

Two other equations of state might be considered here, the Thomas-Fermi equation and the Hugoniot equation. The former is appropriate for a degenerate Fermi gas and will not be discussed since its range of validity is in the megabar region. The Hugoniot equation will be considered in section 5.

b. The Equation of State Including Temperature

In all of the above equations, the parameters must in general be considered as functions of temperature. The temperature-dependent equation of state has been discussed by Gilvarry (1957) and Bernardes and Swensen (1963). Gilvarry concludes that the above isothermal equations should be quite good along any isotherm as long as the appropriate parameters are chosen for that isotherm. He also points out that n and m in equation (11) are essentially independent of T and then using the Mie-Gruneisen theory determines the temperature dependence of B_0 and V_0 and proposes a generalized Birch equation of state. This equation is then compared to Swensen's P, V, T results for the alkali metals with quite good agreement. Swensen points out that in general the thermal contribution to the free energy is small and thus the compressibility is approximately dependent on volume only. Since the thermal pressure in most cases will be small compared to the lattice pressure, an approximate temperature equation of state is quite satisfactory once the pressure along an isotherm is well established.

The most common equation of state including temperature is the Mie-Gruneisen equation (Gruneisen, 1926)

$$P = -\frac{dU}{dV} + \frac{\gamma_e E}{V} \quad (12)$$

where U is the lattice potential energy, E the vibrational energy, and γ_e a parameter defined by

$$\gamma_e = \frac{\sum \gamma_i E_i}{E} \quad (13)$$

in which

$$E = \sum E_i, \quad (14)$$

$$E_i = \frac{\hbar \omega_i}{2} + \frac{\hbar \omega_i}{e^{\hbar \omega_i/kT} - 1},$$

and

$$\gamma_i = -\frac{d \ln \omega_i}{d \ln V}. \quad (15)$$

These equations follow from the quasi harmonic approximation in which the thermal energy of the crystal is taken as that of a set of weakly coupled harmonic oscillators with ω_i the angular frequency of the i th normal mode of vibration. The parameter γ_e is not identical to the γ defined by the Gruneisen relation

$$\gamma = \frac{\alpha V}{C_v K} \quad (16)$$

where α is the volume thermal expansion, K is the isothermal compressibility, and C_v the specific heat at constant volume. Pautamo (1963) shows that the γ in (16) is given by

$$\gamma = \frac{\sum \gamma_i C_{vi}}{C_v} \quad (17)$$

where

$$C_{vi} = \left(\frac{\partial E_i}{\partial T} \right)_V. \quad (18)$$

He also demonstrated that γ_e is nearly temperature independent while γ is quite temperature dependent at low temperature. For $T > \Theta/2$, $\gamma_e = \gamma$ for the materials studied by Pautamo.

Equation (12) is the Mie-Gruneisen vibrational equation of state. If the first term in (14), which is the zero point energy, is assumed independent of temperature and lumped with the potential energy, then

$$P = -\frac{dU'}{dV} + \frac{\gamma_T E_T}{V} \quad (19)$$

follows which is the thermal Mie-Gruneisen equation (Fumi and Tosi, 1962). The value γ_T is now defined by

$$\gamma_T = \frac{\sum \gamma_i E_{Ti}}{E_T} \quad (20)$$

where E_{Ti} is the second term on the right hand of (14). In general γ_T will not be the same as γ_e .

The Hildebrand equation (Hildebrand, 1931)

$$P + \frac{dU}{dV} = \frac{T\alpha}{K} \quad (21)$$

has also been suggested as a reliable approximation for an equation of state. Fumi and Tosi (1962) argue that the approximations leading to the Hildebrand equation are not as accurate as those of equation (12) except at very high temperatures. Since the Mie-Gruneisen equation is always better than or as good as the Hildebrand equation, the Hildebrand equation will not be considered further.

The vibrational energy in (12) can be calculated using a Debye model for the distribution of normal modes. Above the Debye temperature this should be a rather good approximation. The only major problem is to determine the dependence of γ_e upon T and V . It is often considered to be a constant but a better approximation to the correct equation of state is obtained if an estimate of the volume dependence of γ_e is found (Pautamo, 1963). The parameter γ is related to the anharmonicity of the lattice potential and can break down for an extremely anharmonic potential. Pastine (1967), however, argues that the lattice potential becomes more harmonic at elevated pressures making the Mie-Gruneisen equation even a better approximation at high pressures.

Leibfried and Ludwig (1961) have derived the Mie-Gruneisen equation from the approach of lattice dynamics. They demonstrate that this equation follows if one truncates the expansion of the lattice potential after fourth order terms. This limits the usefulness of their approach to that of low compression where the potential can be reasonably approximated by four terms in the expansion. As was pointed out earlier, the potential energy is more prominent than the vibrational kinetic energy in determining the relation between P and V at temperatures which are not excessive. Thus, it is imperative to use the best possible potential energy term in the Mie-Gruneisen equation and estimate the kinetic energy contribution using the quasi harmonic approach. Thomsen and Anderson (1969) have demonstrated that a consistent approach using the fourth order expansion for the potential is not sufficient for NaCl above 70 kbar.

c. Equations of State for Specific Materials

The equations discussed above were based on macroscopic measurements of the bulk modulus and its derivatives but were not concerned directly with interatomic forces. There are, however, certain materials for which the predominant interaction forces are simple enough to allow a calculation of an equation of state from an atomic viewpoint. These are the alkali metals and the alkali halide ionic crystals. The alkali halides are much easier to use experimentally but the alkali metals provide a more stringent test of the theory because they are highly compressible.

d. Alkali Metals

These metals can be approximated by a model consisting of closed shell, positively charged ions distributed in a negative charge sea of nearly free electrons. The cohesive energy contains the terms (Bardeen, 1938a, 1938b)

$$E = E_0 + E_f + E_c + E_l. \quad (22)$$

E_0 is the kinetic energy of the conduction electrons in their lowest-energy momentum state. E_f , the Fermi energy, is the interaction energy of the electron sea and the discrete positive charges. E_c is the correlation energy of the interaction of an electron with the space charge density of the negative sea and accounts for the fact that the electrons tend to avoid each other. E_l comes from the ion-ion overlap and van der Waals terms. E_0 is calculated by solving the Schroedinger wave equation in a Wigner-Seitz cell (1934). The volume dependence of E_f is quite straightforward and can be found in any solid state text (Kittel, 1966).

The two other terms in (22) have either been ignored or empirically estimated. Since these last two terms are relatively small for the alkali metals, the cohesive energy versus volume can be determined quite accurately. Temperature effects are included in the theory by using a Debye model for the free energy of the lattice vibra-

tions. At room temperature and above, the procedure should be quite accurate for sodium.

Bardeen (1938a, b) calculated $E(V)$ and then differentiated to get the compressibility as a function of volume for sodium and lithium. The results agree with experiment for sodium but are consistently low in the case of lithium.

Bardeen (1938a, b) also proposed a semi-empirical equation of state for the alkali metals at absolute zero by combining Frolich's (1937) formula for E_0 with an expression for E_f which assumed the effective number of free electrons per atom remains constant. This equation is

$$E = Ay^3 + By^2 + Cy \quad (23)$$

where $y = (V_0/V)^{1/3}$. The parameter A is purely empirical but B and C can be determined theoretically. The equation can be reduced to one parameter with the requirement that E is a minimum at $y=1$ and by using the measured value of the initial bulk modulus B_0 (Bernardes and Swenson, 1963).

$$P = B_0 y^4 (y-1) \left[3 + \frac{A}{B_0 V_0} (y-1) \right] \quad (24)$$

where V_0 is the zero pressure volume. The fit to experimental data (Swenson, 1955; Beecroft and Swenson, 1961) is well within experimental error for all the alkali metals if A is left arbitrary.

Since the correlation term is better understood now (Kittel, 1963), the new calculation for these materials carried out by Pastine (1968) is welcomed. Pastine also gives a good description of the origin of the various contributions to the $P-V$ isotherm and his results agree quite well with experiment. It is hoped that more accurate experimental work will be done on sodium to better evaluate the theory.

e. Ionic Compounds and in Particular NaCl

The Born model (Born and Goepfert-Mayer, 1933) has given very good results for the cohesive energy of alkali halides. This model assumes the solid is composed of closed shell positive and negative ions of integer charge. The largest contribution to the energy is the coulomb energy of the ionic charge configuration. This energy is well understood. This attraction term is balanced by an overlap repulsion term as the ion shells are forced against each other. The approximation assumes a given empirical form for the overlap term, in that it arises from two-body central forces. In addition to these terms, van der Waal's dipole-dipole and dipole-quadrupole interaction terms may also be included (Mayer, 1933). Tosi (1964) has shown that the inclusion of these terms, even though there is no accurate expression for them, definitely improves the results. Koliwad, Ghate, and Ruoff (1967) seem to disagree with this conclusion, however. Several good review articles are written on this subject;