

THERMODYNAMIC REPRESENTATIONS FOR SOLID/MELT SYSTEMS AT HIGH PRESSURE AND TEMPERATURE

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Abstract. The Vinet “universal” equation of state (EoS) has been modified and extended to enable the description of solid and melt phases for the high pressure – high temperature conditions that occur in some realms of geophysics and condensed phase detonations. Free energies calculated with this equation as well as melting points are in good agreement with experimental data for a variety of inorganic materials. A detailed comparison has been undertaken for diopside ($\text{CaMgSi}_2\text{O}_6$). Monte Carlo methods have been employed for some metal oxides and halides to estimate the few parameters (compressibility and its pressure derivative, and thermal expansion coefficients) used in these simple EoS where these are not available.

INTRODUCTION

The thermodynamics of high temperature and high pressure solids and fluids, for applications such as those that occur in geophysical and explosives systems, can be routinely simulated using a variety of computer programs (1,2,3) containing different complete equations of state (EoS) (4,5,6) for each phase. In earlier work (7) we have published details of the application of a Vinet “Universal” EoS (8) to solid detonation products over an extended temperature range, both above and below Debye temperatures.

In this work we have successfully modelled the diopside ($\text{CaMgSi}_2\text{O}_6$) for both solid and melt phases. Monte Carlo calculations are reported for two metal oxides and to demonstrate an approach for determining unknown EoS parameters.

SOLIDS EoS AND IDEAL DETONATION CODES

The ideal detonation behaviour of an explosive is governed by the thermodynamics of its detonation product molecules. Much effort has been expended on accurate fluid EoS and its representation in modelling computer codes, since

this phase constitutes the majority of the product of condensed phase detonations. In a number of oxygen negative high explosives EoS for carbon (graphite, diamond and liquid) have been used in these studies (1,2,3)

(i) Cowan EoS (4)

The largely empirical Cowan EoS for solids is of the form

$$P = p_1(\lambda) + a(\lambda) + b(\lambda)T^2 \quad (1)$$

where pressure, P , is represented by polynomials in λ (the ratio of density to initial density) - p_1, a, b . These are based on thermal expansion and compressibility coefficients and Hugoniot data fits.

(ii) Murnaghan EoS (5)

The solid molar volume, V , is given by

$$V = V_0 [1 + B'_0 P / B_0]^{-1/B'_0} \quad (2)$$

where B_0 and B'_0 are the bulk modulus and its pressure derivative: V_0 is the reference molar volume of the solid.

(iii) Parsifar Mason EoS (6)

The pressure, P , is given by,

$$P = \left(\frac{1}{2}\right)(V_0/V)^2 B_0[(B'_0-7) - 2(B'_0-6)(V_0/V) + (B'_0-5)(V_0/V)^2] \quad (3)$$

(iv) **Vinet EoS (8)**

The pressure, P , is given by

$$P = 3B_0 \frac{(1-X)}{X^2} e^{\eta(1-X)} \quad (4)$$

where $\eta = \frac{3}{2}[(B'_0-1)]$ and $X = (V/V_0)^{\frac{1}{3}}$

In earlier work (7), the Vinet EoS was extended to cover a range of temperatures above the Debye temperature, resulting in the form

$$P = P(T_R) + \alpha(T_R)B_0(T_R)(T - T_R) \quad (5)$$

where α is the thermal expansion coefficient and T_R is the reference temperature. The extension of this equation or T_R to below the Debye temperature has been discussed elsewhere (8).

PHASE TRANSITIONS AND THE APPROXIMATE MELT EoS FOR DIOPSIDE

Due to the high temperatures that prevail in a detonation it is necessary to include possible solid-melt phase transitions for products such as alkali halides and oxides. A full thermochemical analysis will therefore require solid and melt phases in addition to the fluid mixture. In previous work, the Vinet EoS has been successfully used for phase changes in molten alkali metals (8), giving particularly good agreement with the known $P-V-T$ surface. We have developed a computer code based on a combination of the Vinet EoS for the solid phase and its modified form for the melt phase in order to predict thermochemical quantities for any system. Entropies are calculated assuming the classical limit for heat capacity and that αB_0 is independent of volume. The code is able to determine the most thermodynamically stable phase and, as a result, make accurate predictions of melting points: this is achieved by calculating Gibbs energies of the two phases and selecting that with the lowest energy.

As an example, we have studied diopside, $\text{CaMgSi}_2\text{O}_6$ for which a full set of experimental data exist (Table 1). Figure 1 shows the variation of the Gibbs energies of the two phases with temperature. The predicted melting point (1500 K at $P=0$) is in reasonable agreement with the

experimental value of 1665 K, taking into account the similar gradients of the two curves and the sensitivities to EoS parameters chosen.

Figure 2 illustrates a comparison of predicted $P-V-T$ data for both the melt and solid phases of diopside and experimental Hugoniot data (9). Agreement between experiment and prediction is good. The variation in volume as a function of temperatures for a range of pressures is shown in Figure 3. The clear increase in molar volume upon melting of about 20 % is in good agreement with experiment as is the effect of pressure on melting point of approximately 180 K GPa^{-1} .

TABLE 1. Input parameters for diopside – solid and melt - (Vinet EoS)

Diopside	Solid	Melt
T_R K	1664	1664
$\alpha \times 10^{-6}$ K	3.2	6
B_0 GPa	90.7	21.9
B'_0	4.5	6.9
V_R $\text{m}^3 \text{mol}^{-1}$	69.11×10^{-6}	82.95×10^{-6}
U_R kJ mol^{-1}	-3206.2	-2656.5
S_R J (K mol)^{-1}	142.9	619.8

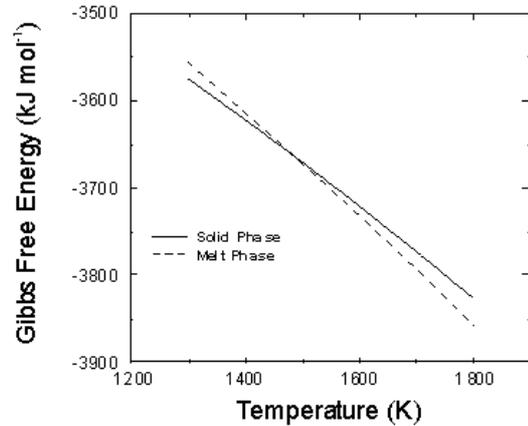


FIGURE 1. Variation of Gibbs energies of the solid and melt phases of diopside at $P=0$.

As a final validation the Gibbs energies of both the solid and melt phases of diopside are plotted along with experimental data (9) over a range of temperature in Figure 4. Agreement is excellent and the comparison comprises a stern test of the model

given the several thermodynamic quantities involved.

Clearly an approach has been developed which, with suitable input parameters, provides an accurate equation of state for both solid and melt phases for a wide variety of systems. A remaining problem is the sparsity of data for the parameters the Vinet EoS requires.

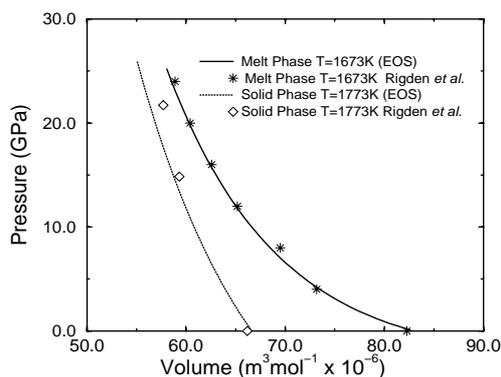


FIGURE 2. EoS of solid and molten diopside at $T = 1773$ and 1663 K respectively. Solid lines show calculations using the Vinet EoS and point data represent experimental Hugoniot results (9).

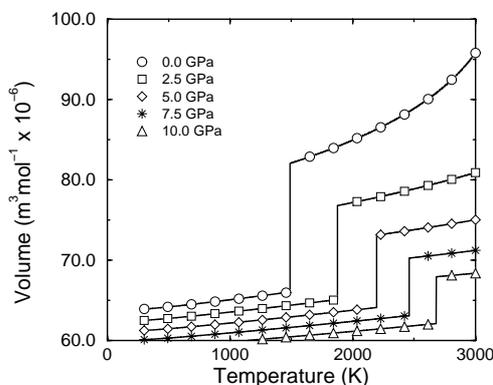


FIGURE 3. Variation of volume with temperature of diopside for a range of pressures.

THE LIQUID EoS: PARAMETERISATION USING MONTE CARLO SIMULATIONS

We have run a series of Monte Carlo simulations for some representative oxides and halides to try and evaluate the required Vinet EoS parameters for the melt. In particular, there is a need for a technique to determine scarce parameters

(B_0 , B'_0 and α). Monte Carlo simulations were performed under constant pressure and typically ran for 20,000 iterations of which half were used for the equilibration stage. Initial values for molar volumes were taken from lattice dynamics simulations or from preceding Monte Carlo calculations at a nearby temperature.

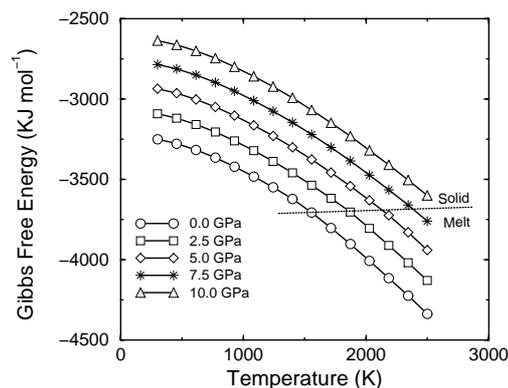


FIGURE 4. Variation of Gibbs free energy with temperature for diopside at $P = 0$. Diamonds and circles show solid and melt experimental data respectively [10].

Figure 5 illustrates a typical calculated pressure-volume-temperature plot for an oxide. A clear phase change is evident at high temperature though the melting temperature (at zero pressure) is 1500 K higher than experimental value. This is most likely a consequence of either superheating of the solid phase in the calculation or lack of any suitable nucleation site.

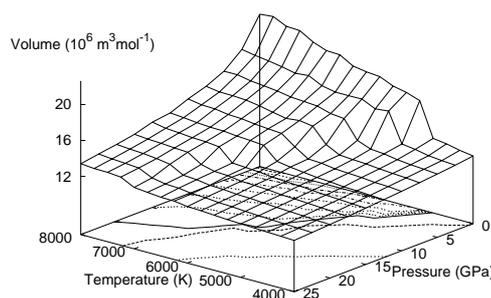


FIGURE 5. PVT relationships from Monte Carlo calculations for periclase, MgO.

Above the calculated melting temperature a series of calculations were undertaken to determine

B_0 and B'_0 . The molar volume and thermal expansion were obtained from an extended set of Monte Carlo calculations.

Table 2 shows the calculated Vinet parameters for the melt phases of two oxide systems (MgO and CaO), extrapolated back to melting point temperatures. Experimentally measured solid state parameters are included for comparison. Predicted transition temperatures of 3020 and 2912 K for CaO and MgO are in reasonable agreement with measured data of 3200 and 3105 K respectively.

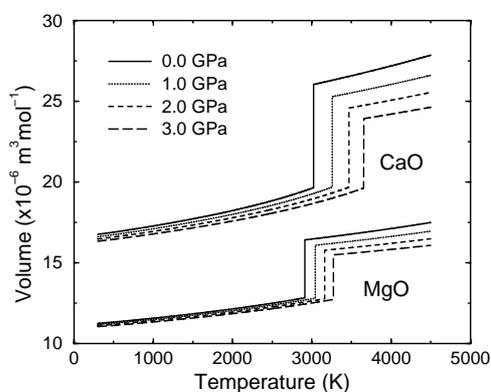


FIGURE 6. Variation of volume with temperature for CaO and MgO at pressures of 0, 1, 2 and 3 GPa.

TABLE 2. Vinet Parameters for solid and melt phases of CaO and MgO.

	T_R K	α 10^{-6} K^{-1}	B_0 GPa	B'_0
CaO(l)	3200	42.4	24.2	2.75
CaO(s)	298	33.6	111.2	4.20
MgO(l)	3105	36.4	37.5	3.9
MgO(s)	800	42.6	3147	3.9

At their respective calculated melting temperatures, the value of B_0 for molten CaO is approximately 35 % smaller than that for molten MgO: the behaviour in the solid phase is similar, with a difference of 25 %. Figure 6 shows the V, T relationship for the two oxides at different pressures.

It is particularly encouraging that the predicted melting temperatures for these two alkali oxides are in both good relative and absolute agreement.

CONCLUSIONS

We have developed a code which uses a modified version of the Vinet equations of state and successfully predicts the thermodynamic properties of any solid or liquid which fits the universal binding energy curve. This approach requires a small data set for each phase. Calculated thermodynamic properties and melting points are in good agreement with experimental data.

In the absence of experimental data for the melt phase, we have demonstrated that Monte Carlo simulations provide a useful means of estimating Vinet parameters. Future work will implement these procedures in ideal detonation (thermochemical) computer codes.

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