

**SOLVEQ-XPT : A Computer Program
for Computing
Aqueous-Mineral-Gas Equilibria**

Version 2.23

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June 2016

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FOREWORD

Program SOLVEQ was the first in a series of programs that we have developed since the mid-1970's for calculating equilibria in aqueous systems. Although SOLVEQ has been substantially improved since it was first written, and even though it has spawned some sophisticated and versatile descendents, such as CHIM-XPT and GASWORKS, it still meets a need for its original essential function of calculating the distribution of aqueous species and mineral saturation indices in natural waters and waters from hydrothermal experiments.

SOLVEQ's new version, SOLVEQ-XPT, is an improvement over its predecessor for its capability to compute equilibria at any specified pressure and temperature up to 5kb and 600°C. Otherwise, SOLVEQ is applied to compute homogeneous equilibrium (distribution of aqueous species) in any aqueous fluid, given pH (or other measure of H^+) and a water analysis. It also computes partial heterogeneous equilibrium, wherein equilibration of a given water with specified minerals or gas fugacities can be forced. The forced equilibria are then used to fix the total concentrations of specified component species. SOLVEQ's forced mineral equilibrium capability and its ability to calculate pH at high temperature and pressure from a low-T-P pH measurement make it useful for geothermometry, geobarometry, and other studies of geothermal and sedimentary formation waters and for processing hydrothermal experimental run products to derive thermodynamic data or evaluate mineral equilibria. The numerical simplicity of the homogeneous equilibrium calculations make them particularly straightforward to compute with SOLVEQ. Forced mineral equilibrium calculations with SOLVEQ can be more troublesome numerically, but, with a little care, they can be carried out successfully.

One of the principal applications of SOLVEQ is computation of mineral solubility indices ($\log Q/K$), which are applied to understand potential scale minerals in geothermal systems and for geothermometry and geobarometry. The latter are executed by plotting $\log Q/K$ for various minerals against P or T to identify P and T conditions of mineral equilibrium with the fluid and with each other. SOLVEQ is also helpful for preparing starting waters for CHIM-XPT calculations.

SOLVEQ is accompanied by program GEOCAL, whose function is to convert raw water analyses or water-plus-gas analyses into an input files for SOLVEQ.

A quality thermodynamic data base such as SOLTHERM-XPT is essential to meaningful model calculations. We have endeavored to make SOLTHERM-XPT accurate, large and current, but the task of making it comprehensive enough to treat everyone's chemical problems is enormous. I hope users will add new or improved data to their own versions of the SOLTHERM data base, including appropriate documentation. Then, if users send their improvements to me from time, I can incorporate them into a master data base. I also encourage all users to notify me about possible problems (bugs or errors, hassles) in SOLVEQ and SOLTHERM so that they can be corrected.

-MHR//4 April 2012

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Chapter 1. Introduction

SOLVEQ-XPT is a FORTRAN computer program for computing multicomponent homogeneous chemical equilibria in aqueous systems (Reed, 1982, 1998). It is used primarily as a work horse for processing water analyses of all types, but it is also useful for certain types of geochemical process modeling. For a given temperature and total composition of a homogeneous aqueous solution, SOLVEQ-XPT computes the activities of all aqueous species, the saturation indices of solids, and the fugacities of gases. SOLVEQ-XPT also calculates partial heterogeneous equilibrium, wherein equilibration of a given water with specified minerals or gas fugacities can be forced. The forced equilibria fix the total concentrations of specified component species. For example, an unknown total concentration of aluminum in a given natural water can be computed by forcing equilibrium with kaolinite. This capability combined with SOLVEQ's ability to calculate pH at high temperature from a low-T pH measurement (Reed and Spycher, 1984; Pang and Reed, 1998) also make it useful for processing hydrothermal experimental run products and for geothermometry and other studies of geothermal and oil field waters, as laid out by Palandri and Reed (2001).

SOLVEQ-XPT solves a system of mass-balance and mass-action equations by the Newton-Raphson numerical technique (Reed, 1982; Reed, 1998). In SOLVEQ, the chemical system is defined in terms *component species*. Other species (complexes, redox species), referred to as *derived species*, are expressed in terms of linear combinations of these component species. Minerals and gases are also expressed in terms of component species. The total chemical composition of the system is thus given as the total molar amount of each component species in that system (e.g. if HCO_3^- is the component species for carbonate, total HCO_3^- includes HCO_3^- , H_2CO_3 , CO_3^{2-} , etc.).

The SOLVEQ-XPT execution file (Solveq-xpt.exe) is about 420 Kbytes in size, and thus requires minimal RAM for execution. The program is small and fast, and runs easily on personal microcomputers.

1.1 Testing Execution

Try out the demonstration files (solrunxpt.dm*, where "*" refers to numbers 1-7) that were distributed with the program. The easiest way to do this is to place all of the Solveq-related files in the same directory, then execute the program. Take the following steps (adapted for a windows operating system; but analogous instructions apply to others):

- Place the following files in one directory: solveq-xpt.exe, soltherm.dat, solrunxpt.dm*. If the soltherm file that you have is not named "soltherm.xpt" (e.g. it might be soltherm.h06 or soltherm.joh) it is likely for the old version of SOLVEQ and will not work with SOLVEQ-XPT. SOLVEQ-XPT reads only "soltherm.xpt".
- Copy (do not "rename") one of the solrun.dm* files to the name "solrun.dat". If you "rename", the file will be lost the next time you create a solrun file, e.g. from GEOCAL-XPT.
- Type "solveq-xpt", solveq-xpt in a command line window, and watch it execute; alternatively, double-click the solveq-xpt icon in Windows Explorer and watch it execute. The advantage of the command line is that error messages can be read.
- Use a text editor (e.g. TextPad (recommended) or Notepad) to examine the output file, solout.dat. TextPad is available at <http://www.textpad.com/>.
- If you wish to save the output file, copy it to another name, e.g. "solout demo1.txt"

- f) Repeat steps b,c,d,e with the other demonstration files.

Chapter 2. Format and Content of Input File SOLRUN

SOLRUN.DAT contains the data specific to each run. As such, it also contains the user's instructions on how SOLVEQ-XPT is to address the water composition that you provide in the file. This takes some thought, and in many instances, some creative ideas. See Chapter 4 for more help on such ideas.

For most users, the SOLRUN is the only input file that will have to be created or modified prior to running SOLVEQ. Details for the other input file, SOLTHERM (containing thermodynamic data) are given in Appendix 2. Program GEOCAL-XPT can be used to create SOLRUN, starting from a raw water analysis in units of ppm, mg/l, or molality. Commonly the user runs GEOCAL-XPT, then edits GEOCAL-XPT's SOLRUN to suit. In this chapter, the formats of each record, and the definition of each variable in the SOLRUN file are given. Refer to chapter 4 for details about the specific use of input parameters for various types of calculations. Six example SOLRUN files are given at the end of this section.

2.1 Example SOLRUN file

Record Number										
1	Demonstration input file for program SOLVEQ					Japanese Geothermal Water				
2	Calculate Al from equilibration w/ muscovite					SOLRUN Demonstration 4				
3										
4	< eprc ><	pH	>< unact	>< alkali	>< tempc	>< rm	>< pr_min	>< pfluid	>	
5	.1000E-11	5.44	.0000E+00	.0000E+00	300.	.0000E+00	0.0	0.0		
6										
7	l/v:0		i chg	n ichg	i igeo	it		a		
8	hiP:1	nmtt	step	bal	loop	bal	sunk	thrm	ref	neut
9	0	1	0	1	40	3	0	1	0	0
10										
11	saq>	< name >	<	mtot	><	mtry	><	gamma	>	
12	1	H+		0.163232117E+00		0.199526694E-04		1.0000		
13	2	H2O		0.327951908E+01		0.100000000E+01		1.0000		
.	3	Cl-		0.643617690E+00		0.100000005E-03		1.0000		
.	4	SO4--		-0.147330528E-02		0.100000022E-06		1.0000		
.	5	HCO3-		0.139322102E+00		0.100000022E-06		1.0000		
.	6	HS-		0.274162218E-01		0.100000022E-06		1.0000		
.	7	SiO2		0.161905289E-01		0.100000022E-06		1.0000		
.	8	Al+++		0.100000000E-05		0.100000000E-15		1.0000		
.	9	Ca++		0.299401172E-01		0.100000022E-06		1.0000		
.	10	Mg++		0.867510447E-03		0.100000022E-06		1.0000		
.	11	Fe++		0.260451779E-04		0.100000022E-06		1.0000		
.	12	K+		0.802097321E-01		0.100000022E-06		1.0000		
11+n	13	Na+		0.521970809E+00		0.100000022E-06		1.0000		
11+n+1										
11+n+2	< force equil. with> ieq> log act>									
11+n+3	muscovite 8									

SOLRUN.dat files are text files normally generated by program GEOCAL from user input of water composition. SOLVEQ users are expected to use a text editor such as TextPad to edit SOLRUN files beyond what GEOCAL produces, or to edit an existing SOLRUN file to suit a new run. The descriptions in Section 2.2, below, provide the information needed to edit solrun,

including Fortran input formats, given in parentheses for each record. Users do not need to understand the input formats as long as the number styles in edited versions do not depart from those in the template file. Guidelines:

- a) All integer and real variables must exist, separated by at least one blank or a comma. By “exist” we mean that a number must be present, e.g. blank space cannot be used to represent zero; “0” must represent zero.
- g) Integer variables must not include a decimal point.
- h) Real or E-format numbers must include a decimal point (E.g. 2.5e-12, or 3.33), but need not be exactly aligned beneath the <...> field delimiters, but they must be separated by a space. The “E” part of E-format numbers may be omitted if it is E00; i.e. “0.0022” is OK in place of “0.22E-2” in an E-format space.
- i) mineral names under “<force equil. with>” must be spelled exactly as in SOLTHERM-XPT, and must begin in column 1.

2.2 Input Variables in the Run File: SOLRUN.DAT (IN1)

A description of this file content and formats follows. Refer to the record numbers in the example file, above.

* Records 1 and 2 (10A8): TITLE, two 80-character lines.

Use this space to record a water source AND a few details on what this particular run does that distinguishes it from other runs on the same water composition. Title notes become your primary record of what you are doing in making this run.

* Records 3 and 4: skipped by SOLVEQ-XPT on input. Record 4 contains field labels for the following line of input. When GEOCAL-XPT generates the SOLRUN file, it outputs records such as 3 and 4, which contain format indicators for the next record. These records can be left blank.

* Record 5 (list-directed format, or free format: space or comma separates numbers): ERPC, PH, UNACT, ALKALN, TEMPC, RM, PR_MIN, PFLUID

ERPC: Convergence limit on mass-balance and mass-action equations (default value is 10^{-12}). When all equations are solved within ERPC precision, the program assumes convergence. When setting ERPC, keep in mind that most computer systems have 16 significant digits in double precision, and SOLVEQ-XPT might fail to converge if ERPC is less than 10^{-11} . Convergence will definitely fail if ERPC is smaller than 10^{-16} . In some instances where convergence fails with ERPC set at 10^{-12} , try 10^{-11} or 10^{-10} to see if it enables convergence. In such instances, be wary of possible errors in component species with very small concentrations. Check the step-by-step convergence residuals to see that they close in on very small values (see variable “ISTEP” for help on residuals).

pH: pH of the solution. If specified, the total molar amount of H^+ ion in solution will be computed and outputted in the “Tot Moles” column of SOLOUT. If zero, the pH will be calculated from the given total amount of H^+ ($M^+(H^+)$).

UNACT: Activity of a component species, if its activity is known instead of its total molar amount. The species itself is identified by the index ISUNK, below. Note that you should use pH, not unact, to input hydrogen ion activity.

ALKALN: Alkalinity of the solution, if known, to be used instead of total molar amount of carbonate, which is then computed from the alkalinity in concert with other alkalinity-producing species, e.g. bisulfide, acetate, etc. The units for ALKALN are molality (molality of H^+ equivalents determined from titration alkalinity).

TEMPC: Temperature at which equilibrium is computed, in degrees Celsius.

RM: Parameter between 0 and 1 to multiply mass-balance/action equations to help convergence in calculations that do not converge otherwise. This forces the residuals to decrease during convergence. RM must be set to zero unless there are convergence problems. Use only as last resort (see chapter 5), as RM non-zero might cause convergence to fail in a system that would normally converge with $RM = 0$.

PR_MIN: Real parameter specifies the minimum molality of derived species to be written in SOLOUT. Ordinarily, set pr-min to a value three orders smaller than the smallest total molality (MTOT) to reduce file size.

PFLUID: Pressure of the system (bars). Check SOLTHERM-XPT data file for the current pressure limits for a given temperature, of thermodynamic data if one is modelling systems at elevated pressures.

* Records 6, 7 and 8: skipped by SOLVEQ-XPT on input, as for records 3 and 4.

* Record 9 (free format): l/v-HiP, NMTT, ISTEP, CHGBAL, NLOOP, ICHGBAL, ISUNK, IGEOThRM, ITREF, NEUT, AWATR

l/v:hiP: Zero means use P-T of H_2O liquid-vapor curve (i.e. use thermodynamic data for T specified by TEMPC at P of H_2O liquid/vapor saturation; ignores PFLUID); one means use thermodynamic data at the P and T point specified by TEMPC and PFLUID

NMTT: If zero, this index disables the calculation of saturation indices and fugacities. Set to non-zero to compute these values. ($NMTT = 0$ also skips reading mineral and gas data in the SOLTHERM data file).

ISTEP: If not zero, printing of extra output for closer inspection of the calculation progress will occur. Generally, ISTEP is only used for debugging purposes, but it is instructive for beginners to examine the additional output, particularly to see the convergence residuals changing size as the system converges.

CHGBAL: If non-zero, charge balance is calculated and adjusted by changing the molar amount of the charge balance ion (ICHBAL index, below). Note that charge balance adjustments are automatically accomplished even if CHGBAL is zero, if pH is given (pH non-zero), if the

UNACT option is used, or if equilibration with a mineral is specified to compute the activity of a component species (FORCE EQUIL. WITH, below, non-blank). Otherwise, the charge balance is not verified and adjusted, unless CHGBAL is non-zero.

NLOOP: Maximum number of Newton-Raphson iterations allowed when converging to a solution. If SOLVEQ-XPT has not converged after NLOOP iterations, the execution is aborted because non-convergence is assumed (some results are still printed to help in debugging). NLOOP = 40 is preferred. Most cases are solved after 10 to 20 iterations (loops), although some might require more. Generally, a case not solved after 70 iterations will not converge.

ICHGBAL: Component species ion to be used for charge balance. ICHGBAL is the sequence position of the selected ion in the list of component species in SOLTHERM data file. Generally, ICHGBAL = 3 (for Cl^-) is used, but in certain instances it may be better to choose 4 for sulfate or 5 for bicarbonate or 13 for Na^+ ion, etc., depending on which is dominant or which is to be set using charge balance instead of analytical information. The total molality of this ion will be adjusted to compensate for a charge imbalance of the solution. If ICHGBAL is zero and PH, UNACT, or FORCE EQUIL. WITH are not given, the adjustment of the ICHBAL ion does not take place. Notice that essentially all raw water analyses are out of charge balance owing to analytical errors and inadequate analyses in one way or another. SOLVEQ-XPT requires charge balance, making it possible to use this constraint to address incomplete analyses, in some instances (see Section 4.4). Typically, the charge balance should be set on an abundant species such as Na^+ or Cl^- .

ISUNK: If value for UNACT, above, was specified, ISUNK must be input to identify which species has the activity given by UNACT. Just as for ICHGBAL, above, ISUNK is the sequence position of the selected ion in the list of component species in SOLTHERM data file. For example, ISUNK = 6 specifies HS^- .

IGEOTHRM: If non zero, IGEOTHRM enables the calculation of equilibration temperature from the Na/K/Ca geothermometer.

ITREF: This parameter is used to activate iterative refinement when solving the system of non-linear equations. ITREF should always be set to zero (no iterative refinement), unless convergence problems arise. ITREF = 1 results in computing residuals, but not iterative refinement. In order to print these residuals, ISTEP must also be set to 1. ITREF = 2 results in minimizing the residuals by one or more iterative refinements, in order to help achieve convergence. This is a last resort option (see chapter 5).

NEUT: Use to control setting of gammas for neutral species and all species to unity.

neut = 0 Set gammas for species flagged in SOLTHERM by azero = 9.99 to $\gamma(\text{CO}_2)$. Used for dissolved gases (CO_2 , H_2S , etc.). Gammas for all other neutral species (SiO_2 , AgCl , etc.) set to 1.0.

neut = 1 Set gamma for all neutral species to 1.0

neut = 2 Set gamma for all neutral species to $\gamma(\text{CO}_2)$

neut = 3 Set gamma for all species to one.

AWATR: Control gamma for water

awatr = 1 Set gamma for water to = 1.0

awatr = not 1 Use subroutine LIETZKE to compute $a(\text{H}_2\text{O})$

Note: NEUT = 3 overrides this option.

* Records 10 and 11: skipped by SOLVEQ-XPT on input, as for records 3 and 4.

* Record 12 and following. The number of the next records depends on how many component species are included in the chemical system (one record per component species).

(15, 13X, 2E19.13, G19.13): SAQ(i), NAME(i), MTOT(i), MTRY(i), GAMMA(i)

SAQ is an integer that uniquely identifies component species. The unique identity is the sequence position of component species as listed in the SOLTHERM data file. (e.g. H^+ is 1, H_2O is 2, Cl^- is 3, SiO_2 is 7, etc..). SAQ, and not NAME, below, identifies which component species will be used for the present calculation. As explained further below, you cannot use both HS^- (SAQ = 6) and O_2 (SAQ = 31) simultaneously to specify composition in this system of components.

NAME contains the names of the selected components species identified by SAQ above. NAME here is a dummy variable which is skipped by SOLVEQ-XPT on input. It is part of the record only to improve the clarity of the SOLRUN file. Program GEOCAL reads the names of component species from SOLTHERM data file (as specified by the values of SAQ above), and writes these names in the NAME field above when creating a SOLRUN file. Therefore, if you set up a SOLRUN file from scratch, NAME here can be left blank.

MTOT or TOTAL MOLES contains the total number of moles of component species SAQ in the system. For water, TOTAL MOLES must be in kilograms. TOTAL MOLES defines the total composition of the chemical system, including aqueous species, and dissolved gases, if any. TOTAL MOLES values are generally positive, but may also be zero or negative if the system contains derived species that are expressed in terms of a negative amount of a component species (e.g. $\text{NaOH} = -1 \text{ H}^+ + 1 \text{ Na}^+ + 1 \text{ H}_2\text{O}$, therefore contains negative H^+ , thus an alkaline solution may have a negative value for TOTAL MOLES for H^+). If the mineral equilibration option is to be used (see FORCE EQUIL. WITH, below), the value given for TOTAL MOLES of the species (IEQ, see below) to be set by the mineral equilibrium need not be given since it will be computed by SOLVEQ-XPT.

Notice that since TOTAL MOLES is in units of moles, not molality, the values themselves do not equal molalities, except when TOTAL MOLES of H_2O is specified as one kilogram (technically, even then they are not quite molality, since some of the H_2O may be consumed in making non-solvent water species). Using moles (and kg, for water) instead of molality simplifies dilution and un-dilution runs, wherein the value of TOTAL MOLES of H_2O is increased or decreased, respectively, without changing TOTAL MOLES of other species.

MTRY or TRIAL MOLALITY contains the trial molalities of component species SAQ. SOLVEQ-XPT solves for these molalities of component species, starting with the trial molalities specified here. In contrast to the TOTAL MOLES, the TRIAL MOLALITY cannot be less than zero.

The closer the initial trial values are to the actual (unknown) molalities, the better are the

chances for SOLVEQ-XPT to converge to a solution. TRIAL MOLALITY values must be estimated, but values of 10^{-7} for all but H_2O , which is set to 1.0, make a good start. Generally, the system will converge even when TRIAL MOLALITY's are orders of magnitude off, however, for some species, notably Al^{3+} , Au^+ , Hg^{2+} , O_2 (in reduced waters), and HS^- (in oxidized waters), and Fe^{2+} (in oxidized waters) much smaller trial molalities are commonly needed, such as 10^{-12} or 10^{-15} . See further discussion in Section 2.3.

GAMMA contains trial activity coefficients of component species SAQ. For an initial run, these must be estimated. Default GAMMA values are 1.

* Record $11+n+1$ (where n is the number of components in this run) MUST BE BLANK to indicate end of component species data.

* Record $11+n+2$: field label line, skipped by SOLVEQ-XPT on input, as for record 4.

*Records $11+n+m$ (where m is the number of minerals (or gases) being forced to equilibrium). These last records need to be supplied only if one is computing the total molar amount and activity of a component species, by forcing equilibration with a mineral or gas containing that species. The number of these records (m) depends on how many equilibrated minerals or gases are specified (one mineral or gas per record).

(A20,2X,I4,F10.3): FORCE EQUIL. WITH(i), IEQ, LOG ACT

Each FORCE EQUIL. WITH contains the name of a mineral or gas that is forced to be in equilibrium with the solution. FORCE EQUIL. WITH must match exactly the spelling of phases in the SOLTHERM data file, or else SOLVEQ-XPT will stop execution and let you know of the mismatch.

IEQ is the index of the species (SAQ, above) contained in mineral or gas FORCE EQUIL. WITH, for which you want to compute the total molar amount and activity. Species IEQ must be among the component species in the SAQ list above. Also notice that if you wish to fix pH using mineral equilibrium, specify IEQ=1 for the mineral (FORCE EQUIL. WITH) you choose to use to fix pH.

LOG ACT is the log of the activity or fugacity of the mineral end member or gas specified by eqnam. Zero or blank yields an activity of unity.

2.3 Solrun Demonstration Files

The software package includes demonstration files for six different types of SOLVEQ-XPT calculations. The files are named "solrun.dm1, solrun.dm2 ...solrun.dm7" and are listed below. We suggest that you test and debug your installation of SOLVEQ-XPT using these files by copying one of the demo's into "SOLRUN.DAT", then running it. You may also choose to use these files as templates to make your own SOLRUN's, if your water analysis is in molar form already. If your water analysis is in ppm, mg/l, etc. then it is easier to run GEOCAL-XPT (see below) to set up a SOLRUN file. As explained in Section 1.1, to execute SOLVEQ-XPT at a command prompt or in a Windows Explorer window, be sure to have the following files, with the following names are in the same directory: solveq-xpt.exe, soltherm.xpt, solrun.dat.

2.3.1. Solrun.dm1

```

Geothermal water      Hveragerdi well 4,  No gases added
Data from Arnorsson GCA v47 p549, 1983  SOLRUN Demonstraton 1

< erpc >>  pH      >> unact >> alkalm >> tempc >>  rm      >> pr_min >> pfluid >
.10000E-11  8.82      0.0      0.0      25.      0.0      0.0      0.0

      l/v:0      i      chg      n      ichg      i      igeo      it      a
hiP:1 nmtd step bal loop bal sunk thrm ref neut watr
      0      1      0      0      40      3      0      1      0      0      0

saq> <  name      >>      mtot      >> 0.0001 mtry      >>      gamma      >
1 H+      0.0
2 H2O      0.99930E+00
3 Cl-      0.30886E-02
4 SO4--     0.45492E-03
5 HCO3-     0.16860E-02
6 HS-       0.56338E-03
7 SiO2      0.46771E-02
8 Al+++     0.51887E-05
9 Ca++      0.43164E-04
10 Mg++     0.82264E-07
11 Fe++     0.14325E-06
12 K+       0.34269E-03
13 Na+      0.66682E-02
23 F-       0.95800E-04

< force equil. with>  ieq>

```

File: SOLRUN.DM1. Example file for computing TOTAL MOLES of H^+ for a geothermal water from the room temperature analysis and pH measurement. After running this "without gas" file once in SOLVEQ-XPT to obtain TOTAL MOLES H^+ for the aqueous phase alone, the TOTAL MOLES H^+ thus obtained is added (by hand) to the TOTAL MOLES H^+ for the gas phase that is to be added back to the liquid. The gas TOTAL MOLES H^+ and TOTAL MOLES's of other component species in the gas such as HS^- , are obtained from running GEOCAL-XPT to create a "with gas" SOLRUN file. The complete "with gas" file for this Icelandic geothermal water is given here as SOLRUN.DM2.

2.3.2 Solrun.dm2

```

Geothermal water   Hveragerdi well 4       Gases added
Data from Arnorsson GCA v47 p549, 1983   SOLRUN demonstration 2

< erpc ><      pH      >< unact >< alkalin >< tempc ><      rm      >< pr_min >< pfluid >
.1000E-11      0.      0.0      0.0      25.      0.0      0.0      0.0

      l/v:0      i      chg      n      ichg      i      igeo      it      a
hiP:1 nmtt step bal loop bal sunk thrm ref neut watr
      0      1      0      0      40      3      0      1      0      0      0

saq> <      name      ><      total moles      ><      trial molality ><      gamma      >
1 H+      0.15943E-02      0.1      E-06
2 H2O      1.04080E+00
3 Cl-      0.31660E-02
4 SO4--      0.43659E-03
5 HCO3-      0.38327E-02
6 HS-      0.73982E-03
7 SiO2      0.46771E-02
8 Al+++      0.51887E-05
9 Ca++      0.43164E-04
10 Mg++      0.82264E-07
11 Fe++      0.14325E-06
12 K+      0.34269E-03
13 Na+      0.66682E-02
23 F-      0.95800E-04

< force equil. with>      ieq>      log act>

```

File: SOLRUN.DM2. Example file for computing in situ properties of the Hveragerdi geothermal water, including the gas constituents that boiled out. The value of TOTAL MOLES H^+ given here was computed from the value for the aqueous phase alone obtained from running SOLRUN.DM1 combined with the contribution from the gas itself (see Reed and Spycher, 1984). The gas contributions to the TOTAL MOLES of the total fluid were computed using GEOCAL-XPT on the raw gas compositions reported in the original reference. This file (SOLRUN.DM2) should be run at many temperatures between 25 and 300 in increments of 25 to obtain a set of log (Q/K) values that can be used for geothermometry or to assess mineral equilibria in general in the geothermal system.

2.3.3 Solrun.dm3

Merino (1975) Sample 912-72. Alkalinity test case
Input alkalinity, pH, Compute carbonate, Mth. SOLRUN demonstration 3

```
< eprc >< pH >< unact >< alkaIn >< temp >< rm >< pr_min >< pfluid >
.1000E-11 .7400E+01 .0000E+00 .0434959 .2500E+02 .1000E+01 0.0 0.0
```

```
l/v:0 i chg n ichg i igeo it a
hiP:1 nmtd step bal loop bal sunk thrm ref neut watr
0 1 0 0 40 3 0 1 0 0 0
```

```
saq> < name >< total moles >< trial molality >< gamma >
1 H+ 0.0000000E+00 0.3981071E-07 1.0000
2 H2O 0.9621367E+00 0.1000000E+01 1.0000
3 Cl- 0.5889065E+00 0.1000000E-03 1.0000
4 SO4-- 0.5183133E-03 0.1000000E-06 1.0000
5 CO3-- 0.4337444E-01 0.1000000E-06 1.0000
6 HS- 0.9876020E-04 0.1000000E-06 1.0000
7 SiO2 0.5619174E-03 0.1000000E-06 1.0000
9 Ca++ 0.1980289E-01 0.1000000E-06 1.0000
10 Mg++ 0.8439043E-02 0.1000000E-06 1.0000
11 Fe++ 0.1319677E-03 0.1000000E-06 1.0000
12 K+ 0.2251547E-02 0.1000000E-06 1.0000
13 Na+ 0.5718188E+00 0.1000000E-06 1.0000
21 Sr++ 0.5568363E-03 0.1000000E-06 1.0000
22 Ba++ 0.2941605E-04 0.1000000E-06 1.0000
23 F- 0.1010633E-03 0.1000000E-06 1.0000
```

```
< force equil. with> ieq> log act>
```

File: SOLRUN.DM3. Example use of alkalinity input, here given as .043495 in units of molality. SOLVEQ-XPT uses this value to compute total carbonate at the specified temperature of 25 °C, presumably the temperature at which the alkalinity titration was carried out. If temperature is changed during the SOLVEQ-XPT run, the alkalinity equation is not used at the higher temperatures; instead the newly computed total carbonate and the carbonate mass balance equation are used.

2.3.4 Solrun.dm4

```

Demonstration input file for program SOLVEQ      Japanese Geothermal water
Calculate Al from equilibration w/ muscovite    SOLRUN Demonstration 4

< eprc >< pH >< unact >< alkaln >< tempc >< rm >< pr_min >< pfluid >
.1000E-11 5.44 .0000E+00 .0000E+00 300. .0000E+00 0.0 0.0

      l/v:0      i chg      n ichg      i igeo      it      a
hiP:1 nmtt step  bal loop  bal sunk thrm  ref neut watr
      0      1      0      1      40      3      0      1      0      0      0

saq> < name >< total moles >< trial molality >< gamma >
1 H+ 0.163232117E+00 0.199526694E-04 1.0000
2 H2O 0.327951908E+01 0.100000000E+01 1.0000
3 Cl- 0.643617690E+00 0.100000005E-03 1.0000
4 SO4-- -0.147330528E-02 0.100000022E-06 1.0000
5 HCO3- 0.139322102E+00 0.100000022E-06 1.0000
6 HS- 0.274162218E-01 0.100000022E-06 1.0000
7 SiO2 0.161905289E-01 0.100000022E-06 1.0000
8 Al+++ 0.100000000E-05 0.100000000E-15 1.0000
9 Ca++ 0.299401172E-01 0.100000022E-06 1.0000
10 Mg++ 0.867510447E-03 0.100000022E-06 1.0000
11 Fe++ 0.260451779E-04 0.100000022E-06 1.0000
12 K+ 0.802097321E-01 0.100000022E-06 1.0000
13 Na+ 0.521970809E+00 0.100000022E-06 1.0000

< force equil. with> ieq> log act>
muscovite 8

```

File: SOLRUN.DM4. Example SOLRUN demonstrating the use of forced mineral equilibration to set the total concentration of Al^{3+} at 300 °C in a Japanese geothermal water. Here, muscovite is specified by name, and the SAQ for Al^{3+} , 8, is specified with it. We also added Al^{3+} to the list of species to be considered, providing a bogus TOTAL MOLES and a trial value for the Al^{3+} molality. SOLVEQ-XPT computes a valid TOTAL MOLES Al^{3+} , that can be substituted in here for further calculations. This file represents an intermediate point in the reconstruction of the total geothermal water, starting from a 25 °C analysis of water and gas. It is not until the "with gas" composition, including the correct TOTAL MOLES H^+ is determined that it becomes appropriate to estimate Al^{3+} by equilibration with muscovite at 300 °C, in this case using a pH of 5.44, which was already computed for 300 °C using the correct TOTAL MOLES H^+ . Further reconstruction might entail estimating Pb, Zn and Cu by forcing equilibrium with appropriate sulfide minerals.

2.3.5 Solrun.dm5

Test case for SOLVEQ--oxygenated water (O2 = 7 PPM) Fixing Al+++ by kaol, Fe++ (AND Fe+++) by hematite, Mg++ by dolomite. SOLRUN Demonstration 5

```
< eprc >< pH >< unact >< alkaIn >< tempc >< rm >< pr_min >< pfluid >
.1000E-09 .7340E+01 .0000E+00 .0000E+00 .2120E+02 .00000E+00 0.0 0.0
```

```
l/v:0      i chg      n ichg      i igeo      it      a
hiP:1 nmtt step  bal loop  bal sunk thrm  ref neut watr
      0      1      0      0    40      3      0      1      0      0      0
```

```
saq> < name >< total moles >< trial molality >< gamma >
1 H+      0.0000000E+00 0.4570901E-07 1.0000
2 H2O     0.9993116E+00 0.1000000E+01 1.0000
3 Cl-     0.2059065E-02 0.1000000E-03 1.0000
4 SO4--   0.4788593E-03 0.1000000E-06 1.0000
5 HCO3-   0.2014613E-02 0.1000000E-06 1.0000
31 O2 AQ. 0.2187500E-03 0.1000000E-06 1.0000
7 SiO2    0.1198402E-03 0.1000000E-06 1.0000
8 Al+++   0.1482497E-06 0.1000000E-15 1.0000
9 Ca++    0.1497006E-02 0.1000000E-06 1.0000
10 Mg++   0.1110563E-02 0.1000000E-06 1.0000
11 Fe++    .1 E-09      .1 E-22      1.
12 K+      0.8439465E-04 0.1000000E-06 1.0000
13 Na+     0.3001332E-02 0.1000000E-06 1.0000
15 Zn++    0.4589262E-06 0.1000000E-06 1.0000
21 Sr++    0.2282583E-05 0.1000000E-06 1.0000
23 F-      0.2210759E-04 0.1000000E-06 1.0000
```

```
< force equil. with> ieq> log act>
kaolinite      8
hematite       11
dolomite,ordered 10
```

File: SOLRUN.DM5. Example SOLRUN demonstrating the use of oxygen as a component species and application of forced equilibration with several minerals to fix Al, Fe and Mg. Notice that O₂ is specified as SAQ-31 in the component species list, resulting in the calling from SOLTHERM of all reactions written in terms of O₂ instead of those written in terms of HS⁻.

2.3.6 Solrun.dm6

Test Case for SOLVEQ--Oxygenated water. Fixing O2 by forced set fugacity of O2 gas. Fixing Al+++ by kaol, Fe++ by hematite, Mg++ by dolomite; solrun.dm6

```
< eprc >< pH >< unact >< alkaIn >< tempc >< rm >< pr_min >< pfluid >
.1000E-09 .7340E+01 .0000E+00 .0000E+00 .2120E+02 .0000E+00 .1e-15 0.0
```

```
l/v:0      i chg      n ichg      i igeo      it      a
hiP:1 nmtd step bal loop bal sunk thrm ref neut watr
      0      1      0      0      40      3      0      1      0      0      0
```

```
saq> < name >< total moles >< trial molality >< gamma >
1 H+ 0.0000000E+00 0.4570901E-07 1.0000
2 H2O 0.9993116E+00 0.1000000E+01 1.0000
3 Cl- 0.2059065E-02 0.1000000E-03 1.0000
4 SO4-- 0.4788593E-03 0.1000000E-06 1.0000
5 HCO3- 0.2014613E-02 0.1000000E-06 1.0000
7 SiO2 0.1198402E-03 0.1000000E-06 1.0000
8 Al+++ 0.4391000E-07 0.1000000E-15 1.0000
9 Ca++ 0.1497006E-02 0.1000000E-06 1.0000
10 Mg++ 0.5770000E-03 0.1000000E-06 1.0000
11 Fe++ 0.2120000E-11 0.1000000E-22 1.0000
12 K+ 0.8439465E-04 0.1000000E-06 1.0000
13 Na+ 0.3001332E-02 0.1000000E-06 1.0000
15 Zn++ 0.4589262E-06 0.1000000E-06 1.0000
21 Sr++ 0.2282583E-05 0.1000000E-06 1.0000
23 F- 0.2210759E-04 0.1000000E-06 1.0000
31 O2 aq. 0.2187500E-03 0.1000000E-06 1.0000
```

```
< force equil. with> ieq> log act>
kaolinite 8
hematite 11
dolomite,ordered 10
O2,gas 31 -.699
```

Solrun.dm6 is the same as Solrun.dm5, except that, in solrun.dm6, the oxygen concentration is set by forced equilibration with an oxygen gas phase at a fugacity of $10^{-6.99}$ (atmospheric). The other forced minerals, kaolinite, hematite and dolomite are set for unit activity by leaving their log act fields blank (zero).

2.3.7 Solrun.dm7

Geothermal fluid, Krafla well K15, 0.20 gas frac determined by trial and error. Calculation at P off of L-V saturation. Note conf = 1. Solrun demonstration 7.

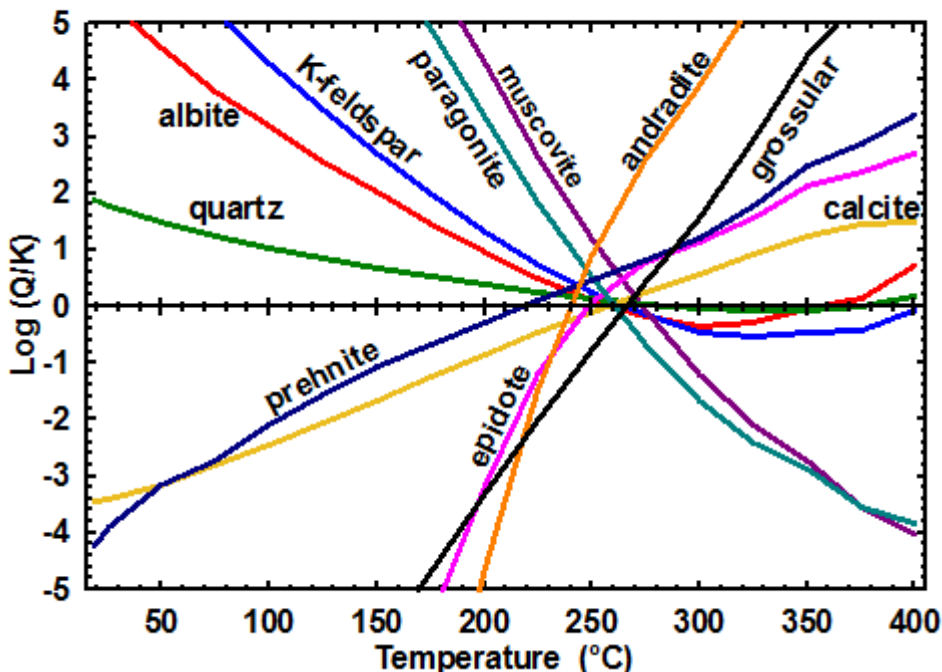
```
< eprc >> pH >> unact >> alkals >> tempc >> rm >> pr_min >> pfluid >
.1000E-11 0.0 .0000E+00 .0000E+00 .1920E+02 .0000E+00 .0000E+00 210.
```

```
l/v:0 i chg n ichg i igeo it a
hiP:1 nmtd step bal loop bal sunk thrm ref neut watr
1 1 0 1 240 13 0 1 0 0 0
```

```
saq> < name >> total moles >> trial molality >> gamma >
1 H+ 6.747792753860E-02 0.102329299228E-05 1.000000000000
2 H2O 0.124468732262E+01 0.100000000000E+01 1.000000000000
3 Cl- 0.690000000000E-03 0.999999974738E-04 1.000000000000
4 SO4-- 0.737613282271E-03 0.100000001169E-05 1.000000000000
5 HCO3- 0.635308868871E-01 0.100000001169E-02 1.000000000000
6 HS- 0.131418689619E-01 0.100000001169E-02 1.000000000000
7 SiO2 0.132700000000E-01 0.100000001169E-02 1.000000000000
8 Al+++ 0.158200000000E-04 0.100000001169E-16 1.000000000000
9 Ca++ 0.400000000000E-04 0.100000001169E-06 1.000000000000
10 Mg++ 0.200000000000E-06 0.100000001169E-07 1.000000000000
11 Fe++ 0.210000000000E-06 0.100000001169E-07 1.000000000000
12 K+ 0.980000000000E-03 0.100000001169E-04 1.000000000000
13 Na+ 0.897000000000E-02 0.100000001169E-03 1.000000000000
21 Sr++ 0.100000000000E-06 0.100000001169E-07 1.000000000000
23 F- 0.830000000000E-04 0.100000001169E-05 1.000000000000
33 H3BO3 0.180000000000E-03 0.100000001169E-04 1.000000000000
```

```
< force equil. with> ieq> log act>
```

File: SOLRUN.DM7. Example SOLRUN demonstrating log Q/K geothermometry. Run at temperatures from 25 to 400 °C. Log saturation indices for alteration minerals such as quartz, epidote, albite, k-fsp, calcite, and muscovite are all near zero at 270 °C. Shown below is a graph of log saturation indices vs. T for this fluid computed with SOLVEQ-XPT for these and some other possible alteration minerals.



2.4 SOLRUN setup

2.4.1 GEOCAL and editing an existing SOLRUN

The easiest ways to set up the SOLRUN file are to run program GEOCAL-XPT, or re-edit an old SOLRUN file. GEOCAL-XPT provides for specifying input data in various units (ppm, mg/l, etc.) and to combine gas analyses with a water analysis to unboil a geothermal water or to replace gases (CO_2 , CH_4) effervesced from a sedimentary water. In many cases, SOLRUN files created by GEOCAL-XPT need further editing, for example, to add forced mineral equilibrations (see below). Program GEOCAL is interactive. It asks straightforward questions about water composition and SOLVEQ-XPT (or CHIM-XPT) run conditions, thus no further guidance is offered here. Whether starting with GEOCAL or editing an old SOLRUN file, it is necessary to make some decisions that direct the calculation. These decisions are expressed in the selection of control parameter settings, as outlined in Section 2.1, above, and further described in Chapter 4. The following are some general guidelines.

2.4.2 TRIAL MOLALITY and GAMMA

For most applications, default initial TRIAL MOLALITY's (or MTRY's) of 10^{-7} or so work fine. However, there are some numerically difficult systems where more carefully chosen estimates are needed to attain convergence. A good MTRY value for hydrogen ion is $10^{-\text{pH}}$. TRIAL MOLALITY for component species such as Fe^{2+} (in oxidized waters) and Al^{3+} can be typically set at 10^{-12} . Generally, very small TRIAL MOLALITY values work better than large values. When specifying equilibrium with a phase (FORCE EQUIL. WITH given in the SOLRUN file), the TRIAL MOLALITY value for the species in this phase (IEQ) must be small, typically 10^{-15} , or convergence may fail. For simple chemical systems, try running SOLVEQ-XPT without specifying TRIAL MOLALITY, in which case these are defaulted to 10^{-10} . Trial GAMMA values also need to be estimated, but in most cases, the default values (GAMMA = 1) are sufficient approximations.

2.4.3 Running

Once a SOLRUN file is set up, run it by executing SOLVEQ-XPT (type "solveq" at a command prompt, or double click on Solveq-xpt.exe in Windows Explorer). If SOLVEQ-XPT fails to run successfully, one or another of the various error messages built into SOLVEQ-XPT will help in determining the error (messages appear on the monitor if you run from the command prompt or in solout.dat, see chapter 5). If SOLVEQ-XPT runs correctly, it outputs some information to the monitor, although with modern personal computers, this output goes by so fast that it can seldom be read except when the execution pauses. One key piece of monitor output is the ionic strength after each iteration. Normally, the ionic strength should converge to a constant value after 10 or 15 iterations. If the ionic strength converges but the iterations reach the loop limit, NLOOP, you might have given a too-small ERPC. $\text{ERPC} = 10^{-12}$ should work without problems. Smaller values are not recommended. Note that in some cases, the ionic strength might converge, but SOLVEQ-XPT still not converge, even if ERPC is set correctly, but we have never found this to occur when ERPC is smaller than 10^{-10} .

After converging, if $L/V\text{-HiP} = 0$, SOLVEQ-XPT gives a choice of changing temperature, changing pH, or stopping. If $L/V\text{-HiP} = 1$, SOLVEQ-XPT gives a choice of changing temperature, changing pressure, changing pH, or stopping. When changing temperature, pressure or pH, make sure not to “jump” to temperatures or pH's very different from the previous ones, or the next convergence attempt might fail. Typical temperature increments are 50 or 100 degrees. Increments of 25 degrees will produce smoother curves for generating log Q/K plots. Notice that SOLVEQ-XPT provides the option simply to hit “enter” for a default choice. Also, it is necessary only to type the first character (y, n, s) to respond the queries with “yes”, “no” or “stop”.

2.5 The thermodynamic data file SOLTHERM (IN2)

The SOLTHERM data file contains all thermodynamic data for aqueous, gas, and mineral species. This file is generally not modified by the user. The file is divided into eight parts: the comment area, the activity coefficients data, the water enthalpy data, the component species data, the derived species data (aqueous), the gas data, the mineral data, and optional miscellaneous data. The content and format of this file are described in detail in appendix A.

Chapter 3. Output Files: SOLOUT, and Others

SOLOUT contains all of the results of the homogeneous equilibrium calculation: distribution of aqueous species and saturation indices of minerals (log Q/K) . SOLOUT is best viewed with a text editor such as TextPad, but NotePad will do. In either case, be sure to use a non-proportional screen font so the columns line up properly, and adjust the screen font of the text editor so that long lines are displayed without wrapping to the next line. This may mean choosing a screen font of size 10 if one's monitor is small. Also, very important, in the rare instances when you print SOLOUT, be sure to adjust the print font size and margins to prevent line wrapping, which makes the output hard to read and doubles paper consumption, thereby wasting more trees from Oregon forests.

SOLOUT results are divided into three parts: a) the title block area, b) the aqueous speciation data, and c) the mineral saturation indexes and gas fugacities. The meaning and interpretation of these sections are explained below.

3.1 Title Block

Pre-title block information (Solrun.dm3)

File SKIP_SPECIES.TXT contains a list of species and minerals omitted from the calculations due to specified T, P and/or option switches in SOLRUN, or suppressed in the SOLTHERM database.

This run is at the P & T of L/V saturation (l/v-hiP not equal to 1).

CuCl4-3 is SUPPRESSED in the SOLTHERM database
arsenopyrite IS SUPPRESSED in the SOLTHERM database
arsenopyrite IS SUPPRESSED in the SOLTHERM database

- Reminders about input P-T data and suppressed or omitted species. (This information is not repeated in subsequent run sections.)

Title Block (Solrun.dm3)

Merino (1975) Sample 912-72. Alkalinity test case
Input alkalinity, pH, Compute carbonate, Mth. SOLRUN demonstration 3
+++++
Number of loops used = 10 Loop limit = 40
Charge balance on Cl- original Mtot value: 0.58891E+00
 changed by: 0.42851E-04

Temperature: 25.00 Degrees C. Pressure: 1.000 Bars

water: 0.9622(Kg.Liq.) 53.4088(Moles Liq.) 53.4065(Moles Total)
 Activity = 0.9799
Stoichiometric Ionic Strength = .6883585E+00 Osmotic Coef. = 0.9269

Ionic Strength = .6526776E+00 Calculated Alkalinity = .4349590E-01
Eh = -0.2435 V. (FROM HS- + 4H2O <=> 9H+ + SO4-- +8e-)
Na-K-Ca Source Temperature : 99. Deg.C. (Fournier & Truesdell, 1973)

The title block shows the title and the following:

- The number of iterations (loops) used to reach convergence. If the number of loops equals the loop limit specified in "nloop", SOLVEQ-XPT stops without having converged on a

solution. You *must* disregard such output, which is printed for debugging purposes only. In some cases, you can re-run with a larger loop limit (see Chapters 4 and 5).

- The charge balance of the solution (if any of ICHGBAL, pH, UNACT, or FORCE EQUIL. WITH are specified)
- Temperature, pressure
- Solvent water quantity: kilograms and moles of liquid (solvent) and total moles of water. The amount of liquid water is the amount of water not including water tied in aqueous species.
- Water activity
- Stoichiometric and true ionic strength, and osmotic coefficient
- Eh If both sulfide and sulfate were input, Eh is computed from the sulfide-sulfate redox pair. If oxygen is specified instead of sulfide, then the O₂-H₂O reaction is used to compute Eh.
- Na-K-Ca geothermometric temperature. If IGEOHRM was set non-zero, the Na/K/Ca geothermometer temperature is given, providing that Na, K, and Ca are part of the component species.

3.2 Species Distribution

Species distribution listing (Solrun.dm3)

Species	Molality	Log(m)	Activity	Log(a)	Gamma
1 H+	0.5404E-07	-7.2673	0.3981E-07	-7.4000	0.7367E+00
2 H2O			0.9799E+00	-0.0088	0.9799E+00
3 Cl-	0.5860E+00	-0.2321	0.3874E+00	-0.4119	0.6610E+00
4 SO4--	0.3035E-03	-3.5178	0.6153E-04	-4.2109	0.2027E+00
5 HCO3-	0.3923E-01	-1.4064	0.2550E-01	-1.5934	0.6501E+00
6 HS-	0.7989E-04	-4.0975	0.5269E-04	-4.2783	0.6596E+00
7 SiO2(aq)	0.5334E-03	-3.2729	0.5334E-03	-3.2729	0.1000E+01
8 Ca++	0.1756E-01	-1.7554	0.3521E-02	-2.4533	0.2005E+00
9 Mg++	0.7366E-02	-2.1328	0.1526E-02	-2.8165	0.2071E+00
10 Fe++	0.1256E-03	-3.9012	0.2576E-04	-4.5891	0.2052E+00
11 K+	0.2337E-02	-2.6313	0.1501E-02	-2.8235	0.6423E+00
12 Na+	0.5691E+00	-0.2448	0.3713E+00	-0.4302	0.6525E+00
13 Sr++	0.4789E-03	-3.3197	0.9520E-04	-4.0213	0.1988E+00
14 Ba++	0.2666E-04	-4.5741	0.5245E-05	-5.2802	0.1967E+00
15 F-	0.9699E-04	-4.0133	0.6790E-04	-4.1681	0.7001E+00
16 BaCO3, aq	0.6972E-07	-7.1566	0.6972E-07	-7.1566	0.1000E+01
17 Ba(HCO3)+	0.2177E-05	-5.6620	0.1391E-05	-5.8566	0.6389E+00
18 BaCl+	0.1006E-05	-5.9974	0.6455E-06	-6.1901	0.6416E+00
19 BaF+	0.3642E-09	-9.4386	0.2337E-09	-9.6313	0.6416E+00
20 CH4, aq	0.3330E-07	-7.4776	0.3210E-07	-7.4936	0.9639E+00
21 C2H6, aq	0.2532E-17	-17.5965	0.2441E-17	-17.6125	0.9639E+00
22 C3H8, aq	0.1155E-25	-25.9374	0.1113E-25	-25.9534	0.9639E+00
23 C4H10, aq	0.4631E-34	-34.3343	0.4464E-34	-34.3503	0.9639E+00
24 CO, aq	0.5341E-14	-14.2724	0.5341E-14	-14.2724	0.1000E+01
25 CO2, aq	0.2379E-02	-2.6236	0.2293E-02	-2.6396	0.9639E+00
list continues with more than 100 species					

The speciation for all aqueous species follows the title block. Data include molality, activity, and activity coefficients and logarithms of these quantities. The Molality column shows the computed molalities of component species and derived species. For the component species, which are listed at the top of the column (through 15, F⁻, above), these molalities are the converged concentrations, starting from the TRIAL MOLALITY's provided in the SOLRUN file. Beneath the component species are the molalities of derived species, starting with BaCO₃, above. pH is not separately output, but can be read in the Log (a) column for H⁺ (7.40 in above example).

3.3 Summary of Component Species

Following the list of species and molalities, etc. the mass balance characteristics of the components species are summarized. The Total Moles column specifies the composition of the system, showing the total moles of component species in the chemical system, as given in the SOLRUN file.

Component Species Summary (Spokane water)					
Species	Molality	Tot Moles	ppm	Tot Molality	Alpha
1 H+	0.5336E-07	0.1534E-03CM	0.154583E+00	0.1535E-03	0.000348
2 H2O	0.1000E+01	0.5547E+02	0.999075E+06	0.5551E+02	0.018015
3 Cl-	0.1360E-01	0.1362E-01AD	0.482917E+03	0.1363E-01	0.997236
4 SO4--	0.3369E-03	0.4789E-03	0.459892E+02	0.4792E-03	0.703140
5 HCO3-	0.1776E-02	0.2015E-02	0.122897E+03	0.2016E-02	0.880753
6 O2 aq.	0.2189E-03	0.2188E-03	0.699836E+01	0.2189E-03	1.000000
7 SiO2(aq)	0.1195E-03	0.1198E-03	0.719888E+01	0.1199E-03	0.996086
8 Al+++	0.1559E-15	0.3402E-09EQ	0.917585E-05	0.3404E-09	0.000000
9 Ca++	0.1455E-02	0.1497E-02	0.599829E+02	0.1498E-02	0.971454
10 Mg++	0.4988E-02	0.5190E-02EQ	0.126154E+03	0.5194E-02	0.960423
11 Fe++	0.1337E-21	0.1200E-11EQ	0.670152E-07	0.1201E-11	0.000000
12 K+	0.8433E-04	0.8439E-04	0.329922E+01	0.8445E-04	0.998567
13 Na+	0.2995E-02	0.3001E-02	0.689838E+02	0.3003E-02	0.997317
14 Zn++	0.3846E-06	0.4589E-06	0.299930E-01	0.4592E-06	0.837520
15 Sr++	0.2205E-05	0.2283E-05	0.199953E+00	0.2284E-05	0.965195
16 F-	0.2076E-04	0.2211E-04	0.419901E+00	0.2212E-04	0.938330

CM means total moles of that species was computed from input of its activity
 AD means total moles of that species was adjusted for charge balance
 EQ means total moles computed at forced saturation with the phase component below. Log(act) shown beneath name of phase component.
 kaolinite hematite dolomite,ordered
 0.000 0.000 0.000
 Al+++ Fe++ Mg++

For each component species, the “Tot Moles” values are the sum of the molar amounts of all aqueous species containing that component species (as defined by the stoichiometries read in the SOLTHERM data file). Total moles were input in the SOLRUN file as TOTAL MOLES. As explained in the text beneath the number columns, the letters CM and EQ that might appear after a value in the Tot Moles column are printed if the total molar amount of a component species was not given, but computed from its known input activity, or from assuming equilibrium with a mineral or gas containing that species, respectively. In the latter case, the mineral or gas with which the solution is in equilibrium is listed at the bottom of the list of component species along with the log of its activity, as specified in SOLRUN. The letters AD in the Tot Moles column follow a value that has been adjusted for charge balance. The Tot Molality column is equivalent to the Tot Moles column renormalized to one kilogram of solvent water. Alpha is the ratio of the individual ion molality to its total molality, giving a measure of how much of the component species is tied up in various complexes. Other columns are self explanatory.

3.4 Gas Fugacities and Mineral Saturation Indices

Fugacities of gases and mineral saturation indices are given beneath the component species summary (unless NMTT was set to a non-zero value in SOLRUN). Minerals are supersaturated if $\log(Q/K) > 0$, exactly saturated if $\log(Q/K) = \text{zero}$, and undersaturated if $\log(Q/K) < \text{zero}$.

Supersaturated minerals are listed first, and undersaturated phases next. Phases exactly saturated may appear in either list with $\log (Q/K) = 0$. Any minerals that were forced to equilibrate should have a computed $\log (Q/K)$ of zero.

Gas fugacities				
Gas	Log K	Log Q	Log f	fugacity
H2O,gas	1.6026	-0.0002	-1.6028	0.2496E-01
CO2,gas	-7.7953	-10.1613	-2.3660	0.4305E-02
CH4,gas	143.2738	-2.8377	-146.1114	0.7737-146
CO,gas	39.3423	-8.3303	-47.6726	0.2125E-47
H2,gas	43.6314	1.8308	-41.8005	0.1583E-41
H2S,gas	132.3022	-11.0829	-143.3851	0.4120-143
SO2,gas	38.4545	-16.5758	-55.0302	0.9328E-55
S2,gas	203.3657	-25.8275	-229.1933	0.6408-229
HCl,gas	6.4663	-9.2776	-15.7439	0.1803E-15
HF,gas	1.0769	-12.0938	-13.1707	0.6750E-13
O2,gas	-2.8773	-3.6620	-0.7847	0.1642
Sum of fugacities =				0.1934
This solution is SUPERSATURATED with the following minerals				
Mineral	Log K	Log Q	Log Q/K	
fCO2-3.5	-11.3180	-10.1613	1.1567	
fCO2-3.0	-10.8200	-10.1613	0.6587	
Mg-carpholite	14.4825	15.5680	1.0855	
clinochlore	57.0431	60.1246	3.0815	
dolomite,ordered	3.3833	3.3833	0.0000	
goethite	-8.4563	-8.3671	0.0892	
hematite	-16.7340	-16.7340	0.0000	
heulandite	-6.5590	-4.5807	1.9783	
kaolinite	3.4481	3.4481	0.0000	
Ca-nontronite	-29.1714	-27.3557	1.8157	
Mg-nontronite	-29.2025	-27.2676	1.9350	
Na-nontronite	-29.1303	-27.7015	1.4289	
quartz	-4.1287	-3.9228	0.2059	
stilbite	-7.5073	-4.5808	2.9265	
kf-ab-equil	-3.1806	-1.5501	1.6305	
This solution is UNDERSATURATED with the following minerals				
Mineral	Log K	Log Q	Log Q/K	
fO2-0.7	-3.5960	-3.6620	-0.0660	
acmite	-8.5184	-11.4675	-2.9491	
akermanite	47.6185	27.4462	-20.1723	
albite-high	2.5157	-1.3763	-3.8920	
albite	1.4784	-1.3763	-2.8547	
almandine	40.3853	-22.8289	-63.2142	
amesite	64.4226	63.2215	-1.2011	
andalusite	12.9562	7.3712	-5.5850	
andradite	16.5852	6.2554	-10.3298	
grossular	47.5779	34.2834	-13.2945	
anhydrite	-4.2683	-6.8208	-2.5526	
ankerite	-0.2148	-16.1882	-15.9734	
annite	29.9530	-25.2811	-55.2341	
phlogopite	38.1126	33.4333	-4.6793	
anorthite	23.2866	15.0344	-8.2522	
an20Ab80	5.6222	1.9058	-3.7164	
an25ab75	6.6867	2.7264	-3.9603	
an30ab70	7.7552	3.5469	-4.2083	
anthophyllite	71.1099	53.4569	-17.6530	
Fe-anthophyllite	41.9986	-83.5432	-125.5418	
antigorite	486.4269	448.3762	-38.0507	
aragonite	2.0101	1.4246	-0.5855	

3.5 Additional Output

If the ISTEP option is enabled in the SOLRUN file, additional data is listed for debugging purposes. This includes a dump, at the start of the output, of the component species read in SOLRUN and of all aqueous species read in SOLTHERM with their log K's. ISTEP non-zero also results in the output of the following: a) matrix of partial derivatives of mass-balance and mass-action equations after the first and second iterations, b) aqueous species data after the second iteration, c) at each iteration, the ionic strength and the molality of each component species, d) listing of the array containing the change in TRIAL MOLALITY values from the previous iteration to the current one (these become very small as SOLVEQ-XPT converges). If the ITREF option in SOLRUN is set non-zero, the residuals of the mass-balance and mass-action equations are also output. A beginner would find it useful to set ISTEP to a non-zero value to see some of the above numerical features involved in the calculation.

SOLOUT can be quite large if calculations are carried out at many temperatures. Also, if the ISTEP option is activated (ISTEP $\neq 0$, see SOLRUN file) SOLOUT will be larger.

3.6 Plot files SOLOUT and SOLPLOT

Graphs of $\log Q/K$ vs T can be useful for geothermometry and evaluations problems in water compositions (e.g. Reed and Spycher, 1984; Pang and Reed, 1998; Palandri and Reed, 2001; Spycher *et al.*, 2014). To produce the $\log Q/K$ vs T graphs, the best procedure is to apply N. Spycher's program MINTAB-xpt to read the SOLOUT file and produce a flat file suitable for plotting with a spreadsheet, Grapher, or SigmaPlot.

Chapter 4. Types of Calculations with SOLVEQ-XPT

SOLVEQ-XPT enables a wide range of calculation types to address many kinds of problems, from determining the *in situ* pH of an experimental run product at 300°C, to figuring out whether Lake Nyos is nearing CO₂ supersaturation. In this chapter, the types of calculations that can be addressed with SOLVEQ-XPT are briefly discussed. A description of the input parameters discussed in this chapter is given in Chapter 2.

4.1 Temperature Change

For many applications such as geothermometry on geothermal or oil field waters, or simply to compute the characteristics of a high temperature geothermal, oil field or experimental run water that was analyzed at room temperature (as most are), it is useful to compute properties first at room temperature then at higher temperatures. For such applications, temperature can be changed interactively while running SOLVEQ-XPT, and the user may select any temperatures between 25 and 350 C if $l/v\text{-hiP} = 0$, or 0.01 to 600 °C if $l/v\text{-hiP} = 1$ and PFLUID is large enough for the selected temperature. Avoid changing temperature by increments greater than 50 C, to avoid convergence problems. If SOLVEQ-XPT converges easily on the first run, but then fails to converge on successive runs, change the temperature by a smaller increment, and try again.

When computing speciation at various temperatures, SOLVEQ-XPT uses the method described by Reed (1982) and Reed and Spycher (1984) to compute pH at high temperatures. When pH is input, SOLVEQ-XPT computes the total molar amount of hydrogen ion in the solution, TOTAL MOLES(H⁺). This amount does not change with temperature, and is subsequently used to compute pH at other temperatures. For an analyzed water, pH is generally known. It is essential to know the temperature of the pH measurement. This temperature is the temperature at which to run SOLVEQ-XPT initially with the measured pH. If a hot spring water analysis is reported at 25 C, for example, but the pH was measured in the field at, say 80 C, first run this water analysis at 80°C at the measured pH, to compute the correct total molar amount of hydrogen ion; then interactively decrease the temperature and compute the pH at 25°C, or at any other temperatures.

4.2 pH Changes

The pH can be changed interactively when running SOLVEQ, just as for temperature. If pH is changed, the total molar amount of hydrogen ion is recomputed, and the charge balance is readjusted for each run. Interactive changing of pH is useful for studying the effects of pH change on equilibria, and for correctly computing mineral saturation indices at a series of temperatures in doing geothermometry, as explained by Pang and Reed (1998).

4.3 Alkalinity

SOLVEQ-XPT provides the option of specifying alkalinity, using variable, ALKALN (see above). The units are molality (moles of H⁺ equivalents per kilogram of solvent water). If this option is used, an alkalinity equation is substituted for the carbonate mass balance equation and total carbonate is computed. The species in the alkalinity equation are identified by "44" in the I=1 position of SPEC(NS,I) in the derived species read in SOLTHERM (see Appendix 2). The

alkalinity species include bicarbonate, carbonate, and many others that contribute to alkalinity, such as organic acid anions, acetate, propionate, succinate and oxalate. Inclusion of the organic acid anion provides for accurate calculations of carbonate and alkalinity sources in oil field waters. Issues and problems with alkalinity data on natural waters are addressed by Palandri and Reed (2001).

4.4 Computing an Unknown Concentration Using Charge Balance

As a practical matter, computing an unknown concentration of a minor species by charge balance cannot really be done except in the context of a model manipulation, as described in a following paragraph. All analyses of natural waters are out of charge balance owing to analytical errors. Charge imbalance from analytical error is addressed by arbitrarily adjusting the concentration of one species to yield charge balance. Thus, in essentially all runs, the concentration of one species, chosen by the user, is determined by charge balance (specified by input parameter “C”, Section 2.1). The best species for charge balance is generally one in large concentration such as Cl^- or Na^+ , for which a small relative error in analysis results in an absolute error that may be large compared to the small concentrations of minor components, such as Mg^{2+} or Sr^{2+} , for example. If the species whose concentration is unknown is a major species such as Na^+ , or Cl^- (or even H^+ in a hyper-acidic fluid such as a volcanic gas condensate) its concentration can be computed directly and simply by charge balance, using “ICHGBAL”. Further, if the user is quite confident that the errors in the analytical values of major species are small relative to the magnitude of the unknown species concentration, the above procedure can be used to compute concentration of a species that is not among the dominant.

Another kind of apparent charge imbalance in a raw analysis results from the conventions used in reporting some species, such as carbonate. For example, if the water has a pH greater than 10.4, but all dissolved carbonate is reported as bicarbonate, HCO_3^- , then there would be an excess of positive charge in the raw analysis since the actual dominant carbonate species would be CO_3^{2-} , not HCO_3^- . The carbonate issue is addressed automatically in SOLVEQ-XPT by the distribution of species at specified pH. A similar kind of problem arises in acidic waters, where H^+ is an abundant species, but is not listed, as such, in a typical analysis. This one, too, is automatically addressed by the equilibrium calculation. The important issue here is that charge balance on any fluid cannot be computed properly *without* a distribution of species; i.e. it cannot be properly executed on the raw water analysis, although an approximation of it can be inferred under favorable circumstances.

Given the considerations described above, it is apparent that a calculation by charge balance of the concentration of a minor species (e.g. one whose concentration is less than ~20% of the dominant species) is not likely to be reliable. For example, it does not make sense to compute the concentration of a minor species such as HCO_3^- by charge balance if the error on a major species concentration, e.g. Cl^- , is larger than (or a significant fraction of) the minor species concentration. This means, for practical purposes, that computing the concentration of a minor species by charge balance can only be done in the context of a model system manipulation, in which the system is put in charge balance initially by a proper calculation (SOLVEQ-XPT run) in which the species of unknown concentration is omitted or guessed. From that run, the charge balance species concentration is set (e.g. TOTAL MOLES of Cl^-), then copied into a new SOLRUN file that is used to explore a change in conditions.

To illustrate, consider an oil field water in which the straight analysis at measured pH yields calcite supersaturation in the formation (e.g. Palandri and Reed, 2001). If we hypothesize that the water should be truly in equilibrium with calcite in the formation, and that the apparent supersaturation results from escape of CO_2 from the sample before carbonate analysis, we can stuff CO_2 back in and calculate the correct carbonate concentration as follows:

- 1) Run the water in SOLVEQ-XPT at the temperature of the pH measurement, with charge balance set on Cl^- .
- 2) Copy the corrected $\text{M}^+(\text{Cl}^-)$ into SOLRUN from the SOLOUT. This step is very important.
- 3) In the new SOLRUN, reset charge balance to be done on bicarbonate ($\text{C} = 5$).
- 4) Run at the formation temperature, interactively changing pH to a series of lower values (more acidic because more CO_2 is assumed to be present).
- 5) Examine calcite $\log(\text{Q/K})$ values in the SOLOUT listing to see what calcite saturation has done. Eyeball a pH at which $\log(\text{Q/K})$ for calcite would be near 0, then re-run at the estimated pH.

By setting charge balance in bicarbonate in the above procedure, then changing pH downward, the effect is adding CO_2 to the system. The amount of added CO_2 is the difference between the initial $\text{TOTAL MOLES}(\text{HCO}_3^-)$ and the final one, as given in the component species summary of SOLOUT (see Section 3.3). The addition of CO_2 is accomplished implicitly by setting charge balance on HCO_3^- while changing pH.

4.5 Including a Gas Analysis in the System Composition

Program GEOCAL-XPT can be used to create input files for SOLVEQ-XPT that include a gas that may have separated from the water. For a geothermal water, for example, both water and gas analysis might be available, and one might want to compute speciation in the deep water where all gas is actually dissolved in a homogeneous aqueous phase (e.g. Reed and Spycher, 1984; Pang and Reed, 1998). After entering both water and gas analyses in GEOCAL-XPT, GEOCAL-XPT produces two SOLRUN files for SOLVEQ: one containing only the water analysis, and the other containing the water and gas analysis recombined.

To run SOLVEQ-XPT with the water + gas analysis, first run SOLVEQ-XPT with only the water analysis, at the temperature at which the pH was measured (see Reed and Spycher, 1984). In this way, obtain a value for $\text{TOTAL MOLES}(\text{H}^+)$ for the degassed water. Then *add* this $\text{TOTAL MOLES}(\text{H}^+)$ value to the $\text{TOTAL MOLES}(\text{H}^+)$ value calculated by GEOCAL-XPT for the water + gas analysis, and put the sum into the $\text{MTOT}(\text{H}^+)$ space in the SOLRUN file that contains the water+gas analysis. Now run SOLVEQ-XPT with the water+gas analysis, making sure, this time, that the pH is not specified ($\text{pH} = 0$). SOLVEQ-XPT will then compute the pH of the un-degassed water, as well as the speciation of aqueous species in the un-degassed case. A *common error* in such gas-water reconstructions is omission of the addition step, above, resulting in erroneous final results.

If a large fraction of the added-back gas is methane, e.g. from sedimentary waters, it might be that a substantial amount of methane should form a gas phase at depth, and an attempt to compute homogeneous equilibrium with all this gas dissolved in a homogeneous aqueous phase fails. In this case, add the gas analysis to the water analysis little fractions at a time, until the sum of all gas fugacities equals the pressure of the reservoir at depth. The chemical composition determined in this way is a good approximation of the composition of the aqueous solution in equilibrium with the gas phase at depth. For more sophisticated reactions involving aqueous,

solid, and gas phases, program CHIM-XPT might be needed instead of SOLVEQ-XPT.

4.6 Computing pH and Concentrations by Forcing Equilibrium with Specified Minerals and/or Gases

By including one or several mineral mass action equations in the system for simultaneous solution in place of specified component mass balance equations, SOLVEQ-XPT provides for computing forced equilibrium of the water with specified minerals. This is particularly useful for computing pH or the concentrations of elements that are otherwise unknown from the water analysis, or for determining the solubility of various minerals in waters of specified composition.

This option is activated by specifying FORCE EQUIL. WITH and IEQ at the bottom of the SOLRUN file. One may also specify LOG ACT, which contains the log of the activity of the mineral end member in FORCE EQUIL. WITH or the log fugacity of the gas in FORCE EQUIL. WITH (see solrun.dm6, above). One can specify as many minerals and species as desired, but avoiding a violation of the phase rule. Each component species for which a computed concentration is sought (species IEQ) must be entered in the list of MTOT values in the SOLRUN file. TOTAL MOLES values input for these species need not be specified, but do input TRIAL MOLALITY values for these species.

Forced mineral equilibrium commonly causes convergence problems. In many instances, these problems are avoided if TRIAL MOLALITY values for IEQ species are set small, typically 10^{-15} . Generally, we recommend that one first compute equilibrium without this option, thus leaving out the species for which concentrations are unknown. This yields a set of good TRIAL MOLALITY values for the species for which concentrations are known. Then, run SOLVEQ-XPT specifying FORCE EQUIL. WITH and IEQ. Remember that some cases may never converge simply because the constraints of pH, charge balance, and composition are such that forced equilibration with a given mineral or gas is thermodynamically impossible.

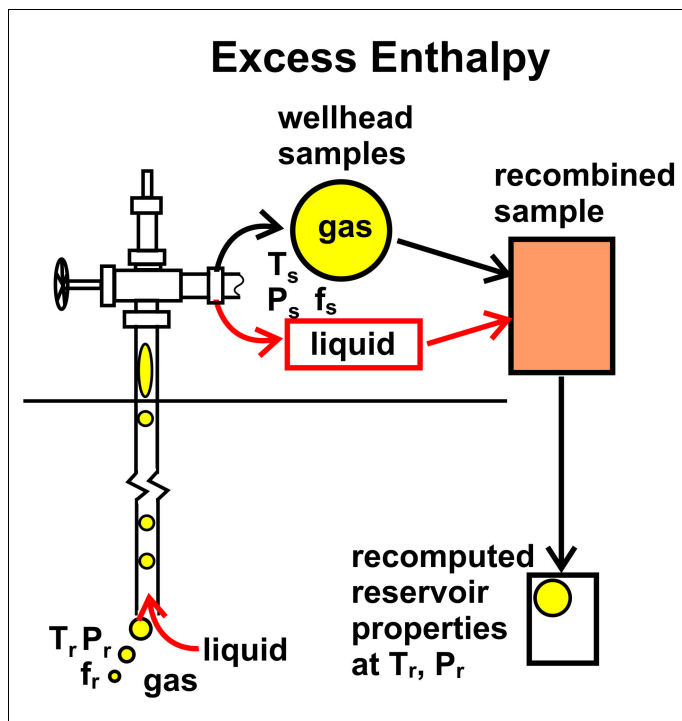
The forced mineral equilibration option is particularly useful for estimating the pH of a sub-surface water where it can be assumed that the water was in equilibrium with a particular mineral assemblage. For example, if an oil field water analysis includes Ca^{2+} and carbonate, but not pH, and if calcite equilibrium at depth is likely, forced equilibrium with calcite (FORCE EQUIL. WITH = calcite) to fix H^+ (IEQ=1) will yield a value for pH. It also yields a value for TOTAL MOLES(H^+) which can then be used to compute pH at other temperatures.

4.7 Oxidized waters

In oxidized waters, the absolute concentrations of sulfide species are so small (less than 10^{-70}) that many computers cannot handle the numbers. In such waters, however, the concentration of aqueous O_2 is substantial, so it can be used in place of sulfide-sulfate to express redox equilibria. This is accommodated in SOLTHERM by the inclusion of two sets of equilibria for redox species and minerals (e.g. Fe^{3+} , Cu^{2+} , Au^{3+} , CH_4 , hematite, native copper, galena, etc.), one expressed in terms of O_2 - H_2O - SO_4^{2-} - H^+ and the other set expressed in terms of HS^- - SO_4^{2-} - H_2O - H^+ . Thus all redox, sulfide and some oxide species and minerals are listed twice in SOLTHERM. On any given run, however, the user specifies composition of the system only in terms of O_2 or only in terms of sulfide, so SOLVEQ-XPT uses only the relevant equilibria out of SOLTHERM. If there is redox dis-equilibrium, as there commonly is in natural waters, the user must choose whether to treat the water as oxidized or reduced.

4.8 Excess-enthalpy geothermal waters

Excess enthalpy geothermal wells produce an amount of steam relative to liquid that exceeds what could have come from boiling of liquid-alone that entered the well at depth. The steam fraction in such wells exceeds the amount produced by isenthalpic boiling of liquid in the well, starting at the well-bottom temperature. Starting from wellhead samples of steam (gas) and liquid with excess enthalpy, the computation of pH, oxidation state, and mineral saturation characteristics in the geothermal reservoir is complicated because the wellhead steam cannot simply be replaced in the liquid to compute the reservoir liquid properties, as we do for normal enthalpy wells. The particular composition of the steam and liquid at depth cannot be known directly from the compositions at the wellhead because the minor gases partition differentially as a function of pressure and temperature. To address this issue, we use the excess enthalpy steam fraction and compositions of gas and liquid from wellhead samples to compute a single bulk analysis of the two-phase reservoir fluid composition, then compute a gas-liquid equilibrium for the reservoir pressure and temperature, as illustrated in the adjacent figure.



The procedure is to use the well headhead enthalpy to determine the steam fraction at the sampling P-T, then to recombine all of that gas with the wellhead liquid. First run the sample liquid and gas compositions in GEOCAL to obtain two solrun.dat files, solrun.gas and solrun.dat. Then run SOLVEQ on the solrun.dat file, which is for the liquid, alone, to determine the liquid $M(aq, H^+)$. Then add that $M(aq, H^+)$ to the $M(t, H^+)$ value in the solrun.gas ("with gas" file) to obtain combined bulk composition of the fluids that entered the well at depth. This "recombined sample" composition can now be run in CHIM-XPT at the reservoir P-T and using the wellhead enthalpy measurement to compute the partitioning of the gas and liquid in the reservoir, as well as the composition of each phase.

Chapter 5. Problems and Errors: Helpful Tips

SOLVEQ-XPT generally runs easily, and, providing that all input data are in the right shape, and that the chemical system is not too messy, problems should be rare. In this chapter, we review the most common problems encountered with SOLVEQ. These problems can be divided into three categories: (a) “clean stops”, which are execution stops and error messages built into SOLVEQ, and that are not related to other system errors, (b) “bombs” (execution abortions) related to input/output errors, and (c) “bombs” resulting from convergence problems. Most “bombs” result from simple problems, such as mistakes in the input data, and are easily corrected. Other more serious bombs relate to numerical problems and machine precision, and might require more effort to solve.

5.1 Clean Stops and Built-in Error Messages

All execution stops built into SOLVEQ-XPT are accompanied by a message indicating why the execution was aborted. Other error messages do not lead to a program interruption. These stops and messages are reviewed below. Messages are given in the same order as they appear in the program. Routine MAIN indicates the main program.

WARNING! THE NUMBER OF COMPONENTS GIVEN IN SOLRUN EXCEEDS THE CURRENT ARRAY DIMENSION (___). CHECK SOLRUN DATA FILE.

From routine: MAIN. Execution stop: YES

SOLVEQ-XPT accepts only up to a certain number of component species (current limit is 40). Notice that the value of any SAQ can exceed 50, but the total number of species specified cannot exceed the array dimension, currently 50. This message might also occur if there are not two blank lines after the component species data in the SOLRUN file.

WARNING! SAQ(____) = ____; MAXIMUM VALUE ALLOWED IS ____

From routine: MAIN. Execution stop: YES

Self explanatory. SAQ values must not exceed the array dimensions specified in SOLVEQ-XPT (current limit is 50). Check for format mistakes in the SOLRUN file, or for an invalid SAQ number.

SELECTED CHARGE BALANCE ION _____ IS UNCHARGED ! SELECT A PROPER ION (ICHGBAL).

From routine: MAIN. Execution stop: YES

Self explanatory. This message might also occur if you did not correctly input ICHGBAL in the SOLRUN file.

ABORT. COMPOSITION OVERSPECIFIED. BOTH O AND HS CANNOT BE USED SIMULTANEOUSLY. CHOOSE.

From routine: MAIN. Execution stop: YES.

Self explanatory.

NUMBER OF SPECIES READ IN SOLTHERM EXCEEDS MAXIMUM OF _____. LAST NAME READ IS: _____ (NS = ____).

From routine: MAIN. Execution stop: YES

The total number of aqueous species read in SOLTHERM cannot exceed the dimension of arrays specified in SOLVEQ. The current limit is 300 species, including the component species. Reduce the number of components in your chemical system, or increase the array dimensions in SOLVEQ. Note that NS in this message should equal the current allowed maximum value.

SPECIES _____ IN SOLTHERM HAS TOO MANY COMPONENTS. ITOT FOR THAT SPECIES IS ____; MAXIMUM IS ____

From routine: MAIN. Execution stop: YES

Dissociation reactions in the SOLTHERM data file are limited to a certain number of stoichiometric components (current limit is 12). The number of stoichiometric components to be read is indicated for each reaction by the integer ITOT in the SOLTHERM data file (see appendix A). If ITOT is too large, or improperly aligned, this message will occur.

IEQ FOR _____ IS NOT CORRECTLY SPECIFIED (=____) CHECK INPUT FORMAT.

From routine: MAIN. Execution stop: NO

Self explanatory. Check IEQ in the SOLRUN file. Also, make sure that the right number of blank lines (and/or format indicator lines) are present between the different sections of the SOLRUN file.

FOLLOWING GIVEN MINERAL NOT FOUND IN SOLTHERM: _____

From routine: MAIN. Execution stop: YES

FORCE EQUIL. WITH names specified in the SOLRUN file must spell exactly as in the SOLTHERM data file. A spelling mistake will cause a mismatch. Also, this message will occur if you specify a mineral or gas which has its suppression flag enabled (SUP not blank or 'GAS ') in the SOLTHERM data file (see appendix A).

CHARGE IMBALANCE EXCEEDS THE TOTAL AMOUNT OF _____ AND CANNOT BE ADJUSTED BY THIS ION. CHOOSE AN ION WITH OPPOSITE CHARGE.

From routine: MAIN. Execution stop: YES

Self explanatory. If selecting another charge balance ion (ICHGBAL) does not help, you might have a bad water analysis. Note that this message might also occur because of convergence problems, even though the water analysis is good and the charge balance ion is properly selected.

GIVEN MINERAL _____ DOES NOT CONTAIN _____

From routine: MAIN. Execution stop: YES

If forcing equilibrium with a mineral or a gas (FORCE EQUIL. WITH in solrun file), you must specify which species (IEQ) is fixed by forced equilibration, and, of course, this species must be contained in the specified mineral or gas.

** WARNING ! MOLALITY OF _____ LESS THAN _____

From routine: MAIN. Execution stop: NO

This message is printed if, during the iteration process, the molality of a component species reaches the lowest value allowed by the computer without underflow errors (the current lowest limit is 10^{-200}). Note that convergence will most likely fail if this occurs (even though the ionic strength might converge to a constant value). If this happens with the molality of HS^- , one might have a chemical system that is too oxidized to use sulfide/sulfate as redox species. Change to using O_2 instead (see Chapter 4).

**** NUMBER OF LOOPS REACHED THE GIVEN MAXIMUM OF ____
NON-CONVERGENCE ASSUMED. EXECUTION ABORTED.

From routine: MAIN. Execution stop: YES

If convergence is not reached after NLOOP iterations, SOLVEQ-XPT will stop. If the ionic strength values printed on the screen after each iteration seemed to converge, ERPC might have been set too small. 10^{-12} should be the lower limit and should work in most cases. Some cases might require slightly larger ERPC. If that does not do it, then you have a convergence problem. Repeat the calculation with a smaller step. If starting the first run, check all input data and readjust TRIAL MOLALITY to better estimates. Remember to set TRIAL MOLALITY for the IEQ species to a very small value ($<10^{-15}$) if you force equilibration with minerals (see chapter 4).

NUMBER OF MINERALS READ IN SOLTHERM EXCEEDS MAXIMUM OF ____ . LAST
NAME READ IS: _____

From routine: MINSAT. Execution stop: YES

The total number of minerals read in SOLTHERM cannot exceed the dimension of arrays specified in SOLVEQ. The current limit is a total of 351 minerals and gases (included). Reduce the number of components in your chemical system, or increase the array dimensions in SOLVEQ.

MINERAL _____ IN SOLTHERM HAS TOO MANY COMPONENTS. ITOT FOR THAT
MINERAL IS ____; MAXIMUM IS ____

From routine: MINSAT. Execution stop: YES

Dissociation reactions in the SOLTHERM data file are limited to a certain amount of stoichiometric components (current limit is 12). The number of stoichiometric components to be read is indicated for each reaction by the integer ITOT in the SOLTHERM data file (see appendix A). If ITOT is too large, or improperly aligned, this message will occur.

***** WARNING ***** COMPUTATIONAL SINGULARITY, IER = 0.0

From routine: SIR. Execution stop: YES

This message is printed in case computational singularity occurs. This occurs if the system is overdetermined (e.g. if a component species can be expressed in terms of other component species, or if two component species in matrix are similar). Check to see if, by mistake, similar minerals are specified when forcing equilibration, or if one or more component species repeat in

SOLRUN.

5.2 Input/Output errors

In this section, the most common input/output system errors are reviewed. Numerical problems are discussed in the convergence "bombs" section below.

- END OF RECORD ERRORS (this error has become rare with current (2010) compilers)

These errors commonly occurs when files are not assigned correctly. Because SOLVEQ-XPT does not incorporate file assignment statements, you have make these assignments before running the program. The best way is to incorporate the assignments into a command file. These errors also occur when downloading input files from tapes with variable record format. The files will look perfectly fine, but will need a fixed record length of 80 to be read properly. Check all file assignments and input files record length. Make sure that SOLRUN file is within format specifications. The SOLTHERM data file needs one blank line at the bottom of the mineral data. Check for enough disk space for output files.

- ILLEGAL DECIMAL CHARACTERS

This will happen anytime SOLVEQ-XPT reads something that it is not expected to read. Check all input file formats. The SOLTHERM data file needs a blank line after the component species list, after complexes data and after the mineral data. The input file SOLRUN needs blank lines between the different sections (see chapter 2).

5.3 Convergence Problems

Welcome to the most frustrating part of numerical modeling! Unfortunately, numerical modeling of some chemical systems can be tedious because of numerical difficulties. Convergence problems are generally worse for systems with a large number of components species and saturated minerals (and gases), but this is not necessarily so.

A convergence problem will cause SOLVEQ-XPT to reach the loop limit (NLOOP) without converging, or to "bomb" before that limit is reached. Typical convergence "bombs" consists of OVERFLOWS and UNDERFLOWS, as well as wrong types of arguments for logarithm and exponential functions. If one encounters convergence problems, the first thing to do is to check that all the previously discussed problems are addressed; this will solve of 90% of the problems. Underflow and overflow errors are rare with modern compilers (in fact, we have not seen one in many years).

If starting an original run, convergence problems generally result from poor guesses for TRIAL MOLALITY values (see chapter 2). Specifying too-small TRIAL MOLALITY values seems to be better than specifying large values. Generally, the system will converge even when TRIAL MOLALITY's are many orders of magnitude off, however, for some species, notably Al^{3+} , Au^+ , Hg^{2+} , O_2 (in reduced waters), and HS^- (in oxidized waters), and Fe^{2+} (in oxidized waters) much smaller trial molalities are commonly needed, such as 10^{-12} or 10^{-15} .

If a convergence problem occurs after changing pH or temperature, try to restart the calculation and change temperature or pH by a smaller increment. Convergence problems can also be related to the composition of the aqueous phase. SOLVEQ-XPT brackets all molalities of derived species between 10^{-200} and 10, to avoid over and underflow problems on most computer systems. However, it might happen that the molality of a component species becomes very small, and that convergence problems result. The best example of such a problem is running SOLVEQ-XPT with an oxygenated solution. Redox in SOLTHERM is expressed in terms of HS^- and SO_4^{2-} . The speciation calculation with an oxygenated solution will yield a value for the molality of HS^- that is so small that some computers (compilers) will not be able to handle it, and redox will have to be reexpressed in terms of other species (see chapter 4). Forcing equilibration with minerals (FORCE EQUIL. WITH specified) might also create convergence problems. In this case, small TRIAL MOLALITY values might be required, as discussed in Chapter 4.

If the discussion above did not help, and you are now experiencing the most frustrating moments in your existence, do not give up. There are two more possibilities that might resolve your problems, but first, stop, go get a cup of tea and a lemon-ginger scone, and think about a tropical vacation.

If convergence fails for no apparent reason, there might be numerical difficulties with the Newton-Raphson convergence process itself. There are two options in SOLVEQ-XPT to improve convergence, RM, and ITREF. ITREF will generally not help unless there are precision limit problems with the computer. This should not be the case with most computers if double precision is used. The RM option will try to force convergence by decreasing residuals after each iteration. The way to use the RM option is first to run SOLVEQ-XPT with $\text{RM} = 0.9$. If that does not do it, try again with 0.8, 0.7, etc. This option might cause divergence if used with a system that normally converges. In any case, ITREF and RM should be last resort options. If these options do not help, you might have reached a numerical impossibility, or you might be dealing with an impossible chemical system. Defeat is hard to take, but you will have to accept the harsh facts of reality, and modify the calculations scheme, or the chemical system you are dealing with, or ...

6. MINTAB

Program MINTAB is used to read plot files from CHIM or GASWORKS, or the main output file from SOLVEQ then generates an ASCII file with selected data in tabular (columns) format for input into commercial plotting packages. MINTAB reads an unlimited number of datasets in the CHIM, GASWORKS, or SOLVEQ output files. No maximum number of datasets is imposed because MINTAB does not store all the plot data in memory (the size of the plot file to read is limited only by the amount of disk storage).

6.1 How to use MINTAB-XPT on output from SOLVEQ-XPT

MINTAB-XPT ("MINTAB", for short, herein) is a FORTRAN program that reads the SOLOUT file from program SOLVEQ-XPT and produces an ASCII file with selected data in tabular format. MINTAB is quite interactive -- asking the user to specify what to plot and what style of plotting to use. The type of data to output in tabular format (i.e. temperature, pressure, etc.) can be specified interactively or (better) by a list of command strings entered in an ASCII

file (MINTAB.PAR). This file can be created with a text editor or by running MINTAB. The default name for this file is MINTAB.PAR but any other file name can be specified.

6.1.1 Using MINTAB

- 1) To run MINTAB, type MINTAB-XPT at the command prompt.
- 2) MINTAB asks for the type of data to be read: (1) chim-xpt plot file, (2) gasworks plot file, (3) solveq output file. Enter (3).
- 3) Next, MINTAB prompts for the name of the file to be processed (default = solout.dat). If this file is not in the current directory, the program will keep prompting until a valid filename is entered or until the user aborts the program using control-break or control-C.
- 4) MINTAB prompts for the name of the file in which the results will be tabulated (default = solout.tab).
- 6) MINTAB asks if the user would like to use an existing parameter plot file (default = yes).
 - a) If yes press [enter]. MINTAB will then prompt for the name of that file (default = mintab.par). Enter the file name if it is not the default name. MINTAB will complete execution with no further input.
 - b) Enter 'n' to create a new one.
- 7) MINTAB will present a list of general parameters to be tabulate:

1 = Temp	5 =
2 = Pfluid	6 =
3 = Alkaline	7 =
4 = pH	8 =

Select the parameters you wish to tabulate by typing the integer indices separated by commas or spaces.

- 8) MINTAB will present a list of other parameters to tabulate:

1 = Individual species molalities
2 = Total moles of components
3 = Total aqueous moles component species
4 = Fugacities and log(Q/K) of gases and minerals

Select one integer index.

9) MINTAB will then present a list of items for the option selected. Select the parameters you wish to tabulate by typing the integer indices separated by commas or spaces.

- 10) MINTAB will then ask:
Do you want to tabulate more data ? (default=yes) :> n

If yes, press [enter] and MINTAB will return to step 7, above. If no, enter 'n'.

11) MINTAB will then ask:

Enter name of parameter file to create
(default = mintab.par) :>

Enter the file name, or press [enter] only to use the default. If the file already exists MINTAB will ask whether to replace it. If user answers no, MINTAB will ask for another file name; enter this name. MINTAB will then complete execution.

APPENDIX

Appendix 1. Input and Output File Assignments

SOLVEQ-XPT needs several input and output files to run properly. To enhance compatibility with various computer systems, SOLVEQ-XPT assigns I/O disk file numbers to variables (IN1, IN2, ..., IOUT1, IOUT2, ... and so on) so that current I/O device numbers in the READ and WRITE statements in SOLVEQ-XPT can easily be redefined if necessary. In the current version of SOLVEQ, there are FORTRAN "OPEN" statements that assign certain explicit file names to the various device name variables used in the READ and WRITE statements. This form of assignment is compatible with common Fortran compilers, but some users may choose to remove (or "comment-out") the OPEN statements and assign the files to device numbers in a "COM" or "EXEC" file.

The following table contains a brief description of the files read and created by SOLVEQ, with their corresponding I/O device variables and currently assigned values. If you choose to disable the OPEN statements in SOLVEQ, you will need to assign each disk file to the corresponding device numbers prior to running the program. Chapter 2 explains the formats and content of these files.

Fortran I/O device variable and current value	File specification, uses, etc.
IN1 4	Current file name: SOLRUN. Input data specific to each run. Contains title, input parameters, molalities, activity coefficients, and other parameters. This file can be created by program GEOCAL.
IN 2 1	Current name: SOLTHERM. Thermodynamic data base for aqueous species, gases and minerals (mainly log K's).
IN3 5 (also “*”)	Terminal input (interactive keyboard on PC)
IOUT1 10	Current name: SOLOUT. Contains the results of calculations
“*”	Terminal output (direct computer monitor)
IOUT2 12	Current name: Skip_Species.txt. Minerals and species suppressed in SOLTHERM
IOUT4 7	Current file name: SOLPLOT. Contains mineral saturation indices and gas fugacities, for plotting these variables as a function of temperature. Serves as input for program SOLPLO.

Appendix 2. More about the Soltherm Data File

The SOLTHERM file contains all thermodynamic data for aqueous, gas, and mineral species. This file generally does not have to be modified by the user. SOLTEHRM is divided into eight parts: the comment area, the activity coefficients data, the water enthalpy data, the component species data, the derived species data (aqueous), the gas data, the mineral data, and optional miscellaneous data.

2.1 The Comment Area

The comment area is skipped by SOLVEQ-XPT, and can be of any length. It contains various comments and references for the thermodynamic data. If you are planning to modify this file, the user should read and understand all the comments. Some of the content of the comment area is repeated here. Whenever updating SOLTHERM, it is important to make a note in the comment area concerning the changes or updates. This area is delimited at the bottom by a record with at least 8 stars in the first 8 columns:

* Last record of comment area: ***** (eight *'s or more)

2.2 The Activity Coefficients Data

These data are used by SOLVEQ-XPT to interpolate activity coefficients of charged species. This area contains 156 records, 39 records for each of four Debye-Huckel parameters, ADH, BDH, BINACL and BIL from Helgeson et al. 1981. The first record for each parameter is blank, and the second record is not read by SOLVEQ-XPT. The next 37 records each contain 36 real values. The 37 records correspond to the following pressures in bar:

1.000, 1.0133, 2.321, 4.758, 8.919, 15.537, 25.479, 39.737, 59.432, 85.839, 120.458, 165.212 (liquid-vapor saturation)
200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500, 5000

The 36 real values in each record correspond to the following temperatures in °C:

0.01, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520, 530, 540, 550, 560, 570, 580, 590, 600

These records are Fortran “free format” meaning the alignment of the real values requires only that they be separated by a comma or blank space. Where values equal 99999.999, absence of data is indicated. Data are absent where the density of water is less than 0.35 g/cm³ **This scheme of 37 records with 36 values in each is also used for water enthalpy and log K data for derived species, minerals and gases.**

2.3 Water Enthalpy Data

These data are not used by SOLVEQ-XPT. They are used by CHIM-XPT to compute the final temperature when mixing two fluids of different temperature. This area contains 39 records. The first record for each parameter is blank, and the second record is not read by CHIM-XPT.

The next 37 records or 36 real values contain water enthalpy in kJ/mole using the same T, P scheme described above for activity coefficients.

2.4 The Component Species Data

These data immediately follow the water enthalpy records described in the previous section, and consist of one record per component species, as follows.

* Each record (A20, F2.0, 6X, F3.2,8x, 3F8.4): AQS_NAME, CHG, AZERO, W, ALKALINITY

For each component species, AQS_NAME is the name, CHG the charge, AZERO the effective ionic radius (Helgeson et al. 1981), W the molecular weight, and ALKALINITY protonation coefficient for alkalinity calculations (this last parameter is only used by SOLVEQ-XPT).

The order of these records should not be changed. For the stoichiometries of derived species, gases, and minerals described in the next sections, each component species is identified by its position in the component species data area (H^+ is 1, H_2O is 2, SiO_2 is 7, etc), and the order of component species in this area is critical. The total number of component species in SOLTHERM may vary, but must be consistent with the array dimensions specified in the programs reading this file.

* Last record must be blank.

2.5 The Derived Species Data

This area contains data for aqueous derived species, and follows the component species data area, preceded by one blank line. The data for each derived species is given by 3 records, which are the following:

* 1st record (A20,T81,A4,T91,A4): AQS_NAME, SUP, PTFLAG_AQS

AQS_NAME is the same as for the component species. SUP: any non-blank character read by SUP in columns 81-84 suppresses the species from the calculations.

Derived species, mineral and gas log K data are of two types. The log K data either covers the entire range from 0.01-600 °C, 1-5000 bar, or it is restricted to T and P conditions of liquid-vapor saturation from 25-350 °C (see below). PTFLAG_AQS is a four character string to indicate to the software which type of log K data will be read: "A11 " indicates the entire range, and any other string indicates the restricted range. If the SOLRUN file integer parameter L/V-HiP: is set to one for high pressure calculations, log K data that are restricted to liquid-vapor saturation are skipped.

* 2nd record (8X,F3.0,15X,F5.2,10X,F6.3): CHG, AZERO, ALKALINITY

CHG, AZERO and ALKALINITY are the same as for the component species. The end of this record also indicates a reference code for the data, with the exact reference given in the comment area.

* 3rd record (I2,1X,I2(F10.3,I2): ITOT, COEF(i) and SPEC(i) where $i = 1$ to ITOT

ITOT is the number of component species in the derived species. COEF(i) contains the stoichiometric coefficient for species SPEC(i) in the derived species. SPEC(i) identifies the component species in the derived species, and correspond to the position of component species in the component species area (e.g. SPEC = 1 for H^+ , 7 for SiO_2 , etc.). If a derived species contains

H⁺, H⁺ MUST be entered in the i = 1 position.

* 4th to 40th, or 4th record only (free format; each real value separated by one comma and/or at least one blank space): LOG K's

The records that follow contain log K data: either (1) 37 records with 36 values each where data are available for the entire T, P grid using the same arrangement as described above for activity coefficients, or (2) a single record for species where data are restricted to conditions of liquid-vapor saturation. In the latter case log K values are typically given for the following temperatures: 25, 50, 100, 150, 200, 250, 300 °C, and 350 °C, but in some cases are restricted to a maximum temperature lower than 350 °C; SOLVEQ-XPT will warn the user in the SOLOUT file if T specified in the SOLRUN is above the range given for that derived species, and it can then be suppressed from the calculations.

* Last record: must be BLANK.

The total number of derived species in SOLTHERM may vary, but must be consistent with the array dimensions specified in the program. To insure proper reading of SOLTHERM, a extra blank line has to be inserted after the data for the last derived species:

2.6 The Gas Data

The first 10 records of this area contain data for computing fugacity coefficients and enthalpies of H₂O-CO₂-CH₄ mixtures:

* First 10 records (A8,6E12.5)

These records contain regression coefficients a, b, and c to calculate cross-virial coefficients B_{ij} and C_{ijk} as a function of temperature (for a virial equation in pressure), such that B_{ij} or C_{ijk} = a/T² + b/T + c, with T in K (Spycher and Reed, 1988). For the names in these records (e.g. B12, C123) the numbers 1, 2, and 3 correspond to H₂O, CO₂, and CH₄, respectively. This block is followed by two blank records.

The next records contain data for gases. H₂O, CO₂, and CH₄ must always be the first 3 gases, in this order, in the gas list. The data for each gas are given by 4 records, as follows:

* 1st record (A20, T67,I2,F8.3,T81,A4,T91,A4): MIN_NAME, JSOLS, B, SUP, PTFLAG_MIN

MIN_NAME is the name of gas or mineral species. MIN_NAME for H₂O, CO₂, and CH₄ must always be: "CO2,gas", and "CH4,gas" followed by 13 blanks for a total of 20 characters. Following MIN_NAME beginning in column 21 is an alternate descriptor of the gas that is not read by SOLVEQ-XPT. JSOLS and B are non-zero for gases and mineral solid solutions (see mineral data section). For gases, B is useless, but must always be 1, and JSOLS identifies the species as being a gas species, and must always be 6. If JSOLS is zero for one or more gases, these gases will be treated as minerals, and will not be included in the gas phase if boiling occurs. Gases with JSOLS = 0 do not have a fourth entry, and must be placed after the list of gases which have JSOLS = 6. SUP performs a similar role as for derived species: any non-blank character read by SUP in columns 81-84 suppresses the species from the calculations. PTFLAG_MIN performs the same role as PTFLAG_AQS does for derived species. PTFLAG_MIN is a four character string to indicate to the software which type of log K data will be read: "A11 " indicates the full T-P grid, and any other string indicates the range restricted to conditions of

liquid-vapor saturation. If the CHILLRUN file integer parameter L/V-HiP: is set to one for high pressure calculations, log K data that are restricted to liquid-vapor saturation are skipped.

* 2nd record (T14,F8.3,T59,F6.3): XMOLW

XMOLW is the molecular weight. The end of this record also indicates a reference code for the data, with the exact reference given in the comment area.

* 3rd record (I3,12(F9.3,I3)) ITOT, COEFM(i) and SPECM(i) i = 1 to ITOT

The 3rd records for gases are similar to the 3rd records for derived species (see derived species section).

* 4th record, only if JSOLS = 6 (4x,6f12.5):

This record contains regression coefficients a, b, c, d, e, and f to calculate virial coefficients B and C of pure gases as a function of temperature (for a virial equation in pressure), such that $B = a/T^2 + b/T + c$, and $C = d/T^2 + e/T + f$, with T in K (Spycher and Reed, 1988). For gases with JSOLS = 0, this record must be omitted. For gases with no data available, this record is left blank and ideal gas behavior is assumed.

The total number of gases in SOLTHERM may vary, but must be consistent with the array dimensions specified in the program. If required, additional gases can be added to the mineral data section (see below), but these gases must then have JSOLS set to zero. Generally, O₂ and other gases with very low fugacities have JSOLS set to zero, and are not included in the gas phase in boiling calculations. This is to avoid possible underflow and overflow problems.

* 4th to 40th, or 4th record only. If JSOLS = 6 5th to 50th, or 5th record only (free format; each real value separated by one comma and/or at least one blank space): LOG K's

These records for gases are similar to the 3rd records for derived species (see derived species section).

2.7 The Mineral Data

The data for minerals immediately follows the gas data. The data for each mineral are given by 3 records, which are identical to the 1st, 2nd and 3rd records for gases (see previous section), except that the SUP parameter in the 1st record must be blank. If SUP is not blank or "GAS " (for gas species), the mineral is suppressed from the calculation. Also, the 2nd record contains two more variables, the mineral molar volume, and the mineral density, in g/cm³ for volume calculations, and are not used by SOLVEQ-XPT.

* 1st record (A20, T67,I2,F8.3,T81,A4,T91,A4)

* 2nd record (T14,F8.3,T59,F6.3)

* 3rd record (I3,12(F9.3,I3))

For mineral solid solutions, B represent the exponent for mineral end-member to be used to calculate activity using ideal multi-site mixing, and JSOLS identifies the index of the solid solution (if any) to which this mineral belongs. See the comment area in SOLTHERM to check the current solid solutions and their JSOLS indexes. JSOLS = 6 is reserved for gases, and JSOLS = 10 is reserved for electrum. Solid solution data are used by CHIM-XPT, but not by SOLVEQ-XPT.

The total number of solid solutions and of their end- members must be consistent with the array dimensions specified in the program. The total number of minerals in SOLTHERM may vary, but must also be consistent with array dimensions. To insure proper reading of SOLTHERM, two blank lines have to be inserted after the data for the last mineral:

* Last two records: must be BLANK.

2.8 Optional Miscellaneous Data

This area is not read, and can be used to save various data. It is useful for saving records of SOLTHERM that are not presently used, but that might be needed at some further time.

Appendix 3. More about the Solplot Data File

The solplot file is created by SOLVEQ-XPT and contains the log Q/K of minerals and gases, and was previously used for plotting of mineral log Q/K's. The SOLPLOT file contains the following records.

* Records 1 and 2 (10A8): two lines of title

The next records are arranged in sets, one set per temperature step, with a blank line at the top of each set. There are as many records in a set as there are gases and minerals in the calculation, and as many sets as there are temperature steps. The format of each set is as follow:

* 1st record of set: must be BLANK

* Next records (A8,2F10.5): gas or mineral name, log Q/K, and temperature in C (the temperature is the same for all records of the same set).

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