

THERMOCALC Workshop 2001: Calculating Metamorphic Phase Equilibria

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Background and Information

The aim is for participants to come away from the Workshop with an understanding of some types of phase diagrams (projections, pseudosections. . .), and how they can be calculated with THERMOCALC¹.

In such a short course, I will have to be selective in what is covered, and some material will be covered only briefly, so the better you are prepared, the more you will get out of it. Some material you will only need to do battle with if you have particular aims in your work. The comments with the references below try to provide a guide to what you should read before the course.

The references below are (unashamedly) Holland/Powell ones as THERMOCALC, in a sense, is a distillation of the way we have thought about the calculation of phase equilibria, as represented in the papers we have written. Some aspects do stem primarily from our work, but much is derived from the work of, for example, JB Thompson, AB Thompson, Spear, Hensen, Greenwood, among others. References to this other work is given in the papers listed, and can be followed up by the interested reader.

The THERMOCALC Resource CD-ROM that will accompany the course should contain some of the more difficult material in these references in a more palatable form.

Reading List

Background

In the application of equilibrium thermodynamics, the starting point is usually what I call the “equilibrium relationship”: the relationship for a balanced chemical reaction between the end-members of phases that are in equilibrium with each other:

$$0 = \Delta G^{\circ} + RT \ln K \quad (1)$$

in which ΔG° is the Gibbs energy of the reaction between the pure end-members in the same structure as the phases in which they occur, K is the equilibrium constant, in terms of the activities of the end-members in their phases, T is temperature, and R is the gas constant.

If you are not familiar with this relationship, then read for example Ch 2–6 of

Powell, R, 1978. *Equilibrium Thermodynamics in Petrology* Harper and Row, 284 pp.

or some other introductory text. The G - x diagram approach to phase diagrams in Ch 3 is also useful.

¹THERMOCALC is capitalised, to make the distinction from another, more recent, computer program, calling itself “Thermo-calc”: THERMOCALC originated in my PhD research in the early ‘70’s.

Internally-consistent datasets

Looking at (1), the first practical concern is where we get the numbers from to insert into ΔG° for any particular reaction. There are actually two sides to this: the form that the Gibbs energies of pure end-members should have as a function of P and T , and what the numbers are. These two go hand-in-hand, and in the context of the internally-consistent dataset that THERMOCALC uses, the papers to read are

Powell, R, and Holland, TJB, 1985 An internally consistent thermodynamic dataset with uncertainties and correlations : 1 : Methods and a worked example. *Journal of Metamorphic Geology* **3**, 327–342.

Holland, TJB, and Powell, R, 1985 An internally consistent thermodynamic dataset with uncertainties and correlations : 2 : Data and results. *Journal of Metamorphic Geology* **3**, 343–370.

Holland, TJB, and Powell, R, 1990 An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K_2O - Na_2O - CaO - MgO - MnO - FeO - Fe_2O_3 - Al_2O_3 - TiO_2 - SiO_2 - C - H_2 - O_2 . *Journal of Metamorphic Geology* **8**, 89–124.

Powell, R, and Holland, TJB, 1993. Is Least Squares an appropriate methodology to be used in the extraction of thermodynamic data from experimentally-bracketed mineral equilibria? *American Mineralogist*, **78**, 107-112.

Holland, TJB, and Powell, R, 1998. An internally-consistent thermodynamic dataset for phases of petrological interest. *Journal of Metamorphic Geology* **16**, 309–344.

How much of this you should read depends very much on how much you really think you need to know. If you are going to use THERMOCALC datafiles that we provide, there may be little point getting too involved. If, however, you want to fiddle with the data (via DQF) it is as well to have a clear understanding of the correlations within the data, and also what is *assumed* about activity-composition relationships in the data (as spelt out most clearly in the 1998 paper). If you are interested just in our philosophy of data extraction from experimental work, start with the 1993 paper. If you want to know more, having read the 1993 paper, continue with the 1998 paper, going to the earlier papers if there is something that you don't understand otherwise.

Activity-composition relationships

Looking at (1), the second practical concern is where we get the numbers from to insert into K for any particular reaction. Given that using THERMOCALC involves you (or a wizard) coding the algebraic form of the activity-composition (a - x) relationships of the phases of interest into the datafile that THERMOCALC uses, this side of things is harder to ignore. You may be able to get away with not getting on top of this if you are happy to use datafiles coded by others. There will be an accumulation of coding of a - x relationships on the CD-ROM.

With THERMOCALC 3.x, the a - x coding has been considerably simplified, with the formulation (coding) of non-ideality involving the symmetric formalism (aka macroscopic regular

model) done automatically. All the user does is list the interaction energies, and THERMOCALC does the rest.

References relating to the symmetric formalism are

Powell, R, and Holland, TJB, 1993. On the formulation of simple mixing models for complex phases *American Mineralogist* **78**, 1174–1180.

Holland, TJB, and Powell, R, 1996. Thermodynamics of order-disorder in minerals. 1: symmetric formalism applied to minerals of fixed composition. 2: symmetric formalism applied to solid solutions. *American Mineralogist* **81**, 1413–1437.

Powell, R, and Holland, TJB, 1999. Relating formulations of the thermodynamics of mineral solid solutions: activity modelling of pyroxenes, amphiboles and micas. *American Mineralogist* **84**, 1–14.

The plan in reading these should be to start with the 1993 paper and work forward. Some of this is a little arcane, but the symmetric formalism is central to coding THERMOCALC datafiles.

Examples of the approach in action are

Holland, TJB, Baker, J, and Powell, R, 1998. Mixing properties and activity–composition relationships of chlorites in the system MgO–Al₂O₃–SiO₂–H₂O. *European Journal of Mineralogy*, **10**, 395–406.

Dale, J., Holland, T.J.B. and Powell, R. 2000. Hornblende-garnet-plagioclase thermobarometry: a natural assemblage calibration of the thermodynamics of hornblende. *Contributions to Mineralogy and Petrology* **140**, 353–362.

The DQF approach is of use in general (in combination with the symmetric formalism), and as a THERMOCALC coding mechanism:

Powell, R, 1987 Darken’s quadratic formalism and the thermodynamics of minerals. *American Mineralogist* **72**, 1-11.

Holland, TJB, and Powell, R, 1992 Plagioclase feldspars: activity-composition relations based upon Darken’s Quadratic Formalism and Landau theory. *American Mineralogist*, **77**, 53-61.

Phase diagram geometry and examples

The “must-read” paper is:

Powell, R, Holland, TJB, and Worley, B, 1998. Calculating phase diagrams involving solid solutions via non-linear equations, with examples using THERMOCALC *Journal of Metamorphic Geology* **16**, 577–588.

Note that there are a couple of infelicities in this paper: top of 2nd col of p584, the expression should be $s - n + n + 2$ (not $s - n + p + 2$); and in the muscovite example on p588, the bi subscripts should be mu (ugh), and the definition should be just $y_{\text{mu}} = \text{Al}^{\text{oct}} - 1$.

Whereas up til now the drawing of phase diagrams has involved using Mathematica functions on manually-assembled THERMOCALC output, I am in the process of writing software (called drawPD) that will replace the Mathematica functions, the phase diagrams being output as postscript or pdf. This *will* be ready for the course. (Hopefully not famous last words).

Some recent “example” papers that might also be of interest are:

- Guiraud, M, Powell, R, and Cottin, JY, 1996. Hydration of orthopyroxene-cordierite-bearing assemblages at Laouni, Central Hoggar, Algeria. *Journal of Metamorphic Geology*, **14**, 467–476.
- Worley, B, and Powell, R, 1998. Singularities in the system $\text{Na}_2\text{O}-\text{CaO}-\text{K}_2\text{O}-\text{MgO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. *Journal of Metamorphic Geology* **16**, 169–188.
- Carson, CJ, Powell, R, and Clarke, GL, 1999. Calculated mineral equilibria for eclogites in $\text{CaO}-\text{Na}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$: application to the Pouébo Terrane, Pam Peninsula, New Caledonia. *Journal of Metamorphic Geology* **17**, 9–24.
- White, RW, Powell, R, Holland, TJB, and Worley, B, 2000. The effect of TiO_2 and Fe_2O_3 on metapelitic assemblages at greenschist and amphibolite facies conditions: mineral equilibria calculations in the system $\text{K}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{TiO}_2-\text{Fe}_2\text{O}_3$. *Journal of Metamorphic Geology* **18**, 497–511.
- White, RW, Powell, R and Holland, TJB, 2001. Calculation of partial melting equilibria in the system $\text{Na}_2\text{O}-\text{CaO}-\text{K}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (NCKFMASH). *Journal of Metamorphic Geology*, **19**, March issue.

Thermometry and barometry

Although little time will be spent on thermometry and barometry in the course, the average *PT* approach to thermometry and barometry is covered in the following papers

- Powell, R, and Holland, TJB, 1988 An internally consistent thermodynamic dataset with uncertainties and correlations: 3: application methods, worked examples and a computer program. *Journal of Metamorphic Geology* **6**, 173-204.
- Powell, R, and Holland, TJB, 1994. Optimal geothermometry and geobarometry. *American Mineralogist* **79**, 120-133.
- Worley, B, and Powell, R, 1999. High-precision relative thermobarometry: theory and a worked example *Journal of Metamorphic Geology* **18**, 91–102.

Apart from in the form of (available) Mathematica functions, the ΔPT approach of the last paper is not currently implemented, though the *plan* is to hive off av*PT* from THERMOCALC, incorporate AX, and include ΔPT in new software (to be called optimumPT). The chances of this being ready in time for the course are *small*.

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