**Chapter 11**

**Supplement 11A: Calculation of Interaction Thermodynamic Work**

The ratio of thermodynamic work to the magma’s heat energy (in excess of ambient) is termed the *conversion ratio*, which is a measure of how dynamic a water/magma interaction is. Passive interactions result in little pressure-volume work so that the conversion ratio is a few percent or less while explosive interactions may show conversion ratios reaching 20% or more. Explosive interactions that tend to keep the expanding water and magma fragments in constant contact and thermal equilibrium show higher conversion ratios than do those where the water separates from the magma during expansion.

Calculation of thermodynamic conversion ratios as a function of *R* (water/magma mass ratio) provides a theoretical basis for predicting the effects of hydrostatic pressure. These calculations begin with the following assumptions: (1) water is initially saturated (no vapor present); (2) all heat transferred from the magma during interaction is to the water (adiabatic boundary); (3) liquid water is incompressible; and (4) heat exchange is sufficiently rapid that water and magma reach an equilibrium temperature, *Te*, before the water expands:

 , (11A.1)

where *T* is temperature (subscripts *e* for equilibrium, *w* for water, and *m* for magma), and *c* is constant-volume specific heat, assumed to be constant. Because most of the water stays saturated during attainment of initial thermal equilibrium with magma, its specific heat is nearly constant between *Tw* and *Te* and Eq. (11A.1) also assumes this constancy.

The Hicks-Menzies (1965) assumption of rapid heat exchange includes the idea that water does not experience much volume change in reaching equilibrium with the melt so that volume terms can be ignored in the derivative of entropy *S*:

 , (11A.2)

in which *p* is pressure and *V* is volume. Solving Eq. (11A.2) for constant volume yields:

 , (11A.3)

where the subscripts *i* and *e* denote the initial (ambient) and equilibrium states, respectively.

*Te* and *Se* alone are not sufficient to predict other thermodynamic properties without further considerations. The rapid heating to initial equilibrium temperature and pressure can be idealized as *isochoric* (constant volume), but that idealization is only approached for shock compression of water at low pressure, and it does not allow for the creation of a vapor film at water/melt interfaces, which is documented in MFCI experiments. Accordingly, for the calculated *Te* and *Se* values, equilibrium states of pressure, volume, and other thermodynamic parameters are determined by fitting polynomial functions to steam-table data (e.g., Haar *et al.*, 1984).

With the equilibrium state defined as a function of *R*, calculation of the final expanded thermodynamic state depends upon whether an *isentropic* fluid or *pseudo-isothermal* mixture expansion path is followed during water expansion and the final pressure. For calculations, the *isentropic* case just requires finding thermodynamic parameters for the desired final pressure at the equilibrium entropy (isentropic expansion). The *pseudo-isothermal* case is more complex (Wohletz, 1986), requiring calculation of the slope of the expansion curve in temperature-entropy space and finding thermodynamic parameters for points (if any) where this curve intersects the saturation curve. The total work for the *pseudo-isothermal* calculation then becomes the sum of the work for each leg of the expansion path.

The First Law of Thermodynamics provides a starting point for calculation of thermodynamic work:

 , (11A.4)

for which *U* is the energy of the system, *Q* is heat, *W* is thermodynamic work, such that *dW* = – *pdV*. For a system at constant pressure, *U* = *H – pV*, *dQ* = *cpdT*, and *–W = Uf – Ui*, where *H* is enthalpy, *cp* is the constant pressure heat capacity, and the subscripts *f* and *i* denote the final and initial states of the system, respectively. Furthermore at constant pressure, *dU = dQ – pdV* and *cp = dU/dT + p(dV/dT) = dQ/dT*. Alternatively, for a system at constant volume, *dU = dQ*, and *cv = dU/dT = dQ/dT*.

Using the above thermodynamic relationships and the definition of an isentropic adiabatic process as one where *dQ* = 0, *dW* = *dU*, the mechanical work involved is *dW* = (*Ui – Uf*) so that

 . (11A.5)

For a *pseudo-isothermal* mixture process involving magma and water (where *mm* and *mw* are their respective masses), thermodynamic work is the sum of heat transfer and internal energy change, –*dW* = *dQ – dU*, where heat transfer is *dQ* = (*mmcm*+*mwcw*)*dT* + *pdV*:

 . (11A.6)

Integrating Eq. 11-S6

 , (11A.7)

and combining terms, yields

 . (11A.8)

Expansion within the steam dome (the scientific term for water’s two-phase stability field of liquid and vapor) involves specification of pressure-dependent phase-change enthalpy, *H\**, and volume *V\**, and calculation of steam fractions, *X*, by the ratio of entropy *S* over the phase-change entropy. Whereas calculation of the *isentropic* fluid case by adiabatic expansion is relatively simple, application of Eq. (11A.8) requires careful consideration of thermodynamic path. If expansion does not go through the steam dome, phase-change terms do not apply, so one should use instead:

 . (11A.9)

Numerical implementation of this calculation is available (*KWare* PHM; Wohletz, 2001), and it involves steam-table lookups for which built-in thermodynamic property calculations are made that are accurate within 1% of values listed in steam tables (Lemmon *et al.*, 2001).

**References**

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