SOFTWARE NOTICE

THERMO: A computer program for calculation of mixed-volatile equilibria

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Abstract

THERMO is an interactive computer program that conducts thermodynamic calculations of mixed-volatile equilibria. It was written specifically for microcomputers. Its simple commands, large vocabulary, and ease of operation make it ideal for both teaching and research. Copies of the program, for either an IBM or an Apple operating system, are available on floppy disk. A thermodynamic database with data for over 125 minerals and related substances is available with the program.

Introduction

Slaughter et al. (1976) presented APL programs, and Wall and Essene (unpub.) developed the FORTRAN program EQUILI for thermodynamic calculations of mixed-volatile equilibria. These and other similar programs were written for mainframe computers with their high speeds and large memories. In recent years, there has been a strong shift away from mainframe computers to personal computers. What is presented here is a conversational computer program, written specifically with small computers in mind, for making complex phase-equilibria calculations. Its interactive nature and English vocabulary make it easy to use.

The program was written in FORTRAN77 for the DOS2.10 operating system on an IBM PC or equivalent. Copies formatted for Apple computers will soon be available. The uncompiled program occupies about 60 kbytes of memory, the compiled version about 145 kbytes. Calculations of solid-solid equilibria are rapid. Calculations involving volatile species, which are slower, will run one to two orders of magnitude faster on computers equipped with a math coprocessor chip.

Data storage

A thermodynamic database is stored on disk and read by THERMO every time the program is initiated. Sources of data include standard references such as Birch (1966), Skinner (1966), Robie et al. (1978), and JANAF (1971, et seq.), as well as selected others. Twenty-five pieces of information are stored for each phase. It is possible to have more than one set of thermodynamic values for a given phase. New phases and thermodynamic constants may be entered in the database at any time

using simple commands. At present, the database includes data on over 120 minerals and related compounds.

If function constants are not known, tabulated values may be entered, and the program will fit a function to the data using a least-squares regression. For all functions, residuals and goodness-of-fit statistics are printed out.

There have been many recent studies that have pointed out inconsistencies in tabulated thermodynamic data for minerals. The data supplied with this program have *not* all been checked for consistency. The ΔG_f^0 values are especially suspect, as they have been taken from a variety of sources. Program users should check data sources and evaluate their accuracy themselves.

Calculations

Standard calculations

The main function of THERMO is to evaluate the Gibbs energy (ΔG), equilibrium constant (K), or log of the equilibrium constant (ln K) of a reaction, given a reference value at a known pressure (P_1), temperature (T_1), and mole-fraction H_2O or CO_2 (X_1). The reference value may be entered, or the program will calculate it from stored ΔG_f^0 values. The program then asks for the ranges of pressures (P_2), temperatures (T_2), and mole-fractions H_2O or CO_2 (X_2) over which calculations will be made. The operator is also asked for the kind of table (P-T, T-X, or P-X) and the nature of the values to be output (ΔG, K, or ln K). All input parameters have automatic default values so that questions can be ignored for routine calculations. The Gibbs energy of reaction is then calculated at all P_2, T_2, X_2 by

$$\Delta G_{P_2, T_2, X_2} = \Delta G_{P_1, T_1, X_1} + \sum_i \nu_i \int_{P_1}^{P_2} V_i \, dP$$
$$- \sum_i \nu_i \int_{T_1}^{T_2} S_i \, dT + \nu_{H_2O} \Delta G_{H_2O}$$
$$+ \nu_{CO_2} \Delta G_{CO_2}, \qquad (1)$$

where the summations apply to the solid phases and the ν values are the reaction coefficients. For each of the solids,

$$\int_{P_1}^{P_2} V \, dP = \int_{P_1}^{P_2} V_{298}^0 \left(1 + \frac{\alpha_{\%}}{100}\right)\left(1 - \frac{\beta_{\%}}{100}\right) dP \qquad (2)$$

and

$$\int_{T_1}^{T_2} S \, dT = \int_{T_1}^{T_2} \left[S_{298}^0 + \int_{298}^{T} \frac{C_P}{T} \, dT \right] dT, \qquad (3)$$

where $\alpha_\%$ and $\beta_\%$ are the percentage thermal expansion and isothermal compressibility, respectively.

For H_2O and CO_2,

$$\Delta G_{H_2O} = RT[\ln f_{P_2,T_2,X_2} - \ln f_{P_1,T_1,X_1}]_{H_2O}$$
$$+ [\Delta G^0_{T_2} - \Delta G^0_{T_1}]_{H_2O} \tag{4}$$

and

$$\Delta G_{CO_2} = RT[\ln f_{P_2,T_2,X_2} - \ln f_{P_1,T_1,X_1}]_{CO_2}$$
$$+ [\Delta G^0_{T_2} - \Delta G^0_{T_1}]_{CO_2}. \tag{5}$$

Functions for the fugacities of H_2O and CO_2 at elevated pressures are based on modified Redlich-Kwong equations of Kerrick and Jacobs (1981). The specific subroutines have been modified from those of Jacobs and Kerrick (1981) and apply over a temperature range of about 300–1200°C and pressures of 1–12000 bars. The standard Gibbs free energies of H_2O and CO_2 at 1 bar are evaluated using equations based on the data of Robie et al. (1978). Functions for C_P, thermal expansion (expressed in percent), and isothermal compressibility (expressed in percent) have the forms

$$C_P = A + BT + CT^{-1/2} + DT^{-2} \tag{6}$$

$$\alpha_\% = E(T - 293) + F(T - 293)^2 \tag{7}$$

$$\beta_\% = GP + HP^2, \tag{8}$$

where A through H are constants.

If the operator desires $\ln K$ or K values to be output, they are evaluated as

$$\ln K = -\Delta G/RT \tag{9}$$

$$K = \exp(-\Delta G/RT). \tag{10}$$

Values of V^0_{298}, S^0_{298}, and the constants in Equations 6, 7, and 8 are taken from the thermodynamic database. However, the operator has the option to change any of them at any time.

Entropies, volumes, and H_2O-CO_2 properties

THERMO will conduct several other types of calculations in addition to those already described. For example, tables of entropy as a function of temperature, and of volume as a function of temperature and pressure, may be calculated. Perhaps of more use, THERMO will calculate and print out tables of the thermodynamic properties (standard Gibbs free energies, fugacities, or activities) of H_2O and CO_2. Such tables may be created for pure (end-member) H_2O and CO_2 or for supercritical mixtures.

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NOTICE

JANAF Thermochemical Tables, third edition, published by NBS

The National Bureau of Standards (NBS) of the U.S. Department of Commerce has published the third edition of the (Joint Army–Navy–Air Force) *JANAF Thermochemical Tables*. The JANAF tables provide scientists in government, industry, and universities with important information on the performance of materials at high temperatures.

The JANAF tables project was established in late 1959 at the Dow Chemical Thermal Research Laboratory (Midland, Michigan) as a way to compile and publish consistent tables of thermodynamic data required for rocket-propellent performance calculations by industry and Department of Defense agencies. Today the database is located in the NBS Chemical Thermodynamics Data Center and contains critically evaluated data on the thermodynamic properties of approximately 1800 substances. It includes all evaluated data done under the program through October 1985.

The database includes recommended temperature-dependent values for the thermodynamic properties of inorganic substances and for organic substances containing only one or two carbon atoms. These tables cover the thermodynamic properties of materials over a wide temperature range (0 to 6000 kelvins) with single-phase and multiphase tables for crystal, liquid, and ideal-gas state. The properties tabulated are heat capacity, entropy, Gibbs energy function, enthalpy of formation, Gibbs energy of formation, and the logarithm of the equilibrium constant for formation of each compound from the elements in their standard reference states. All values are given in SI units and are for a standard-state pressure of 10^5 pascals (1 bar).

The *JANAF Thermochemical Tables* also are available in a computer-readable format that will be updated each year as new information becomes available.

The *JANAF Thermochemical Tables* are published as Supplement No. 1 to Volume 14 of the *Journal of Physical and Chemical Reference Data* (1985). The journal and its supplements are published under a cooperative agreement among NBS, the American Institute of Physics, and the American Chemical Society. The two-volume set is available for $130 (prepaid) from the American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D.C. 20036, U.S.A.

The computer-readable database, the *JANAF Thermochemical Tables* (1985), NBS Standard Reference Database 13, is available for $1200 from the Office of Standard Reference Data, A323 Physics Building, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A. (telephone, 301-975-2208).