K_S}\frac{\partial K_S}{\partial \rho}\right)_P$$

$$= (K_S\alpha)^{-1}\left(\frac{\partial K_S}{\partial T}\right)_P = \delta_S \qquad (2)$$

The elastic moduli of a solid are affected by temperature both implicitly, through the volume, and explicitly. Thus, for example,

$$K_T = K_T(V,T)$$

and

$$d \ln K_T = (\partial \ln K_T/\partial V)_T\, dV + (\partial \ln K_T/\partial T)_V\, dT \qquad (3)$$

The measured variation of K_T with temperature is, then,

$$\frac{d \ln K_T}{dT} = \left(\frac{\partial \ln K_T}{\partial V}\right)_T \frac{dV}{dT} + \left(\frac{\partial \ln K_T}{\partial T}\right)_V$$

$$\left(\frac{d \ln K_T}{d \ln V}\right)_P = \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T + \alpha^{-1}\left(\frac{\partial \ln K_T}{\partial T}\right)_V \qquad (4)$$

where $(\partial \ln K_T/\partial T)_V$ is the intrinsic temperature dependence of K_T. $(\partial \ln K_S/\partial T)_V$ is positive. There is a general tendency for $(\partial \ln K_T/\partial T)_V$ to be smaller at high T/θ.

Experiments show

$$\left(\frac{\partial \ln K_S}{\partial \ln V}\right)_P < \left(\frac{\partial \ln K_S}{\partial \ln V}\right)_T$$

$$\left(\frac{\partial \ln K_S}{\partial \ln V}\right)_P < \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P$$

and

$$\left(\frac{\partial \ln K_S}{\partial \ln V}\right)_T < \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T$$

all of which are useful when trying to estimate the effects of pressure, volume, and temperature on the adiabatic bulk modulus. Note that these are all experimental and thermodynamic inequalities and are independent of the equation of state. We also note that

$$\delta_S < K' < \delta_T$$

$$\delta_T - \delta_S \approx \gamma$$

The seismic parameter Φ is simply

$$\Phi = K_S/\rho$$

so that

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_P = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P - 1 \qquad (5)$$

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_T = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T - 1 \qquad (6)$$

The pressure in the mantle rises to about 1500 kbar, which, for $(dK/dP)_T = 4$, corresponds to a 6000-kbar increase in the bulk modulus. Temperature can therefore be treated as a small perturbation on the general trend of bulk modulus, or Φ, with depth, at least in the deeper part of the mantle.

THERMAL EXPANSION AND ANHARMONICITY

Because the attractive and repulsive potentials have a different dependence on the separation of atoms, the thermal oscillation of atoms in their (asymmetric) potential well is anharmonic or nonsinusoidal. Thermal oscillation of an atom causes the mean position to be displaced, and thermal expansion results. (In a symmetric, or parabolic, potential well the mean positions are unchanged, atomic vibrations are harmonic, and no thermal expansion results.) The Debye model is restricted to assemblages of harmonic oscillators and, strictly speaking, cannot be used to discuss anharmonic effects such as thermal expansion. Anharmonicity causes atoms to take up new average positions of equilibrium, dependent on the amplitude of the vibrations and hence on the temperature, but the new positions of dynamic equilibrium remain nearly harmonic. At any given volume the harmonic approximation can be made so that the characteristic temperature, θ, and frequency are not explicit functions of temperature. This is called the quasi-harmonic approximation. If it is assumed that a change in volume can be adequately described by a change in θ, then the frequency of each normal mode of vibration is changed in simple proportion as the volume is changed. The Grüneisen parameter

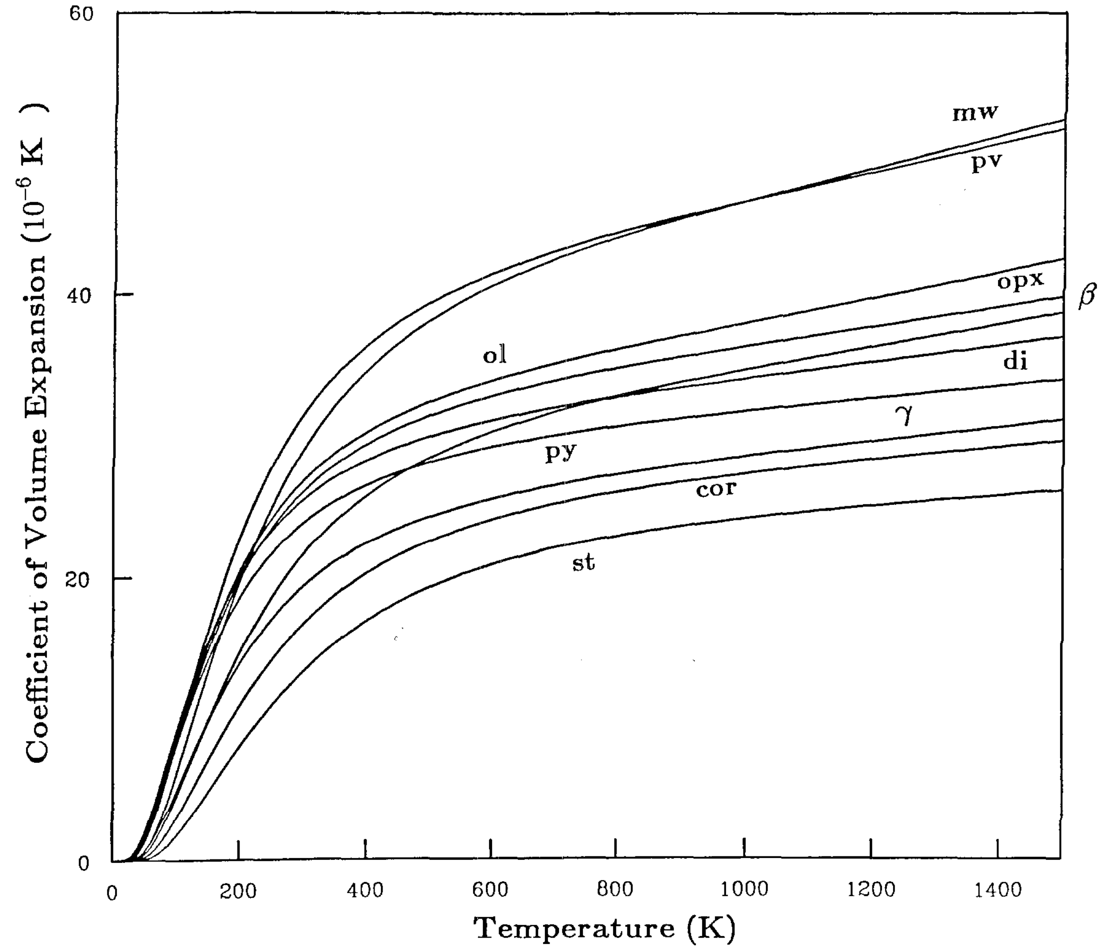

FIGURE 5-1
Coefficient of thermal expansion of mantle minerals, representing theoretical fits to available experimental data (after Duffy and Anderson, 1988).

$$\gamma = -\frac{\mathrm{d}\ln\theta}{\mathrm{d}\ln V}$$

is then a measure of anharmonicity.

From one of Maxwell's thermodynamic relations,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right) \bigg/ \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \alpha K_T$$

we have the volume coefficient of thermal expansion

$$\alpha = \frac{\gamma C_V}{K_T V} = \frac{\gamma C_P}{K_S V}$$

where C_V and C_P are molar specific heats and V is the molar volume. If the specific heats per unit volume are used, then V will not be present in these equations. The Grüneisen equation then shows that thermal expansion will only arise as a consequence of anharmonicity through the parameter γ, and if γ is itself independent of temperature, and we can ignore any explicit temperature dependence of K_T, then γ should be proportional to C_V in its temperature dependence. Since C_V is constant at high temperature (in "classical behavior"), then α should be as well; α should increase with temperature but level off at high T/θ, as shown in Table 5-4 and Figure 5-1.

The change of α with pressure is given by the thermodynamic identity

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{K_T^2}\left(\frac{\partial K_T}{\partial T}\right)_P$$

Thermal expansion decreases with pressure and reaches fairly low values at the base of the mantle. According to *Birch (1938, 1952), α at the core-mantle boundary is only* about 30 percent of its near-surface value. Birch (1968) showed that

$$\alpha/\alpha_0 = 1 + \frac{P}{K}\left[\frac{1}{\alpha_0 K_0}\frac{\mathrm{d}K_0}{\mathrm{d}T}\right] = 1 - \frac{\delta P}{K}$$

TABLE 5-4
Thermal Expansion of Minerals

Mineral	$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$ (10^{-6}/°C) 20°C	400°C	800°C	1500K
Quartz	34	69	−3	—
Coesite	8	11	14	—
Stishovite	16.5	22	23	24
Feldspar	12	19	24	—
Olivine	26	32	34	52
Pyroxene	24	28	32	—
Garnet	19	26	30	33
Al_2O_3	16.3	26	27	28
MgO	31.5	42	45	52
Spinel	16.2	28	29	31
β-spinel	20.6	31	34	37
γ-spinel	18.6	27	28	30
$MgSiO_3$-perovskite	—	37	42	—

Clark (1966), Jeanloz and Knittle (1986).

where the subscripts denote $P = 0$, and showed that

$$\frac{1}{K}\left(\frac{\partial K}{\partial T}\right)_P = \frac{1}{K_o}\frac{dK_o}{dT}\left[1 - \frac{P}{K}\left(\frac{\partial K}{\partial P}\right)_T\right]$$

If δ is independent of pressure $[(\delta = (\partial \ln K/\partial \ln \rho)_P)]$, then

$$\alpha/\alpha_o = (V/V_o)^{\delta}$$

and

$$\frac{1}{K}\left(\frac{\partial K}{\partial T}\right)_P = \frac{\alpha}{\alpha_o}\frac{1}{K_o}\frac{dK_o}{dT} = \left(\frac{V}{V_o}\right)^{\delta}\frac{1}{K_o}\frac{dK_o}{dT}$$

implying that $\partial K/\partial T$ is independent of pressure and $\partial K/\partial P$ is independent of temperature.

In shock-wave work it is often assumed that $\gamma C_V/V$ is independent of pressure. This gives

$$\alpha/\alpha_o = K_o/K$$

or αK is independent of pressure.

The Grüneisen theory for thermal expansion can be written

$$\alpha = (\partial E/\partial T)_P/[Q_o(1 - kE/Q_o)]^2$$

where E is the thermal or vibrational lattice energy,

$$Q_o = K_oV_o/\gamma$$

and

$$k = (1/2)(K_o' - 1)$$

where K_o, K_o' and V_o are the bulk modulus, its pressure derivative and volume, respectively. The thermal energy can be calculated from the Debye model or the Nernst-Lindemann formula,

$$E(T,\theta) = (3pR\theta/4)\,[2(e^{\theta/T} - 1)^{-1} + (e^{\theta/T} - 1)^{-1}]$$

where p is the number of atoms in the molecular formula and θ is a characteristic temperature. In fitting experimental data for α as a function of T, the parameters Q_o, k and θ can be treated, if necessary, as adjustable parameters or, if $\alpha(T)$ is to be estimated for unmeasured materials, these parameters can be estimated from other types of measurements. Both theory and experiment show that α increases rapidly with temperature and then levels off at high temperature ($T/\theta > 1$). Most of the mantle is at high temperature, but most laboratory measurements are made at relatively low temperatures. It cannot be assumed that *α is constant with temperature, or varies linearly with* temperature.

The theory of thermal expansion and a realistic estimate of its variation with temperature are essential in modeling the density and elastic properties of the mantle and in calculating mineral equilibria. The elastic properties of minerals have both an intrinsic and an extrinsic temperature dependence. The former is the variation of a property at constant volume, an experiment that requires a change in temperature and a compensating change in pressure. Most of the variation of the elastic properties is a result of the change in volume, and therefore it is important to understand the variation of α with temperature and to allow for this variation in modeling high-temperature phenomena. The functional forms of $\alpha(T)$ and $C_P(T)$ are related, and this is why γ is relatively independent of temperature.

In general, the coefficient of thermal expansion α is less for high-pressure phases than for low-pressure phases. Of the important mantle minerals, olivine and periclase have high thermal expansivities and γ-spinel and stishovite have relatively low coefficients. (Mg,Fe)SiO_3-perovskite violates this trend (Kuittle and others, 1986), having a relatively high α, at least for the metastable form.

There is a close relationship between lattice thermal conductivity, thermal expansion and other properties that depend intrinsically on anharmonicity of the interatomic potential. The atoms in a crystal vibrate about equilibrium positions, but the normal modes are not independent except in the idealized case of a harmonic solid. The vibrations of a crystal lattice can be resolved into interacting traveling waves that interchange energy due to anharmonic, nonlinear coupling.

In a harmonic solid:

1. *There is no thermal expansion.*
2. Adiabatic and isothermal elastic constants are equal.
3. The elastic constants are independent of pressure and temperature.
4. The heat capacity is constant at high temperature ($T > \theta$).

These consequences are the result of the neglect of anharmonicity (higher than quadratic terms in the interatomic displacements in the potential energy). In a real crystal the presence of one phonon, or lattice vibration of a given type, causes a periodic elastic strain that, through anharmonic interaction, modulates the elastic constants of a crystal. Other phonons are scattered by these modulations. This is a nonlinear process that does not occur in the absence of anharmonic terms.

Perhaps the simplest departure from linear or harmonic theory is to assume that the frequencies, ω_i, of lattice vibrations depend on volume. In the harmonic theory the free energy is independent of volume. The mode Grüneisen parameter expresses this volume dependence

$$\gamma_i = -(\partial \ln \omega_i / \partial \ln V)$$

and is a useful measure of anharmonicity. The crystal anharmonicity is a suitable average of all the modal γ_i. The Grüneisen approximation is that all γ_i are equal, but this is not generally true. A better approximation is to consider the longitudinal and shear modes separately, giving

$$\gamma = (1/3)(\gamma_p + 2\gamma_s)$$

where γ_p and γ_s are the longitudinal and transverse components, respectively, and all shear modes are assumed to have the same volume dependence, or, alternatively, separate averages are made of the two mode types. The above γ is sometimes called the acoustic or high-temperature γ. It is clearly dominated by the shear modes. In principle, the variation of the elastic constants with volume provides an estimate of γ or the anharmonicity and, therefore, higher order properties of the interatomic potential.

At high temperature ($T > \theta$) all phonons are excited and the acoustic γ is a weighted average of all modes. At lower temperature the value of γ is largely controlled by the lower frequency transverse waves.

According to the Mie-Grüneisen theory of the thermal expansion of solids,

$$\gamma = \frac{\alpha K_T}{C_V \rho}$$

and, in the Debye theory,

$$\gamma = -\partial \ln \theta / \partial \ln V$$

In terms of the interatomic potential function, U,

$$\gamma \approx -r^2 U''' / 3U''$$

where U'' and U''' are related to the elastic constants and their volume derivatives, respectively. Note that if $\alpha = 0$ or $U''' = 0$ (that is, no pressure dependence of elastic moduli), then $\gamma = 0$ and there is no anharmonicity. If $\gamma = 0$, the lattice thermal conductivity is infinite.

Actually, the concept of a strictly harmonic crystal is highly artificial. It implies that neighboring atoms attract one another with forces proportional to the distance between them, but such a crystal would collapse. We must distinguish between a harmonic solid in which each atom executes harmonic motions about its equilibrium position and a solid in which the forces between individual atoms obey Hooke's law. In the former case, as a solid is heated up, the atomic vibrations increase in amplitude but the mean position of each atom is unchanged. In a two- or three-dimensional lattice, the net restoring force on an individual atom, when all the nearest neighbors are considered, is not Hookean. An atom oscillating on a line between two adjacent atoms will attract the atoms on perpendicular lines, thereby contracting the lattice. Such a solid is not harmonic; in fact it has negative α and γ.

The quasi-harmonic approximation takes into account that the equilibrium positions of atoms depend on the amplitude of vibrations, and hence temperature, but that the vibrations about the new positions of dynamic equilibrium remain closely harmonic. One can then assume that at any given volume V the harmonic approximation is adequate. In the simplest quasi-harmonic theories it is assumed that the frequencies of vibration of each normal mode of lattice vibration and, hence, the vibrational spectra, the maximum frequency and the characteristic temperatures are functions of volume alone. In this approximation γ is independent of temperature at constant volume, and α has approximately the same temperature dependence as molar specific heat C_V.

ISOTHERMAL-ADIABATIC TRANSFORMATIONS

Seismic data are adiabatic in the sense that the time scale of seismic waves is short compared to the time scale required for the temperature to equilibrate between the compressed and dilated parts of the wave. To relate isothermal theories and experiments with adiabatic data, laboratory or seismic, requires *isothermal-adiabatic transformations*, all of which follow from

$$K_S = K_T(1 + \alpha\gamma T) \tag{7}$$

A large amount of ultrasonic data on solids at moderate pressures has accumulated in the past decades, and these transformations are also required to interpret the data in terms of isothermal equations of state.

From equation 7 we can write

$$\frac{(\partial \ln K_S/\partial T)_P}{(\partial \ln \rho/\partial T)_P} = \frac{(\partial \ln K_T/\partial T)_P}{(\partial \ln \rho/\partial T)_P} - \frac{K_T}{\alpha K_S}\left(\frac{\partial \alpha\gamma T}{\partial T}\right)_P \tag{8}$$

$$\frac{(\partial \ln K_S/\partial P)_T}{(\partial \ln \rho/\partial P)_T} = \frac{(\partial \ln K_T/\partial P)_T}{(\partial \ln \rho/\partial P)_T} + \frac{\alpha\gamma T K_T}{K_S} \times \left[\left(\frac{\partial \ln \gamma}{\partial \ln \rho}\right)_T - \left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P\right] \tag{9}$$

The Grüneisen ratio, γ, is relatively independent of temperature, and the coefficient of volume thermal expansion α is independent of temperature at high temperatures. The second term on the right of equation 8 is, therefore, of the order of γ and is negative. The volume dependence of γ can be written:

$$\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T = \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P + 1$$

$$= -\frac{1}{\alpha}\left(\frac{\partial \ln K_T}{\partial T}\right)_V + 1 \qquad (10)$$

if we take $(\partial \ln C_V/\partial \ln V)_T = 0$, appropriate for high temperatures. Note that the multiplicative factor $(\alpha\gamma T K_T/K_S)$ in equation 9 can be written $(K_S - K_T) \div K_S$, which is a small number of the order of 0.001 for most materials at room temperature. The derivative $(\partial \ln \gamma/\partial \ln \rho)_T$ is of the order of -1 and $(\partial \ln K_T/\partial \ln \rho)_P$ is of the order of 6, so the second term on the right-hand side of equation 8 is of the order of -0.007 or about 1 percent of the first term.

The following relations are useful:

$$\frac{(\partial \ln K_T/\partial P)_T}{(\partial \ln \rho/\partial P)_T} = \left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_T = \left(\frac{\rho\, \partial K_T}{K_T\, \partial \rho}\right)_T$$

$$= \left(\frac{\partial K_T}{\partial P}\right)_T = K_T' \qquad (11)$$

$$\frac{(\partial \ln K_S/\partial P)_T}{(\partial \ln \rho/\partial P)_T} = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T$$

$$= \left(\frac{\rho\, \partial K_S}{K_S\, \partial \rho}\right)_T = \frac{K_T}{K_S}\left(\frac{\partial K_S}{\partial P}\right)_T \qquad (12)$$

CALCULATION OF DENSITY IN THE EARTH

The variation of density ρ with radius in the Earth r can be written

$$\frac{d\rho}{dr} = \left(\frac{\partial \rho}{\partial P}\right)\frac{dP}{dr} + \left(\frac{\partial \rho}{\partial T}\right)\frac{dT}{dr} + \left(\frac{\partial \rho}{\partial \phi}\right)\frac{d\phi}{dr} + \left(\frac{\partial \rho}{\partial c}\right)\frac{dc}{dr} \qquad (13)$$

that is, density is a function of pressure, temperature, phase (ϕ) and composition (c). For a homogeneous adiabatic self-compressed region, we have

$$\frac{d\phi}{dr} = 0, \quad \frac{dc}{dr} = 0$$

$$\frac{dP}{dr} = -g\rho, \quad g = \frac{GM(r)}{r^2}$$

In a convecting mantle the mean temperature gradient, away from thermal boundary layers, is close to adiabatic:

$$\frac{dT}{dP} = \left(\frac{\partial T}{\partial P}\right)_S = \frac{T\alpha}{\rho C_P} \qquad (14)$$

It is therefore convenient to write the temperature gradient as

$$\frac{dT}{dr} = \frac{T\alpha}{\rho C_P}\frac{dP}{dr} - \tau \qquad (15)$$

where τ is the superadiabatic (or subadiabatic) gradient. Adiabatic compression of a material is given by the adiabatic bulk modulus, K_S

$$K_S = \left(\rho\frac{\partial P}{\partial \rho}\right)_S$$

Seismic waves are also adiabatic, and hence we can use

$$V_P^2 - (4/3)V_S^2 = K_S/\rho = (\partial P/\partial \rho)_S = \Phi$$

to calculate the variation of density with depth in a homogeneous, adiabatic region for which we have seismic data. Making the above substitutions,

$$\frac{d\rho}{dr} = -g\rho/\Phi + \alpha\rho\tau$$

$$= -g\rho/\Phi\,(1 - \gamma C_P \tau/g) \qquad (16)$$

These are the Williamson-Adams equations as modified by Birch (1938, 1952).

A useful test of homogeneity (Birch, 1952) is provided by

$$1 - g^{-1}\,d\Phi/dr = dK_S/dP + \alpha\Phi\tau/g \qquad (17)$$

The Bullen parameter (Dziewonski and Anderson, 1981),

$$\eta = \frac{dK}{dP} + \frac{1}{g}\frac{d\Phi}{dr}$$

should be near unity for homogeneous regions of the mantle that do not depart too much from adiabaticity.

In the upper mantle the temperature gradients are high, decreasing from a high conductive gradient at the surface to the convective gradient in the deeper interior. There are also probably chemical, mineralogical and phase changes in the shallow mantle. The latter include partial melting and basalt-eclogite and garnet-pyroxene reactions. At greater depth the olivine-spinel, pyroxene-majorite and garnet-perovskite phase changes keep the mantle from being homogeneous in the Williamson-Adams sense. Any chemical layers also cause thermal boundary layers and superadiabatic gradients. The Bullen parameter is consequently far from unity at depths less than 670 km, and the Williamson-Adams equations cannot be used over most of the upper mantle (Butler and Anderson, 1978). The parameter dK/dP is another measure of homogeneity. It is generally close to 4 at $P = 0$ and decreases smoothly with pressure. This behavior is exhibited by the mantle below 770 km except for the region near the core-mantle boundary.

FINITE-STRAIN EQUATION OF STATE

Finite-strain theory has been applied extensively to problems in geophysics. The resulting equations are called semi-empirical because they contain parameters that have to be determined from experiment. The theory relates strain, or compression, to pressure.

The relation between strain ε and volume V or density ρ is

$$V_o/V = \rho/\rho_o = (1 - 2\varepsilon)^{3/2} = (1 + 2f)^{3/2}$$

where $f = -\varepsilon$ refers to compression, a positive quantity.

The first few terms in the Birch-Murnaghan equation of state (Birch, 1938, 1952) are

$$P = \frac{3}{2} K_o \left[(\rho/\rho_o)^{7/3} - (\rho/\rho_o)^{5/3}\right] \times \{1 - \zeta[(\rho/\rho_o)^{2/3} - 1] + \cdots\}$$

K_o is the bulk modulus at $P = 0$ and can refer to either isothermal or adiabatic conditions depending on whether an isotherm or an adiabat is to be calculated. K_o and ζ are parameters that are functions of temperature alone. In terms of strain,

$$P = 3K_o f(1 + 2f)^{5/2}(1 - 2\zeta f)$$

$$K = K_o(1 + 2f)^{5/2}[1 + 7f - 2\zeta f(2 + 9f)]$$

The term ζ can be found in terms of $(\mathrm{d}K/\mathrm{d}P)_o = K_o'$;

$$K_o' = 4 - \frac{4}{3}\zeta$$

This equation of state has been fitted to a large amount of shock-wave data on oxides and silicates, and K_o' is found to be generally between 2.9 and 3.6 (Anderson and Kanamori, 1968; Sammis and others, 1970; Davies and Anderson, 1971). K' generally decreases with pressure. In the lower mantle $K'(P)$ varies from about 3.8 to 3.1. Ultrasonic measurements of K_o' on minerals generally give values in the range 3.8 to 5.0. Note that for $\zeta = 0$, $K_o' = 4$, a typical value.

For quick, approximate calculations, the Murnaghan equation is useful:

$$P = \frac{3K_o}{n}\left[\left(\frac{\rho}{\rho_o}\right)^n - 1\right]$$

where $n = K_o'$. This diverges from the Birch-Murnaghan equation at high compressions but is useful at low pressures.

Finite-strain equations can also be developed for the variation of seismic velocity with pressure (Birch, 1961b; Burdick and Anderson, 1975). These have been used in the interpretation of velocity and density profiles of the mantle (Butler and Anderson, 1978; Davis and Dziewonski, 1975; Jeanloz and Knittle, 1986). The equations are:

$$V_p^2(P) = V_p^2(0)(1 - 2\varepsilon)[1 - 2\varepsilon(3K_oD_p - 1)]$$

$$V_s^2(P) = V_s^2(0)(1 - 2\varepsilon)[1 - 2\varepsilon(3K_oD_s - 1)]$$

where

$$D_{p,s} = (\partial \ln V_{p,s}/\partial P)_T$$

at $P = 0$. Pressure is calculated from

$$P = -3K_o(1 - 2\varepsilon)^{5/2}(1 - 2\varepsilon\zeta)\varepsilon.$$

The ζ parameter satisfies

$$\zeta = (9/4) - (3/2)\rho_o[V_p^2(0)D_p - (4/3)V_s^2(0)D_s]$$

The expressions to the next order in strain have been given by Davies and Dziewonski (1975). In order to apply these, the higher order pressure derivatives of K_S, V_p and V_s are required, and these are generally not available. However, the higher order terms for the lower mantle can be determined by fitting these equations to the seismic data for the lower mantle, assuming it is homogeneous and adiabatic. The zero-pressure properties of the lower mantle can therefore be estimated.

The "fourth-order" finite-strain equations can be written

$$\rho V_p^2 = (1 - 2\varepsilon)^{5/2}(L_1 + L_2\varepsilon + 1/2L_3\varepsilon^2 + \cdots)$$

$$\rho V_s^2 = (1 - 2\varepsilon)^{5/2}(M_1 + M_2\varepsilon + 1/2M_3\varepsilon^2 + \cdots)$$

$$P = -(1 - 2\varepsilon)^{5/2}(C_1\varepsilon + 1/2C_2\varepsilon^2 + 1/6C_3\varepsilon^3 + \cdots)$$

where L_i, M_i and C_i are constants.

By evaluating the above equations and their derivatives at $\varepsilon = 0$, it is possible to relate the above coefficients to the $P = 0$ values of the elastic moduli and their pressure derivatives. There is some question as to whether the finite-strain equations converge at high pressure and which order is appropriate for application to the lower mantle. There are significant differences in the inferred $P = 0$ properties of the mantle depending on whether third-order or fourth-order finite-strain equations are used.

Unfortunately, there has been little progress in determining equations of state for V_p and V_s from first principles. The bulk modulus and seismic parameter, $K_S/\rho = \Phi$, however, can be determined by simple differentiation of a wide variety of equations of state. $\Phi = \partial P/\partial\rho$ can also be determined from static-compression and shock-wave measurements. Therefore, most discussions of the composition and mineralogy of the mantle depend upon the seismic values for ρ, K_S and Φ, rather than V_p and V_s. Unfortunately, it is the velocities that can be determined most accurately.

Other potential functions in common use are the Bardeen potential:

$$U(r) = \frac{a}{r^3} + \frac{b}{r^2} - \frac{c}{r}$$

giving

$$P = X^{4/3}(X^{2/3} - 1)\left[\frac{3}{2}K_o + D(X^{2/3} - 1)\right]$$

$$K = \left(\frac{4}{3}D - 2K_o\right)X^{4/3} + (3K_o - 4D)X^2 + \frac{8}{e}DX^{8/3}$$

where $X = \rho/\rho_o$, D is an empirically determined constant and

$$K_o' = \frac{10}{3} + \frac{8}{9}\frac{D}{K_o}$$

For an exponential repulsive term in the potential function,

$$U(r) = -\frac{a}{r} + b\exp\left(-\frac{r}{c}\right)$$

giving

$$P = AX^{2/3}\exp[B(1 - X^{-1/3})] - AX^{4/3}$$

$$K = \frac{AX^{2/3}}{3}(BX^{-1/3+2})\exp[B(1 - X^{1/3})] - \frac{4}{3}AX^{4/3}$$

$$K_o = \frac{1}{3}A(B - 2)$$

and

$$K_o' = \frac{1}{9}\frac{A}{K_o}(B^2 + 3B - 12)$$

ZERO-PRESSURE VALUES OF LOWER-MANTLE SEISMIC PROPERTIES

Butler and Anderson (1978) fitted a variety of equations of state to the lower mantle in order to test for homogeneity and to obtain estimates of lower-mantle properties at zero pressure. Their results are summarized in Table 5-5. The first row gives the extrapolated zero-pressure values, based on the assumption that the lower mantle is homogeneous and adiabatic. These assumptions, for the Earth model they used, were only valid between radii of 4825–5125 km and 3850–4600 km; and I have taken the average here. In the Earth model PREM the homogeneity-adiabaticity assumption seems to hold below 5700 km radius. For comparison the Earth model PREM yields $\rho_o(T) = 3.99$–4.00 g/cm^3, $K_o(T) = 2.05$–2.23 Mbar, $K_o' = 3.8$–4.4, $G_o = 1.30$–1.35 Mbar and $G_o' = 1.5$–1.8.

In subsequent rows various temperature corrections have been made, using temperature derivatives given at the bottom of the table. In the lower part of the table, measurements or estimates of the zero-pressure, room-temperature values for various candidate lower-mantle minerals are given. Note that "perovskite" (the high-pressure form of $MgSiO_3$) and corundum (Al_2O_3) give good fits. If the mantle is homogeneous and contains abundant olivine, $(Mg,Fe)_2SiO_4$, in the upper mantle, then the lower mantle will contain substantial magnesiowüstite, (Mg,Fe)O, thereby decreasing the moduli and velocities compared to perovskite.

THE EQUATION OF STATE

The general form of an equation of state follows from considerations of elementary thermodynamics and solid-state physics. A wide variety of theoretical considerations lead to equations of state that can be expressed as

$$P = 3K_o(m - n)^{-1}[(V_o/V)^{(m+3)/3} - (V_o/V)^{(n+3)/3}] \quad (18)$$

$$K_T = K_o(m - n)^{-1}[(m + 3)(V_o/V)^{(m+3)/3} - (n + 3)(V_o/V)^{(n+3)/3}] \quad (19)$$

The choice of exponents $m = 2$, $n = 4$ leads to Birch's equation, which is based on finite-strain considerations; if $m = 1$, $n = 2$ we obtain Bardeen's equation, which was derived from quantum mechanical considerations. If $m = -3$ we obtain Murnaghan's finite-strain equation. A generalized form of the equation of state of a degenerate electron gas obeying Fermi-Dirac statistics can also be cast into this form. Equations of state based on the Mie form of the potential energy $U(r)$ of an atom in a central interatomic force field, given as

$$U(r) = -Ar^{-m} + Br^{-n}$$

where the two terms on the right correspond to an attractive and a repulsive potential and r is an interatomic distance, yield the general form of the equation of state by differentiation. The choice $m = 1$ is appropriate for electrostatic interactions, and $m = 6$, $n = 12$ is the Lennard-Jones potential, appropriate for Van der Waals or molecular crystals.

The foundations of the atomic approach were laid near the beginning of this century by Born, Van Karman, Grüneisen, Madelung, Mie and Debye. The basic premise of the theory is that ionic crystals are made up of positively charged metal atom ions and negatively charged electronegative atom ions that interact with each other according to simple central force laws. The electrostatic, or Coulomb, forces that tend to contract the crystal are balanced by repulsive forces, which, in the classical theory, are of uncertain origin. Dipole-dipole and higher order interactions, the Van der Waals forces, provide additional coupling between ions. They dominate the attraction between closed-shell atoms but are a minor part of the total attractive force in mainly ionic crystals. The Van der Waals forces are also of much shorter range than electrostatic forces.

An ionic crystal is a regular array of positive and negative ions that exert both attractive and repulsive forces on each other. The attractive force is the Coulomb or electro-

TABLE 5-5
Extrapolated Values of Lower Mantle Properties

$-\Delta T$ (°C)	ρ (q/cm^3)	K_S (Mbar)	μ (Mbar)	V_P (km/s)	V_S (km/s)	K_S'	μ'
0	3.97	2.12	1.34	9.93	5.83	3.9	1.5
1400	4.14	2.48–2.62	1.67–1.72	10.7–10.9	6.3–6.4		
1600	4.16	2.53–2.68	1.71–1.76	10.8–11.0	6.4–6.5		
1800	4.18	2.57–2.74	1.74–1.80	10.8–11.1	6.5–6.6		
			Minerals				
$(Mg_{0.8}Fe_{0.2})O$ (mw)	4.07	1.66	1.05	8.7	5.08	4.0	2.5
Stishovite (st)	4.29	3.16	2.20	11.9	7.16	4.0*	1.1*
Al_2O_3 (cor)	3.99	2.53	1.63	10.83	6.40	4.3	1.8
Perovskite* (pv)	4.10	2.60–2.45	1.43–1.84	10.5–10.9	5.9–6.7	4.1–4.5	2.1–2.6

*Estimated.

Temperature corrections:

$$(\partial \ln K_S/\partial \ln \rho)_P = 4.0\text{–}5.5$$
$$(\partial \ln \mu/\partial \ln \rho)_P = 5.7\text{–}6.5$$
$$\alpha = 3 \times 10^{-5}/°\mathrm{C}$$

static force between the ions, and the force that keeps the crystal from collapsing is the repulsion of filled shells. For a simple salt the attractive potential between any pair of ions with charges q_1 and q_2 is

$$U_1 = -q_1q_2e^2/r$$

where r is the distance between the centers of the ions and e is the electronic charge. This potential must be summed over all pairs of ions in the crystal to get the total cohesive energy. The result for the attractive potential energy of a crystal is

$$U = aU_1$$

where a (or A) is the Madelung constant, which has a characteristic value for each crystal type. The repulsive potential is much shorter range and usually involves only nearest neighbors.

The calculation of the exact form of the interatomic force law or the potential energy of an assembly of particles as a function of their separation is a difficult problem and has been treated by quantum mechanical methods for only a few cases. For many purposes it is sufficient to adopt a fictitious force law that resembles the real one in some general features and that can be made to fit it in a narrow region around the equilibrium point. The total energy U must satisfy

$$\left(\frac{dU}{dV}\right)_{V_0} = 0 \quad \text{and} \quad = \left(\frac{d^2U}{dV^2}\right)_{V_0} = \frac{K_T}{V_0}$$

which are the conditions that the crystal be in equilibrium with all forces and that the theoretical bulk modulus, K_t, should be equal to the observed value. These conditions serve to determine the constants in the fictitious force law and assure that the slope and curvature of this law are proper at the equilibrium point.

The attractive forces in a crystal are balanced by the so-called overlap repulsive forces that oppose the interpenetration of the ions. Perhaps the simplest picture is a rigid ion surrounded by a free-electron gas. The effect of hydrostatic pressure is to reduce the volume of the electron gas and to raise its kinetic energy. The kinetic energy varies as r^{-2} where r is the nearest neighbor separation. The repulsive force between ions is very small until the ions come in contact, and then it increases more rapidly than the electrostatic force. In his early work on ionic crystals, Born (1939) assumed that the repulsive forces between ions gave rise to an interaction energy of the type

$$U(r) = b/r^n$$

for the whole crystal where b and n are constants and r is the distance between nearest unlike ions. Investigations of interionic forces based on quantum mechanics indicate that a repulsive potential of this type cannot be rigorously correct, although it may be a good approximation for a small range of r. Later work has used a repulsive potential of the form

$$U(r) = be^{-r/a}$$

where b and a are constants.

Regardless of the details of the various attractive and repulsive potentials and their dependence on interatomic spacing, the Mie-Lennard-Jones potential

$$U(r) = -Ar^{-m} + Br^{-n}, \quad n > m$$

is a simple useful approximation for a restricted region of the potential energy curve and, in particular, the vicinity of the potential minimum. Constants A, B, m and n will be determined at a point in the vicinity of interest by requiring that the interatomic spacing and the bulk modulus both be appropriate for the pressure at this point.

TABLE 5-6
Thermodynamic Properties of Minerals and Metals

Substance	γ	$\left(\frac{\partial \ln K}{\partial \ln \rho}\right)_T = (\partial K/\partial P)_T$	$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P = \delta_T$	$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P = \delta_S$	$\left(\frac{\partial \ln K_S}{\partial T}\right)_V$ $\times 10^5/K$	$\left(\frac{\partial \ln G}{\partial \ln \rho}\right)_T$	$\left(\frac{\partial \ln G}{\partial \ln \rho}\right)_P$	$\left(\frac{\partial \ln G}{\partial T}\right)_V$ $\times 10^5/K$
MgO	1.53	3.89	6.18	3.61	0.842	3.13	5.58	7.72
Mg_2SiO_4	1.18	5.39	7.60	5.38	0.025	2.83	6.50	9.19
Fe_2SiO_4	1.25	5.97	6.95	5.15	2.14	—	—	—
Al_2O_3	1.32	3.99	5.14	3.41	0.945	2.73	6.85	6.72
$MgAl_2O_4$	1.13	4.19	6.14	3.97	0.389	1.31	5.89	7.42
Garnet	1.43	5.45	6.88	5.00	1.062	2.61	5.40	6.07
Cu	1.96	5.62	5.69	3.23	10.89	—	—	—
Ag	2.40	6.21	6.19	3.26	15.38	—	—	—
Au	3.03	6.50	7.03	3.92	9.64	—	—	—

Using the interatomic potential

$$U = -\frac{A}{r^m} + \frac{B}{r^n}, \quad n > m$$

and setting the molar volume of the solid $V = \overline{M}/\rho$ equal to a constant times r^3 and using the relations

$$P = -\left(\frac{\partial U}{\partial V}\right)_T$$

and

$$K_T = -\left(\frac{V\,\partial P}{\partial V}\right)_T$$

for the pressure and bulk modulus, respectively, we obtain the equations previously given as equations 18 and 19:

$$P = \frac{3K_o}{m-n}\left[\left(\frac{V_o}{V}\right)^{(m+3)/3} - \left(\frac{V_o}{V}\right)^{(n+3)/3}\right]$$

$$K = \frac{K_o}{m-n}\left[(m+3)\left(\frac{V_o}{V}\right)^{(m+3)/3} - (n+3)\left(\frac{V_o}{V}\right)^{(n+3)/3}\right]$$

where V_o and K_o are the molar volume and the bulk modulus at zero pressure.

For small compressions we can expand K about $V = V_o$ to obtain

$$\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T = -\frac{1}{3}(m+n+6) \qquad (20)$$

and can note in passing that

$$\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T = \left(\frac{\partial \ln K/\partial P}{\partial \ln V/\partial P}\right)_T = -\left(\frac{\partial K}{\partial P}\right)_T \qquad (21)$$

so, to a first approximation, the isothermal bulk modulus is a linear function of pressure and a simple power-law relationship holds between the bulk modulus and the density. Table 5-6 summarizes some pertinent experimental data on minerals and metals, which show the relationships between K_S, K_T and rigidity, G, with density and temperature.

For $m = 3$, we have the simple relation (Fürth, 1944)

$$\left(\frac{\partial \ln K}{\partial \ln V}\right)_P = \frac{(\partial \ln K/\partial T)_P}{(\partial \ln V/\partial T)_P} = \left[\frac{\partial \ln K}{\partial \ln V}\right]_T + 1$$

$$= -\frac{1}{3}(m+n+3)$$

Using Grüneisen's approximation for $(\partial \ln K_T/\partial T)_P/(\partial \ln V/\partial T)_P$, we can summarize the important results of the previous sections. For small compressions:

$$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_T = \frac{1}{3}(m+n+6)$$

$$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P = \frac{1}{3}(m+n+9)$$

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T = \frac{1}{3}(m+n+6) + \frac{K_T^2}{K_S}\left(\frac{\partial \alpha\gamma T}{\partial P}\right)_T$$

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P = \frac{1}{3}(m+n+9) - \frac{K_T}{\alpha K_S}\left(\frac{\partial \alpha\gamma T}{\partial T}\right)_P$$

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_T = \frac{1}{3}(m+n+3) + \frac{K_T^2}{K_S}\left(\frac{\partial \alpha\gamma T}{\partial T}\right)_T$$

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_P = \frac{1}{3}(m+n+6) - \frac{K_T}{\alpha K_S}\left(\frac{\partial \alpha\gamma T}{\partial T}\right)_P$$

or

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T = \frac{1}{3}(m+n+6) - \frac{\alpha\gamma T K_T}{K_S}\left[\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P - \left(\frac{\partial \ln \gamma}{\partial \ln \rho}\right)_T\right]$$

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P = \frac{1}{3}(m + n + 9) - \frac{\gamma K_T}{K_S}$$

$$+ \frac{\alpha\gamma T K_T}{K_S}\left[\left(\frac{\partial \ln \gamma}{\partial \ln \rho}\right)_P + \left(\frac{\partial \ln \alpha}{\partial \ln \rho}\right)_P\right]$$

and corresponding equations for $(\partial \ln \Phi/\partial \ln \rho)$.

The Debye theory leads to a nonthermal definition of the Grüneisen ratio (Knopoff, 1963; Brillouin, 1964):

$$\gamma_D = -\frac{1}{6} - \frac{1}{2}\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T \qquad (22)$$

This relation assumes that all the modes of vibration have the same volume dependence or, equivalently, that all the elastic constants depend on volume or pressure the same way. An alternative expression has been suggested by Druyvesteyn and Meyering (1941) and Dugdale and MacDonald (1953) and is hence called the DM expression:

$$\gamma_{DM} = -\frac{1}{2} - \frac{1}{2}\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T = \gamma_D - \frac{1}{3} \qquad (23)$$

and this corresponds physically to a model of independent pairs of nearest neighbor atoms, in a linear chain, rather than to the Debye model of coupled atomic vibrations. This definition of the Grüneisen ratio is often used in the reduction of shock-wave data.

Taking into account the transverse oscillations of atoms leads to the free-volume γ:

$$\gamma_{FV} = -\frac{5}{6} - \frac{1}{2}\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T \qquad (24)$$

This is more exact than the other derivations (Stacey, 1977; Brennan and Stacey, 1979) and is appropriate for high temperatures where the classic assumption of independent vibrations of atoms becomes a good one and where the distinction between longitudinal and transverse modes becomes fuzzy.

The γ's are related by

$$\gamma_{FV} = \gamma_{DM} - \frac{1}{3} = \gamma_D - \frac{2}{3}$$

At finite pressure,

$$\gamma_{FV} = \frac{1}{2}\left(\frac{\partial \ln K_T}{\partial \ln V} - \frac{5}{6} + \frac{2}{9}\frac{P}{K_T}\right)_T$$

$$\div \left(1 - \frac{4}{3}\frac{P}{K_T}\right) \qquad (25)$$

Using the above relations we can write

$$\gamma_D = \frac{1}{6}(m + n + 5)$$

and

$$\gamma_{DM} = \frac{1}{6}(m + n + 3)$$

$$\gamma_{FV} = \frac{1}{6}(m + n + 1)$$

which shows that the exponents in the equation of state are related to the anharmonic properties of the solid since the Grüneisen relation $\gamma = \alpha K_T/\rho C_V$, relating the coefficient of thermal expansion α with the specific heat C_V, is a measure of anharmonicity.

The parameter γ decreases with compression but has a tendency to be higher for the close-packed crystal structures such as face-centered cubic and hexagonal close-pack than it is for the more open structures such as diamond structure and body-centered cubic. For most materials γ is between 1 and 2, which gives a range for $m + n$ of 1 to 7 for the Lorentz-Slater theory and 3 to 9 for the DM theory. The corresponding ranges for $(-\partial \ln K_T/\partial \ln V)_T$ are 2.3 to 4.3 and 3 to 6, respectively. Many minerals have measured or inferred γ in the range 1.1 to 1.5.

In a later section I discuss the role of shear vibrations in a more accurate nonthermal definition of the Grüneisen parameter.

THE SEISMIC PARAMETER Φ

The seismic parameter Φ plays an important role in discussions of the mineralogy, composition and homogeneity of the mantle. It is more amenable to theoretical treatment than the seismic velocities and is available from static compression, shock-wave and ultrasonic experiments. Table 5-7 tabulates mean atomic weight $\overline{M}$ density ρ and Φ for a variety of important minerals and analog compounds.

The Φ for many silicates and oxides is approximately the molar average of the Φ's of the constituent oxides (Anderson, 1967b, 1969, 1970). Using the values for MgO, Al_2O_3 and SiO_2 (stishovite) in Table 5-7, we can estimate Φ for $MgAl_2O_4$ and $MgSiO_3$ as 55.3 and 60.6, respectively. Table 5-8 gives Φ calculated from the molar averaging rule; note the excellent agreement between the predictions and the measurements. This rule is useful in the estimation of Φ for compounds that have not been measured.

EFFECT OF COMPOSITION AND PHASE

We have now established the theoretical form for the expected relationship between seismic parameter Φ and density and have investigated the effect of temperature and pressure. The exponent in the power-law relationship is different for temperature and pressure, meaning that there is an intrinsic temperature effect over and above the effect of temperature on volume. We have not yet specifically allowed for composition except insofar as this information

TABLE 5-7
Mean Atomic Weight, Density and Seismic Parameter of Minerals

Mineral	$\bar{M}$	ρ (g/cm³)	Φ (km²/s²)
Albite	20.2	2.62	20.3
Nephelite	21.1	2.62	17.4
Oligoclase	20.5	2.65	24.9
Orthoclase	21.4	2.58	18.3
Microcline	21.4	2.56	20.2
Quartz	20.0	2.65	17.4
Olivine	20.1	3.22	40.1
Olivine	23.0	3.35	38.7
Orthopyroxene	21.2	3.29	32.5
Diopside	21.6	3.28	34.5
Garnets	21.9	3.73	45.1
	22.6	3.62	47.4
	—	3.64	48.7
Jadeite	22.5	3.35	40.4
Fayalite	29.1	4.14	26.0
β-spinel	20.1	3.47	50.1
γ-spinel	20.1	3.56	51.7
Majorite	20.1	3.52	49.7*
Spinel	20.3	3.58	55.1
$MgSiO_3$-perovskite	20.1	4.10	64.8
$MgFeSiO_3$-perovskite	—	4.21	61.6*
$SrTiO_3$-perovskite	36.7	5.12	34.1
TiO_2	26.6	4.26	50.6
Al_2O_3	20.4	3.99	63.2
MgO	20.2	3.58	47.4
SiO_2-stishovite	20.0	4.29	73.7
$CaSiO_3$-perovskite	24.0	4.13*	55.0*
$CaMgSi_2O_6$-perovskite	22.1	4.12*	57.8*

*Estimated.

is contained in the initial density and Φ_o. Birch (1961a) showed empirically that the mean atomic weight, $\bar{M}$, is an appropriate measure of composition although exceptions to this general rule occur. Knopoff and Uffen (1954) used a "representative atomic number" Z as a measure of composition in applying the Thomas-Fermi-Dirac (TFD) theory to compounds.

McMillan (1985) and Knopoff (1965) made semi-empirical adjustments to the Thomas-Fermi statistical model of the atom in order to obtain the proper low-pressure limit. Their equations can be put in the forms

$$-5(K_oZ^{-10/3})(ZV_o)^{-1} = d(P_{TF}Z^{-10/3})/d(ZV)_{V=V_o}$$

and

$$(K_oZ^{-10/3})(ZV_o)^{7/3} = \text{constant}$$

The latter form can be written approximately as

$$\Phi_o = \text{constant}(\rho_o/\bar{M})^{4/3}$$

Although the Thomas-Fermi model is not appropriate for pressures as low as those existing in the Earth and the extrapolation to zero-pressure conditions is not justified because of the presence of phase changes, this equation does suggest the form of the relationship between Φ_o, ρ_o and composition $\bar{M}$. At this stage the constants are more properly obtained from experiment.

Consider an equation of the general form we treated earlier:

$$P = (N - M)^{-1}K_o\left[\left(\frac{\rho}{\rho_o}\right)^N - \left(\frac{\rho}{\rho_o}\right)^M\right] \tag{26}$$

where M and N are constants, P is pressure, K_o is initial bulk modulus, ρ_o is initial density and ρ is the density at pressure P. Its derivative with respect to density gives

$$\frac{\partial P}{\partial \rho} = (N - M)^{-1}\frac{K_o}{\rho_o}\left[N\left(\frac{\rho}{\rho_o}\right)^{N-1} - M\left(\frac{\rho}{\rho_o}\right)^{M-1}\right]$$

or

$$\Phi = \Phi_o(N - M)^{-1}\left[N\left(\frac{\rho}{\rho_o}\right)^{N-1} - M\left(\frac{\rho}{\rho_o}\right)^{M-1}\right] \tag{27}$$

where the seismic parameter Φ is the ratio of the bulk modulus to the density. The adiabatic Φ for the Earth is available from seismic data. The ratio of Φ for two different densities is then

$$\frac{\Phi_1}{\Phi_2} = \frac{N(\rho_1/\rho_o)^{N-1} - M(\rho_1/\rho_o)^{M-1}}{N(\rho_2/\rho_o)^{N-1} - M(\rho_2/\rho_o)^{M-1}} \tag{28}$$

This is the seismic equation of state (Anderson, 1967a). If the total compression is small, then

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right) = N + M - 1 \tag{29}$$

TABLE 5-8
Seismic Parameter $\Phi = K_S/\rho$ Calculated from Molar Average of Constituent Oxides

		Φ (km²/S²)	
Mineral	**Formula**	**Calculated**	**Measured**
Spinel	$MgAl_2O_4$	54.4	54.5
Spinel	$NiFe_2O_4$	33.6	34.3
Magnetite	Fe_3O_4	33.2	36.0
Ilmenite	$FeTiO_3$	37.7	38.4
	$(Al,Cr)_2O_3$	62.5	61.7
Chromite	$MgCr_2O_3$	44.0	45.7
Titanate	$BaTiO_3$	30.7	27.0
	$SrTiO_3$	34.4	34.1
Perovskite	$MgSiO_3$	59.6*	64.8
	$CaSiO_3$	52.9*	—
Stishovite	SiO_2	—	73.7

*MgO or CaO plus SiO_2 (stishovite).

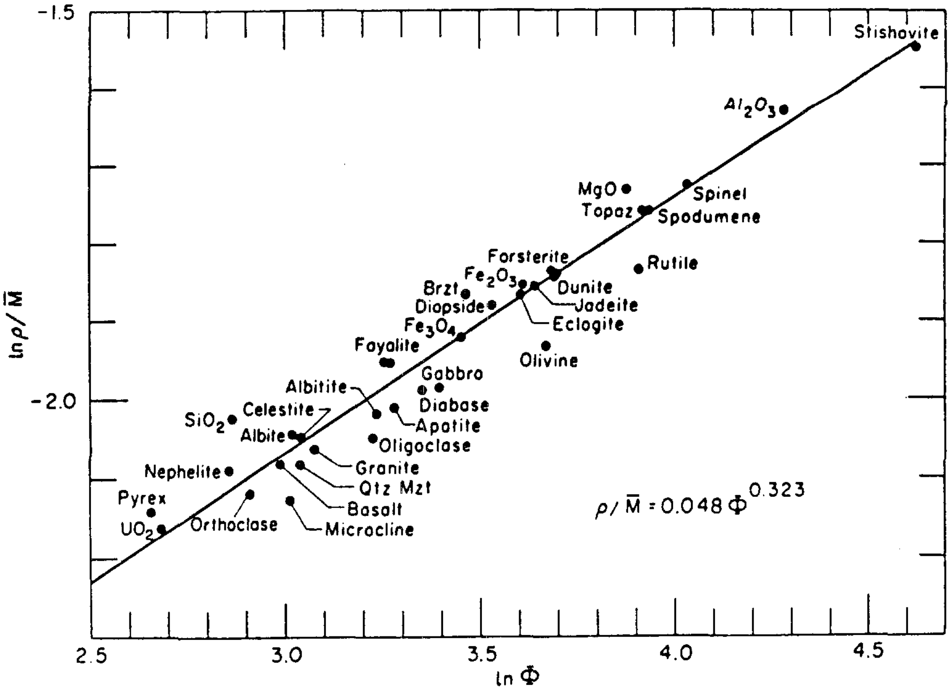

FIGURE 5-2
Seismic parameter Φ, density ρ, and mean atomic weight $\bar{M}$ for rocks, minerals and oxides (after Anderson, 1967a).

Figure 5-2 gives $\bar{M}$, ρ and Φ for selected minerals that vary in mean atomic weight. A least-square fits to these data gives

$$\frac{\rho}{\bar{M}} = 0.048\Phi^{0.323} \tag{30}$$

$$-\left(\frac{\partial \ln \Phi}{\partial \ln V}\right)_{T,P} = 3.10 \tag{31}$$

For comparison, a least-squares fit to the ultrasonic compression data on MgO and Al_2O_3 gives

$$\frac{\rho}{\bar{M}} = 0.048\Phi^{0.335}$$

$$-\left(\frac{\partial \ln \Phi}{\partial \ln V}\right)_{T} = 2.99$$

for MgO and

$$\frac{\rho}{\bar{M}} = 0.052\Phi^{0.318}$$

$$-\left(\frac{\partial \ln \Phi}{\partial \ln V}\right)_{T} = 3.15$$

for Al_2O_3. The agreement of these parameters, which are obtained from compression experiments, with those found above is remarkable. This lends support to the generalization that, as a first approximation, the bulk modulus in silicates and oxides is determined by density and mean atomic weight, or mean molar volume. The effect of changes in bulk modulus and volume at constant temperature and constant pressure are given in Table 5-6. The values for $(\partial \ln K/\partial \ln \rho)$ in that table can be compared with the above values and values computed from

$$(\partial \ln K/\partial \ln V) = (\partial \ln \Phi/\partial \ln V) - 1$$

THE REPULSIVE POTENTIAL

For any solid where the potential U can be separated into an attractive term and a repulsive term, which are functions of the interatomic separation r, we can write

$$U = U_o(r) + f(r)$$

For an ionic crystal with a Born power-law repulsive potential, it can be shown that

$$KV_o = Az_1z_2e^2(n - 1)/9r_o \tag{32}$$

where A is the Madelung constant, z_i is the valence of a constituent ion, and n is the exponent in the power-law repulsive potential. If the exponential form of the repulsive potential is used, the energy per cell can be written

$$U(r) = -A/r + Be^{-r/\sigma}$$

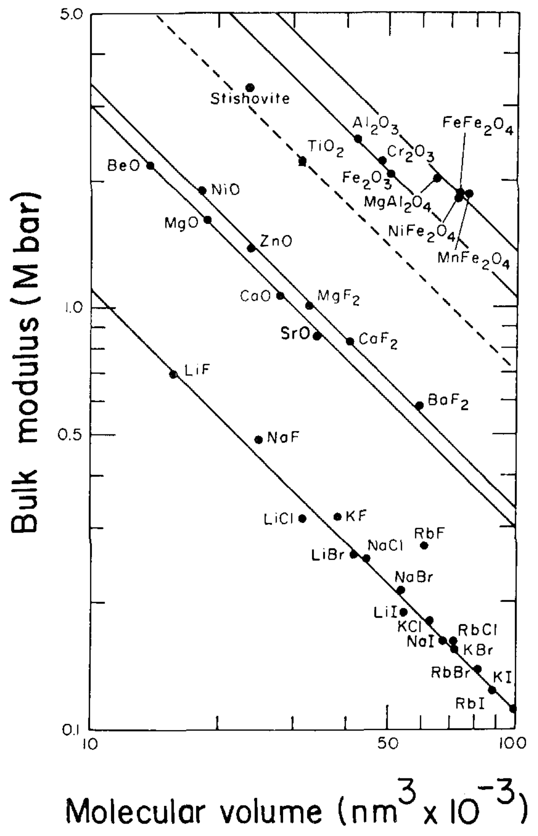

FIGURE 5-3
Bulk modulus versus molecular volume for various crystal structures (Anderson and Anderson, 1970).

where σ is a scale factor. At equilibrium the bulk modulus-volume product can be written

$$KV_o = Az_1 z_2 e^2 (r_o/\sigma - 2)/9r_o \qquad (33)$$

The parameter n in the power-law potential is simply related to σ:

$$n = (r_o/\sigma) - 1 \qquad (34)$$

Data for a number of oxides are presented in Figure 5-3, which demonstrates that KV_o is a constant for a wide variety of oxide compounds. Here V_o is the specific molar volume of the formula and K is the bulk modulus at zero pressure.

The parameter $\psi = KV_o/(z_o z_c e^2)$ is tabulated in the last column of Table 5-9; z_o and z_c are, respectively, the valences of oxygen and the mean cation. Except for ZnO and TiO_2 all of the values fall in the range 0.150–0.165, and the values show no systematic behavior. ZnO and TiO_2 are anomalous in several other respects. The values of Poisson's ratio are high, the shear velocity decreases with pressure, and the oxygen coordination is anomalous for the size of the cation. If these compounds are excluded, the remaining substances for which bulk modulus data are available satisfy

$$\psi = 0.157 \pm 0.005$$

The standard deviation corresponds to an error of 3.3 percent. This is remarkable consistency when one considers that so many structures (halite, wurtzite, spinel, corundum, perovskite, and rutile) and so many cations (Mg, Be, Al, Fe^{2+}, Fe^{3+}, Mn, Ni, Cr, Sr, and Si) are involved, and that no account has been taken of structural factors (the Madelung constant) or range or repulsion parameters. These factors apparently tend to compensate for each other. The KV = constant law is useful for estimating the bulk modulus of high-pressure phases.

The empirical repulsive range parameter σ calculated from the data is also tabulated in Table 5-9. It is relatively constant for each group of compounds and shows a tendency to increase with molecular volume. It can be well approximated, as shown in Table 5-10, by the simple equation

$$\sigma_o = 0.05(1 + R + 3\Delta R) \qquad (35)$$

where R is the cube root of the molecular volume and $\Delta R = R - R_c$, where R_c is the (Pauling) radius of the smallest cation.

The reduced Madelung constant A, also given in Table 5-9, is defined as

$$A_R = A/m(z_c z_o) \qquad (36)$$

where m is the number of ions in the chemical formula. This is a useful parameter since it varies much less from structure to structure than the conventional Madelung constant, and it correlates well with coordination and interatomic distances. For example, it satisfies the relation

$$A_R = 0.20 + 0.45\Delta R \qquad (37)$$

as shown in Table 5-10.

For crystals involving more than one cation, the valence product is defined as

$$z_c z_o = \sum^{p} x_i z_i z_o / p \qquad (38)$$

where x_i is the number of cations in the formula having valence z_i, z_o is the valence of the anion (oxygen), and p is the total number of cations in the formula. z_c is the cation valence.

A check on the form of the repulsive potential is available from ultrasonic measurements of dK/dP. This quantity depends only on the parameters in the repulsive potential, that is,

$$(dK/dP)_o = (n + 7)/3 \qquad (39)$$

$$(dK/dP)_o = [3(2 - r_o/\sigma)]^{-1} \times [14 - (1 + r_o/\sigma)(2 + r_o/\sigma)] \qquad (40)$$

TABLE 5-9
Data for Calculation of Repulsive Range Parameter

Substance	Structure	$(z_c\, z_o)$	V (Å^3)	R (Å)	A	A_R	K (Mbar)	σ (Å)	ψ
MgO	Halite	4	18.67	2.653	8.808	1.10	1.62	0.477	0.164
CaO	Halite	4	27.83	3.030	8.808	1.10	1.06	0.509	0.160
SrO	Halite	4	34.35	3.251	8.808	1.10	0.84	0.54	—
BeO	Wurtzite	4	13.77	2.397	9.504	1.19	2.20	0.482	0.164
ZnO	Wurtzite	4	23.74	2.874	9.604	1.20	1.39	0.490	0.179
$MgAl_2O_4$	Spinel	5.33	65.94	4.040	67.54	1.81	2.02	0.790	0.155
$FeFe_2O_4$	Spinel	5.33	73.85	4.195	65.48	1.75	1.87	0.769	0.161
$NiFe_2O_4$	Spinel	5.33	72.48	4.169	65.53	1.76	1.82	0.790	0.153
$MnFe_2O_4$	Spinel	5.33	76.72	4.249	(66.7)	(1.79)	1.85	0.768	0.165
$SrTiO_3$	Perovskite	6	59.56	3.905	49.51	1.65	1.79	(0.74)	0.154
Al_2O_3	Corundum	6	42.47	3.489	45.77	1.53	2.51	0.674	0.154
Fe_2O_3	Corundum	6	50.27	3.691	45.68	1.52	2.07	0.700	0.150
Cr_2O_3	Corundum	6	48.12	3.637	(45.7)	(1.52)	2.24	0.681	0.155
TiO_2	Rutile	8	31.23	3.149	30.89	1.29	2.24	0.658	0.126

Anderson and Anderson (1970).

A is the Madelung constant; A_R is the reduced Madelung constant.

for the power law and exponential forms respectively. Table 5-11 gives $(\mathrm{d}K/\mathrm{d}P)_0$ evaluated from equations 39 and 40 and, for comparison, the ultrasonic results. The power-law repulsive potential gives better agreement, although the measured values of $(\mathrm{d}K/\mathrm{d}P)_0$ are higher than computed for either potential. The exponential form gives $(\mathrm{d}K/\mathrm{d}P)_0$ from 0.50 to 0.58 units lower than the power-law form. Table 5-12 gives the bulk modulus calculated from the KV_o relation. Figure 5-4 shows experiments and calculations relating K'_o, n and interatomic distance.

SHOCK WAVES

Pressures in the deepest parts of the Earth are beyond the reach of static-compression experiments, although pressures in diamond anvils are getting close. Explosively generated transient shock waves can be used to study material properties to pressures in excess of several megabars (1 Mbar = 10^{11} Pa). The method is to fire a projectile at a target composed of the material under investigation, generating a shock wave that propagates through it at a speed,

TABLE 5-10
Comparison of Repulsive Parameter

	R_c	R	σ_c	σ	ΔR	A_c	A_R
MgO	0.65	2.65	0.48	0.48	2.00	1.10	1.10
CaO	0.99	3.03	0.51	0.51	2.04	1.12	1.10
BeO	0.31	2.40	0.48	0.48	2.09	1.14	1.19
ZnO	0.74	2.82	0.50	0.49	2.08	1.14	1.20
$MgAl_2O_4$	0.50	4.04	0.78	0.79	3.54	1.79	1.81
$FeFe_2O_4$	0.64	4.20	0.79	0.77	3.56	1.80	1.75
$NiFe_2O_4$	0.64	4.17	0.79	0.79	3.53	1.79	1.76
$MnFe_2O_4$	0.64	4.25	0.80	0.77	3.61	1.82	1.79
Al_2O_3	0.50	3.49	0.67	0.67	2.99	1.55	1.53
Fe_2O_3	0.64	3.69	0.69	0.70	3.05	1.57	1.52
Cr_2O_3	0.69	3.64	0.67	0.68	2.95	1.53	(1.52)
TiO_2	0.68	3.15	0.58	0.66	2.47	1.31	1.29
$SrTiO_2$	0.68	3.91	0.73	0.74	3.23	1.65	1.65

Anderson and Anderson (1970).

$\sigma_c = 0.05(1 + R + 3\,\Delta R)$ where $\Delta R = R - R_c$. Also given are the reduced Madelung constants calculated from $A_c = 0.20 + 0.45\,\Delta R$ and the reduced Madelung constant calculated by conventional techniques. R_c is the radius of the smallest cation.

TABLE 5-11
Repulsive Parameters and Corresponding Values of **d*K*/d*P*** for Power-Law and Exponential Repulsive Potentials

Substance	r_o	dK/dP	n	dK/dP	$(dK/dP)_{exp}$
MgO	5.56	3.33	4.56	3.85	3.89
CaO	5.95	3.48	4.95	3.98	5.23
BeO	4.97	3.10	3.97	3.66	5.52
ZnO	5.87	3.45	4.87	3.96	4.78
$MgAl_2O_4$	5.11	3.16	4.11	3.70	4.18
$NiFe_2O_4$	5.28	3.22	4.28	3.76	4.41
Al_2O_3	5.18	3.18	4.18	3.73	3.98
Fe_2O_3	5.27	3.22	4.27	3.76	4.53
SiO_2(st.)	5.02	3.12	4.02	3.67	7*
TiO_2	4.79	3.02	3.79	3.60	6.76

Anderson and Anderson (1970).
*Estimated.

v_s, which is faster than the following material or particle velocity, v; that is, a pressure wave travels through the solid at a speed greater than its speed of sound. The pressure rises in a thin layer to a value set up by the impact. The shock front propagates to the far side of the sample where it is reflected as a rarefaction wave. The equations of conservation of mass, momentum and energy, together with the measured shock-wave and material or particle velocities, allow one to calculate the pressure, density and internal energy of the shocked material. The sample is usually destroyed in the process. A series of shock-wave experiments, using different impact velocities and different, but hopefully similar samples then gives a relation between density, pressure and internal energy from which a shock-wave equation of state can be constructed. It is neither an adiabat nor an isotherm since the temperature and internal energy vary from point to point. Shock compression is not simply adiabatic because the compressed material acquires kinetic energy, and it is not a reversible process. The locus of points is called the Hugoniot, and a major problem is the deduction of an isothermal, or adiabatic, equation of state from this kind of data.

The basic equations are:
Conservation of mass:

$$\rho_o v_s = \rho(v_s - v) \qquad (41)$$

Conservation of momentum:

$$P = \rho_o v_s v \qquad (42)$$

Conservation of energy:

$$Pv = \rho_o v_s \left(\frac{1}{2} v^2 + E - E_o\right) \qquad (43)$$

where $E - E_o$ is the change in internal energy per unit mass.

The rate at which material enters the shock front is $\rho_o v_s$, and it leaves at a rate $\rho(v_s - v)$ per unit area of the shock. The rate at which momentum is generated is equal to the rate of flow of material through the shock front, $\rho_o v_s$, multiplied by the velocity acquired, v, and this is equal to the difference in pressure across the front. The rate at which work is done on the material passing through the shock is equal to the rate of flow through the shock, $\rho_o v_s$, times the change of kinetic energy [1/2 v^2] plus the change in internal energy, both per unit mass. Pv is the rate at which pressure does work on the material, or the rate at which kinetic en-

TABLE 5-12
Comparison of Computed (K_c) and Measured (K) Bulk Modulus

Substance	$(z_c z_o)$	V	R	σ_c	A_c	K_c	K
MgO	4	18.67	2.653	0.48	1.10	1.61	1.62
CaO	4	27.83	3.030	0.51	1.12	1.07	1.06
BeO	4	13.77	2.397	0.48	1.14	2.12	2.20
ZnO	4	23.74	2.874	0.50	1.14	1.28	1.39
$MgAl_2O_4$	5.33	65.94	4.040	0.78	1.79	2.04	2.02
$FeFe_2O_4$	5.33	73.85	4.195	0.79	1.80	1.84	1.87
$NiFe_2O_4$	5.33	72.48	4.169	0.79	1.79	1.86	1.82
$MnFe_2O_4$	5.33	76.72	4.249	0.80	1.82	1.77	1.85
$SrTiO_3$	6	59.56	3.905	0.73	1.65	1.83	1.79
Al_2O_3	6	42.47	3.489	0.67	1.55	2.58	2.52
Fe_2O_3	6	50.27	3.691	0.69	1.57	2.18	2.07
Cr_2O_3	6	48.12	3.637	0.67	1.53	2.30	2.24
SiO_2	8	23.27	2.855	0.56	1.20	3.44	3.16
TiO_2	8	31.23	3.149	0.58	1.31	2.81	2.24

Anderson and Anderson (1970).

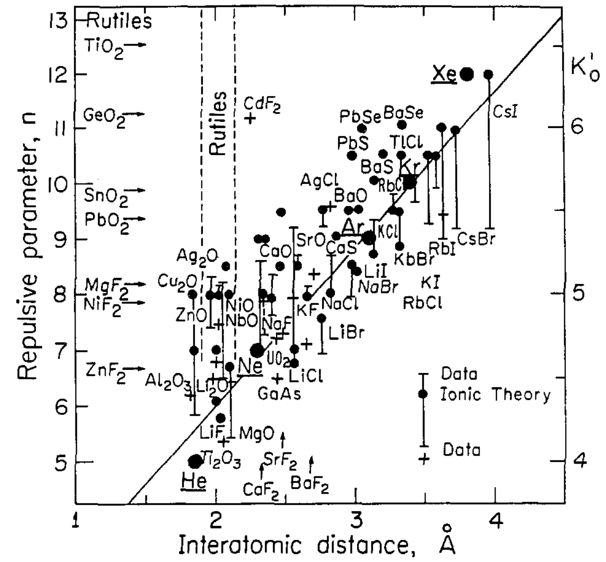

FIGURE 5-4
K_o' and repulsive parameter n versus interatomic distance. The n calculated from K using ionic theory and from compression data are shown. The line is drawn through the rare-gas solids. Ions can be treated as rare-gas atoms plus or minus electrons.

ergy plus internal energy are increased. These equations can be rewritten:

$$v_s = \frac{(P - P_o)^{1/2}}{(V_o - V)}$$

$$v = \frac{1}{2}[(P - P_o)(V_o - V)]^{1/2} \qquad (44)$$

$$E - E_o = \frac{1}{2}(P + P_o)(V_o - V)$$

where $V = 1/\rho$ and the subscript refers to the initial conditions.

In many cases the Hugoniot equations can be simplified since there is an approximately linear relation between v_s and v. In this case

$$v_s = c_o + \lambda v$$

where c_o is the bulk sound speed $(K/\rho)^{1/2}$, to which v_s reduces when the shock is weak, and λ is a constant. This gives

$$P = P_o + \frac{c_o^2(V_o - V)}{V_o - \lambda(V_o - V)^2}$$

Reduction of shock-wave data to an isotherm usually involves the Mie-Grüneisen equation, which relates the difference in pressure at fixed volume between the initial low temperature and a high-temperature state of specified thermal energy:

$$P - P_o = P^* = \alpha K_T T = \gamma \rho C_V T = \frac{\gamma}{V}(E - E_o)$$

where the total pressure, P, is the sum of an initial ambient pressure P_o plus a thermal pressure P^*. The two states (P, E) and (P_o, E_o) have the same volume. Thus, a locus of (P, V) points along a shock compression curve are reduced to a set of (P_I, V) points along an isotherm (T_o) by

$$P_I = P\left[1 - \frac{\gamma}{2}\left(\frac{V_o}{V} - 1\right)\right] - (\gamma/V)\int_{V_o}^{V}[P - \gamma\rho C_V T_o]\,dV$$

where the integral is along the shock compression curve.

The pressure, P_S, along an adiabat is

$$P_S = P[1 - (\gamma/2)(V_o/V - 1)] - (\gamma/V)\int_{V_o}^{V} P_S\,dV$$

This follows from

$$dE = -P_S\,dV$$

and

$$E_S - E_H = -\int_{V_o}^{V} P_S\,dV - \frac{1}{2}P(V_o - V)$$

the internal energy difference between the adiabat and the Hugoniot.

The pressure correction can be substantial for the higher pressure (megabar) experiments, and a reliable value of the Grüneisen ratio γ at high pressure is needed. As shown in previous sections, γ is related directly to the pressure dependence of the bulk modulus and can therefore be estimated from the shock-wave data. However, K_S and dK_S/dP require differentiation of corrected experimental data and are therefore uncertain. Usually the experimental data are fitted with theoretical or semi-empirical equations of state and the differentiations performed on these smooth functions. Shock-wave data remain our best source of information on the bulk modulus, or bulk sound speed, of rocks and minerals at high pressure, particularly high-pressure phases. These properties can be directly compared with seismic data:

$$\Phi = \left(\frac{\partial P}{\partial \rho}\right)_S = \frac{K_S}{\rho} = V_p^2 - \left(\frac{4}{3}\right)V_s^2 = c_o^2$$

Unfortunately, methods have not yet been developed for determining accurate values for the shear velocity under shock conditions.

Shock waves heat as well as compress the sample. Temperatures can be inferred from the equations already given. Temperatures are typically 1400–1700 K at pressures of the order of a megabar for materials that do not undergo phase changes, such as MgO and Al_2O_3. Silicates, which undergo shock-induced phase changes, typically end up at much higher temperature (2500–5000 K) at comparable pressures (Anderson and Kanamori, 1968). In fact, melting may occur under shock conditions.

High-speed pyrometry techniques have permitted the measurement of temperature under shock conditions (Ahrens and others, 1982). Shock-induced temperatures of 4500 to 5000 K have been measured for forsterite in the pressure range 1.5 to 1.7 Mbar. At these pressures Mg_2SiO_4 has presumably converted to MgO and $MgSiO_3$ (perovskite), and hence the temperature is due not only to compression but also due to the energy involved in phase transformation. The measured temperature is close to that calculated on the basis of the equation-of-state data (Anderson and Kanamori, 1968; Ahrens and others, 1969).

When a phase change is involved, the shock temperature T_H is calculated from

$$P(V_o - V)/2 = E_{TR} - \int_{V_o}^{V} P_a\,dV + V(P - P_a)/\gamma$$

$$T_a = T_U \exp\left[-\int_{V_o}^{V} (\gamma/V)\,dV\right]$$

$$V(P - P_a)/\gamma = C_V(T_H - T_a)$$

where P is the shock pressure, P_a is the isentropic pressure of the high-pressure phase, E_{TR} is the transition energy between the low- and high-pressure phases at standard conditions, and T_a is the temperature achieved on the isentrope of the high-pressure phase at volume V. The calculated temperature is therefore sensitive to E_{TR}, which is not always well known, particularly when the nature of the high-pressure phase is unknown.

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