# S1: Introduction to Chemical Equilibria and Activity Modelling

Activity modelling is used to determine equilibrium lines between pairs of minerals in a chemical system, *e.g.*, the reaction between talc (Tlc) and magnesite (Mgs):

Mg3Si4O10(OH)2(s) (Tlc) + 3 CO2(g) + 7 H2O = 3 MgCO3(s) (Mgs) + 4H4SiO4(aq)

[1]

The equilibrium constant of this reaction at a given pressure and temperature () is expressed as the activity of the products divided by the activities of the reactants:

[2]

where represents the activity of a given phase , and the exponent represents the stoichiometric coefficient of the phase. Taking the logarithm of both sides yields:

[3]

Of particular interest is the effect of CO2 fugacity and H4SiO4(aq) activity on the stability of talc *versus* magnesite. Therefore, [3] can be rewritten in the form of with as the independent variable and as the dependent variable:

[4]

Assuming the activities for pure solids and liquids is unity, *i.e.*, (assuming no solid solution) leads to a simplified expression:

[5]

Graphically, this represents a line with a slope of and intercept of . Plotting these lines for each set of phases produces an activity diagram.

To plot this line, the value of must be determined. At equilibrium, is directly proportional to the standard molar Gibbs free energy of the reaction ():

[6]

where is the ideal gas constant (8.314 J∙K-1∙mol-1). The can be determined by stoichiometric sum of the apparent molar Gibbs free energy of formation () values for the products minus those of the reactants.

The of each mineral and phase at the of interest is given by the Legendre transform of the fundamental equation of thermodynamics (first and second laws of thermodynamics; *e.g.*, Berman 1988):

[7]

where = enthalpy of formation at the and of interest; and = entropy at the and of interest.

The values for and are related to the standard state enthalpy of formation measured at reference conditions of 1 bar and 25°C ( and , resp.), by considering the changes in and as a function of and (*e.g.*, Berman 1988):

[8]

where: = reference pressure (1 bar) and temperature (25°C); = pressure and temperature of interest; = heat capacity at constant pressure (*i.e.*, isobaric); and = volume. Note that the superscripted zero refers only to pure standard-state quantities and does not refer to the standard - conditions as usually denoted in physical chemistry. Given the above thermodynamic data, it is possible to calculate for each phase component in the reaction, yielding and , which permits the plotting of the equilibrium line for talc *versus* magnesite in the above example.

From [8], the terms require an equation of state for *vs.* . The value of is variably expressed as polynomial functions of of the form:

[9]

where , , , , , , and are phase-specific empirical coefficients. Commonly used conventions include: (1) Maier-Kelley (, Maier & Kelley 1932), (2) Haas-Fisher (, Haas & Fisher 1976, Robie & Hemingway 1995), (3) Berman-Brown (, Berman & Brown 1985), and (4) Holland-Powell (; Holland & Powell 1985, Powell & Holland 1985). Where heat capacity data are not available, some thermodynamic data use the constant isobaric heat capacity assumption ( or the Van’t Hoff approximation ().

Similarly, the term in [8] requires an equation of state for the relationship between *vs.*  and . Many thermodynamic databases assume constant for solids, given the minor deviations from surface conditions (*e.g.*, up to 5 kbar and 1000 °C). However, it is invalid to extrapolate constant from surface conditions to the greater metamorphic - conditions (*e.g.*, to 100 kbar and 1000 °C), so equations of state for have been implemented in metamorphic databases. For example, Berman (1988) uses the following relation:

[10]

where , , , and are empirical coefficients which describe the isothermal (, ) and isobaric (, compressibilities of the mineral of interest. Holland and Powell (1990, 1998, 2011) use more complex equations of state for , but discussion of these is beyond the scope of this contribution.

For aqueous species, the refined Helgeson-Kirkham-Flowers (HKF) equations of state may be used instead of the heat capacity and volume equations of state listed above (Helgeson *et al.* 1981, Tanger & Helgeson 1988). The equations of state are built on the Born equation, which involves the Born solvation coefficient ω; non-solvation volume coefficients , , , ; and non-solvation heat capacity coefficients , ; and charge (see Sverjensky 2019 for a comprehensive overview; Helgeson & Kirkham 1976).

As a note, caution must be taken when entering and HKF coefficients from a thermodynamic database into a thermodynamic modelling software package because some of the and HKF coefficients are reported in differing orders of magnitude (*e.g.*, for Maier-Kelley coefficients, is commonly multiplied by 10-3 and by 10-5). Equally, it is important to check that the coefficient matches the correct corresponding polynomial in the equation for the coefficients being selected.

Thus, for all chemical species, the following data are needed: , , , and ( can be calculated from the above data). Note that the value used in aqueous geochemistry (Benson 1968, Helgeson *et al.* 1978) follows a different convention than that for metamorphic petrology (Powell & Holland 1985, Berman 1988). In metamorphic petrology, is calculated using the third law of thermodynamics () and does not include the entropies of the elements (), whereas aqueous geochemistry includes the stoichiometric sum () of (), so it is necessary to verify that the database and software are using the same convention. For minerals and gases, both the coefficients expressing as a function , and the equation of state for as a function of and are needed (if no relation for is given, it is assumed to be constant). For aqueous species, the HKF coefficients (, , , , , , ω, and ) may be used. Note thatsome software packages and thermodynamic databases do not use this thermodynamic data *per se*, instead employing the values related to the formation of minerals at various temperatures (*e.g.*, The Geochemist’s Workbench™; Bethke 1995). Additionally, some databases account for the effects of *P* on to < 1 kbar (*e.g.*, *PHREEQC*); Appelo *et al.* 2014).

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