

Users Guide for  
**SOLVGAS: A Computer Program**  
**for Computing**  
**Gas-Solid-Liquid Equilibria**

Edition 2.0

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March 2009 (re-edited by MR)

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## FOREWORD

Program SOLVGAS was developed for computing the equilibrium distribution of gas species in volcanic gases. It is used primarily as a workhorse for processing gas analyses of all types, but it is also useful for certain types of geochemical process modeling. SOLVGAS computes a gas phase species distribution as a function of temperature, pressure, oxygen fugacity, or the fugacity of another gas (e.g., HCl). From the gas species distribution, SOLVGAS determines degree of super- or under-saturation of the gas with respect to solids and liquids that could precipitate from the gas as sublimates or condensates. SOLVGAS is well suited for restoring analyses of volcanic gases, modeling the speciation of gas mixtures, and computing the saturation indexes of potential sublimates.

SOLVGAS descended from program SOLVEQ (Reed, 1982, 1998), which computes the distribution of aqueous species in hydrothermal waters. SOLVGAS was originally written to interpret gas compositions and silica-tube sublimate samples from Merapi Volcano, Indonesia (Symonds, et al., 1987), and has since been applied to many other volcanic gas problems, as listed in the references at the end of this user's guide. GASWORKS is a sister program to SOLVGAS, which computes gas-solid-liquid equilibria and reaction processes.

SOLVGAS runs at a Windows command line in a very straightforward process requiring only the setup of an initial run file, which can be done using program VOLCAL. We hope that this manual will ease the process of learning to use SOLVGAS, which inexperienced users can quickly learn, but of course, a knowledge of geochemistry is helpful for understanding the input and output and for designing meaningful runs. We encourage users to notify us about problems (bugs, errors, hassles) in SOLVGAS and data base GASTHERM.

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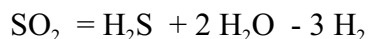
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## CHAPTER I. INTRODUCTION

SOLVGAS is a FORTRAN computer program designed for computing multicomponent homogeneous chemical equilibria in volcanic gases. For a given temperature, pressure, and total composition of a homogeneous gas phase, SOLVGAS computes the fugacities of molecular gas species at equilibrium and the saturation indices of solids and liquids relative to the gas phase. SOLVGAS solves a system of mass-balance and mass-action equations by the Newton-Raphson method, as explained by Symonds and Reed (1993). Calculations are constrained by thermochemical data (Symonds and Reed, 1993) and tabulated in the GASTHERM.DAT file. In SOLVGAS, the chemical system is defined in terms of "component species", actual species in the gas phase that are also used as thermodynamic components, in the strict sense. Gas phase species that are combinations of component species are called "derived species". Solids and liquids are also expressed in terms of component species.

A complete listing of the component species, derived gas species, solids, and liquids are given in the GASTHERM.dat file and in Symonds and Reed (1993). The component species in the present data base are as follows: H<sub>2</sub> H<sub>2</sub>O CO<sub>2</sub> H<sub>2</sub>S HCl HF HBR NaCl KCl FeCl<sub>2</sub> ZnCl<sub>2</sub> AlF<sub>3</sub> CuCl BiCl<sub>3</sub> PbCl<sub>2</sub> H<sub>2</sub>MOO<sub>4</sub> H<sub>2</sub>WO<sub>4</sub> AsCl<sub>3</sub> SbCl<sub>3</sub> SiF<sub>4</sub> MgCl<sub>2</sub> CaCl<sub>2</sub> TiF<sub>4</sub> CrCl<sub>4</sub> CoCl<sub>2</sub>:CO NiCl<sub>2</sub> MnCl<sub>2</sub> VCl<sub>4</sub> SrCl<sub>2</sub> GsCl<sub>3</sub> LiCl RbCl CsCl H<sub>2</sub>Se H<sub>2</sub>Te N<sub>2</sub> SnCl<sub>2</sub> AgCl Au, Hg, Ir.

The bulk chemical composition of the gas system is given as the molar amount of each component species in the system. This calls for re-expressing some major species in an alternative form consistent with the set of component species. For example, derived species SO<sub>2</sub> is expressed in terms of component species H<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>S as



and the mass balance equations for H<sub>2</sub>S, H<sub>2</sub>O, and H<sub>2</sub> each include a term for SO<sub>2</sub>. A related treatment applies to oxygen and oxygen fugacity, which although small is commonly used to express oxidation state. Although O<sub>2</sub> is not a component species, oxygen fugacity may be specified, from which the hydrogen mole number is computed by way of the H<sub>2</sub>O-O<sub>2</sub>-H<sub>2</sub> equilibrium solved in combination with all other equilibria involving H<sub>2</sub>. This procedure is used to compute oxygen fugacities without recourse to mineral buffer constraints at any temperature from knowing (or estimating) fugacity at a single temperature. As for oxygen, where the fugacities of component species are known instead of the mole number, the fugacity can be specified, from which SOLVGAS computes the mole number of that component in the gas.

The actual unknowns that SOLVGAS determines are the "mole numbers" of the various component and derived species. The mole number of any species is the number of moles of that species at equilibrium at the specified temperature, pressure, and bulk composition. In most cases, we set up problems for a total of one mole of gas, thus the species mole number is nearly a mole fraction, and can readily be expressed as a mole fraction as needed. An illustrative example of a SOLVGAS calculation output follows, showing mole numbers under the "moles" column heading.

# Sample output from program SOLVGAS with many species and two columns omitted

AUGUSITNE DOME-3 SAMPLE (SYMONDS ET AL., 1991).  
 AT 870 C AND 1 ATM IN THIS RUN. GASRUN DEMONSTRATION 2.  
 ++++++  
 NO. OF LOOPS USED = 8 LOOP LIMIT = 90  
 TEMPERATURE: 870. DEGREES CENTIGRADE  
 PRESSURE: 1.000 ATM  
 TOTAL MOLES OF GAS = .9997252E+00

SPECIES	MOLES	PARTIAL PRESS.	FUGACITY	LOG(F)	TOT MOLES	PPM
1 H2	0.61489E-02	0.61505E-02	0.61505E-02	-2.21109	0.16910E+00	-0.151188E+05
2 H2O	0.83919E+00	0.83942E+00	0.83942E+00	-0.07602	0.95330E+00	0.761720E+06
3 CO2	0.23987E-01	0.23993E-01	0.23993E-01	-1.61991	0.24200E-01	0.472380E+05
4 H2S(G)	0.10035E-01	0.10038E-01	0.10038E-01	-1.99836	0.71200E-01	0.107610E+06
5 HCL	0.60340E-01	0.60357E-01	0.60357E-01	-1.21927	0.60340E-01	0.975797E+05
6 HF	0.53581E-03	0.53596E-03	0.53596E-03	-3.27087	0.52840E-03	0.468874E+03
7 HBR	0.67517E-05	0.67535E-05	0.67535E-05	-5.17047	0.67800E-05	0.243315E+02
8 NACL	0.13895E-04	0.13899E-04	0.13899E-04	-4.85702	0.14500E-04	0.375860E+02
9 KCL	0.86767E-05	0.86791E-05	0.86791E-05	-5.06153	0.87200E-05	0.288336E+02
10 FECL2	0.15777E-05	0.15781E-05	0.15781E-05	-5.80186	0.15800E-05	0.888264E+01
11 ZNCL2	0.63928E-06	0.63946E-06	0.63946E-06	-6.19419	0.64000E-06	0.386864E+01
12 CD	0.21396E-07	0.21402E-07	0.21402E-07	-7.66954	0.21400E-07	0.106695E+00
13 ALF3	0.41348E-11	0.41359E-11	0.41359E-11	-11.38342	0.27000E-06	0.100566E+01
14 CUCL	0.69394E-07	0.69413E-07	0.69413E-07	-7.15856	0.69500E-07	0.305170E+00
15 BICL3	0.80130E-11	0.80152E-11	0.80152E-11	-11.09609	0.24500E-08	0.342666E-01
16 PBCL2	0.18567E-06	0.18572E-06	0.18572E-06	-6.73113	0.23900E-06	0.294805E+01
17 H2MOO4	0.64666E-07	0.64683E-07	0.64683E-07	-7.18921	0.17800E-06	0.127861E+01
18 ASCL3	0.61360E-08	0.61377E-08	0.61377E-08	-8.21199	0.99200E-06	0.797608E+01
19 SBCL3	0.25716E-07	0.25723E-07	0.25723E-07	-7.58967	0.38200E-07	0.386485E+00
20 SIF4	0.79596E-04	0.79618E-04	0.79618E-04	-4.09899	0.82700E-04	0.381765E+03
21 MGCL2	0.47631E-07	0.47644E-07	0.47644E-07	-7.32199	0.47800E-07	0.201856E+00
22 CACL2	0.46400E-06	0.46412E-06	0.46412E-06	-6.33337	0.46400E-06	0.228409E+01
23 TIF4	0.11263E-12	0.11266E-12	0.11266E-12	-12.94824	0.64700E-08	0.355476E-01
24 CRCL4	0.88831E-10	0.88855E-10	0.88855E-10	-10.05132	0.11900E-08	0.102293E-01
25 NICL2	0.22394E-08	0.22400E-08	0.22400E-08	-8.64976	0.22400E-08	0.128756E-01
26 MNCL2	0.17300E-07	0.17305E-07	0.17305E-07	-7.76183	0.17300E-07	0.965618E-01
27 VCL4	0.20598E-11	0.20604E-11	0.20604E-11	-11.68605	0.15200E-08	0.129949E-01
28 SRCL2	0.53000E-09	0.53015E-09	0.53015E-09	-9.27561	0.53000E-09	0.37652E-02
29 LICL	0.66843E-07	0.66861E-07	0.66861E-07	-7.17483	0.66900E-07	0.125793E+00
30 O2	0.24852E-12	0.24859E-12	0.24859E-12	-12.60452		
31 AL	0.12166E-26	0.12169E-26	0.12169E-26	-26.91474		
32 ALBR	0.46341E-21	0.46353E-21	0.46353E-21	-21.33392		
33 ALBR3	0.76463E-21	0.76484E-21	0.76484E-21	-21.11643		
34 (ALBR3)2	0.49834E-44	0.49848E-44	0.49848E-44	-44.30236		
35 ALC	0.19138E-47	0.19144E-47	0.19144E-47	-47.71798		
36 ALCL	0.13810E-16	0.13814E-16	0.13814E-16	-16.85968		
37 ALCLF	0.62078E-14	0.62095E-14	0.62095E-14	-14.20694		
38 ALCLF2	0.53602E-10	0.53617E-10	0.53617E-10	-10.27070		
39 ALCL2	0.17612E-13	0.17617E-13	0.17617E-13	-13.75406		
40 ALCL2F	0.39912E-09	0.39923E-09	0.39923E-09	-9.39878		
41 ALCL3	0.10416E-08	0.10419E-08	0.10419E-08	-8.98219		
42 (ALCL3)2	0.19673E-19	0.19679E-19	0.19679E-19	-19.70600		
43 ALF	0.32166E-16	0.32174E-16	0.32174E-16	-16.49249		
44 ALFO	0.43255E-13	0.43267E-13	0.43267E-13	-13.36385		
45 ALF2	0.31671E-15	0.31680E-15	0.31680E-15	-15.49922		
46 ALF2O	0.26850E-06	0.26857E-06	0.26857E-06	-6.57094		

~~~ hundreds of derived species omitted here ~~~~

|              |             |             |             |           |  |  |
|--------------|-------------|-------------|-------------|-----------|--|--|
| 436 TICL3    | 0.14602E-09 | 0.14606E-09 | 0.14606E-09 | -9.83547  |  |  |
| 437 (TICL3)2 | 0.17534E-20 | 0.17539E-20 | 0.17539E-20 | -20.75600 |  |  |
| 438 TICL4    | 0.62703E-08 | 0.62721E-08 | 0.62721E-08 | -8.20259  |  |  |
| 440 TIF2     | 0.71251E-15 | 0.71271E-15 | 0.71271E-15 | -15.14709 |  |  |
| 441 TIF3     | 0.24863E-10 | 0.24870E-10 | 0.24870E-10 | -10.60432 |  |  |
| 442 TIO      | 0.27854E-21 | 0.27862E-21 | 0.27862E-21 | -21.55499 |  |  |
| 443 TIOCL    | 0.15712E-16 | 0.15717E-16 | 0.15717E-16 | -16.80364 |  |  |
| 444 TIOCL2   | 0.28666E-10 | 0.28674E-10 | 0.28674E-10 | -10.54251 |  |  |
| 445 TIOF     | 0.29827E-18 | 0.29835E-18 | 0.29835E-18 | -18.52528 |  |  |
| 446 TIOF2    | 0.31547E-14 | 0.31556E-14 | 0.31556E-14 | -14.50092 |  |  |
| 447 TIO2     | 0.39279E-15 | 0.39290E-15 | 0.39290E-15 | -15.40572 |  |  |
| 448 TIS      | 0.39500E-26 | 0.39511E-26 | 0.39511E-26 | -26.40328 |  |  |
| 449 V        | 0.20192E-26 | 0.20197E-26 | 0.20197E-26 | -26.69471 |  |  |
| 450 VBR4     | 0.41109E-27 | 0.41120E-27 | 0.41120E-27 | -27.38594 |  |  |
| 451 VF5      | 0.88737E-31 | 0.88762E-31 | 0.88762E-31 | -31.05177 |  |  |
| 452 VO       | 0.47609E-18 | 0.47622E-18 | 0.47622E-18 | -18.32219 |  |  |
| 453 VOCL3    | 0.15160E-08 | 0.15164E-08 | 0.15164E-08 | -8.81919  |  |  |
| 454 VO2      | 0.19805E-11 | 0.19811E-11 | 0.19811E-11 | -11.70310 |  |  |
| 455 ZN       | 0.71990E-09 | 0.72010E-09 | 0.72010E-09 | -9.14261  |  |  |
| 456 ZNBR2    | 0.36862E-12 | 0.36873E-12 | 0.36873E-12 | -12.43330 |  |  |
| 457 ZNS      | 0.13075E-12 | 0.13079E-12 | 0.13079E-12 | -12.88343 |  |  |

## Hardware and system requirements

The executable version of SOLVGAS runs readily at the command prompt under various Windows incarnations (2000, XP, Vista, etc.). Presumably it also runs fine on Macintosh computers. Output files will consume a few megabytes of hard drive space.

## CHAPTER II. INPUT AND OUTPUT FILE ASSIGNMENTS

SOLVGAS needs several input and output files to run properly. SOLVGAS does not include built-in routines for assignment of I/O disk files. However, I/O device numbers are assigned to variables (IN1, IN2, ..., IOUT1, IOUT2, ... and so on) so that current I/O device numbers in the READ and WRITE statements in SOLVGAS can easily be redefined if necessary. In the current version of SOLVGAS, there are FORTRAN "OPEN" statements that assign certain explicit file names (in DOS-compatible syntax) 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 SOLVGAS, with their corresponding I/O device variables and currently assigned values. If you choose to disable the OPEN statements in SOLVGAS, you will need to assign each disk file to the corresponding device numbers prior to running the program. Chapter III explains the format and content of these files.

### I/O Files

Fortran I/O device variable, current value, file name and explanation

---

IN1 4 Current file name: GASRUN.DAT. Input data specific to each run. Contains title, input parameters, trial mole numbers, total moles of components, fugacity coefficients, and other parameters.

IN2 1 Current name: GASTHERM.DAT. Thermodynamic data base for gases, solids, and liquids (mainly log K's).

IN3 5 Terminal (interactive) input.

IOUT1 6 Current name: GASOUT.DAT. This file contains the results of the calculations.

IOUT2 5 Terminal (interactive) output.

IOUT3 2 Current file name: GASPLOT.DAT. Contains log fugacities of gases for plotting as a function of temperature,  $f_{O_2}$ , or UNACT (e.g., HCl fugacity). Contains log mole fractions of gases if pressure is the variable.

IOUT4 7 Current file name: SUBPLOT. Contains saturation indices ( $\log(Q/K)$ ) of solids and liquids for plotting as a function of temperature, pressure,  $f(\text{O}_2)$ , or U<sub>NACT</sub> (e.g., HCl fugacity).

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### CHAPTER III. FORMAT AND CONTENT OF INPUT AND OUTPUT FILES

To run SOLVGAS, the user specifies a gas composition, pressure and temperature in an input file called gasrun.dat. Results of the calculation are output in file gasout.dat. Other I/O files of immediate interest to the user include gastherm.dat, which contains thermodynamic data, gasplot.dat and subplot.dat. These file are addressed in this chapter. Other input files are addressed in the appendix. For each file described in this chapter, formats are given in parentheses for each record, in standard FORTRAN notation. I/O device number variables are given in parenthesis after each file name heading.

#### The run file: GASRUN (IN1)

GASRUN.dat contains the data and constraints specific to each run. For most users, this file is the only one that they create or modify prior to running SOLVGAS. The file contains format indicators and variable names in lines that are not read by SOLVGAS, which makes it straightforward to create a new gasrun.dat by modifying an existing file to apply to the new run. This chapter addresses the formats and definitions of variables. How to set up this file to accomplish your modeling goals is addressed in chapter IV. Chapter V addresses the specific use of input parameters for various types of calculations and provides example GASRUN files. A description of the GASRUN file follows.

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

\* **Records 3 and 4**: Format indicator lines for record 5; skipped by SOLVGAS on input. Use a previously run GASRUN file to obtain these lines, or input two blank lines.

\* **Record 5** (8E10.5): ERPC, FO2LOG, U<sub>NACT</sub>, GASTOT, TEMPC, PF, RAT

ERPC: Convergence limit on mass-balance and mass-action equations (default value is  $10^{-12}$ ). The program satisfies the convergence test when all equations are solved within ERPC precision. When setting ERPC, keep in mind that most computer systems have 16 significant digits in double precision, and SOLVGAS might fail to converge if ERPC is less than  $10^{-12}$ . Convergence will definitely fail if ERPC is less than  $10^{-16}$ .

FO2LOG: Log fugacity of oxygen. If non-zero, the total molar amount of  $\text{H}_2$  in the gas will is computed as discussed by Symonds and Reed (1993). If input as zero, the  $f(\text{O}_2)$  will be calculated from the mass balances of all the component species including  $\text{H}_2$ .

U<sub>NACT</sub>: Fugacity of a component species, if it is known or estimated in place of the total molar amount. The species itself is identified by the index NSUNK, below. Note that it may be

necessary to input  $f(\text{O}_2)$  (FO2LOG) when using this option to get a valid result for both  $f(\text{O}_2)$  and the unknown other species. UNACT can be changed interactively while running SOLVGAS.

GASTOT: A trial value for the total moles of gas. This is also a factor to aid convergence by setting a ceiling on permissible values of current mole numbers of gas species. Set to the number of moles of gas in the input gas composition, which is about 1 mole in most cases.

TEMPC: Temperature ( $^{\circ}\text{C}$ ) at which equilibrium is computed. TEMPC overrides the preselected temperature variable NTEMP, below. To choose from preselected temperatures (to use NTEMP), TEMPC must be input as zero or blank.

PF: Total fluid pressure in atmospheres. Normally set at 1 atmosphere for studies of fumarolic gases modeled at outlet conditions. However, can be set at higher values or incremented. If you are incrementing pressure, make sure to set NMOLF to 1 (below).

RAT: Arbitrary minimum limit on the size of mole numbers to be printed out. In log units. Set to -300 if you want to print every gas species. Set at a larger number, say -20, to minimize output.

\* Records 6 and 7: skipped by SOLVGAS on input. Similar to records 3 and 4.

\* **Record 8** (12I5): BSTOT, NTEMP, NMTT, NMOLF, IGAMP, NLOOP, NSUNK, IPRINT, ITREF

BSTOT: Number of component species in GASTHERM data file, currently 42.

NTEMP: Indices of preselected temperatures. Set NTEMP to: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13, to accomplish calculations at  $25^{\circ}$ ,  $100^{\circ}$ ,  $200^{\circ}$ ,  $300^{\circ}$ ,  $400^{\circ}$ ,  $500^{\circ}$ ,  $600^{\circ}$ ,  $700^{\circ}$ ,  $800^{\circ}$ ,  $900^{\circ}$ ,  $1000^{\circ}$ ,  $1100^{\circ}$ , or  $1200^{\circ}\text{C}$ , respectively. This option is disabled if TEMPC, above, is non-zero.

NMTT: If zero, this index disables the calculation of saturation indices of solids and liquids. Set to non-zero to compute these values. (NMTT = 0 also skips reading solid and liquid data in the GASTHERM data file).

NMOLF: Setting NMOLF to 1 will also cause log mole fractions (instead of log fugacities) to be printed in the GASPLOT data file. It will also enable one to increment pressure. Set to zero to disable this option.

IGAMP: Not used. Set to zero.

NLOOP: Maximum number of Newton-Raphson iterations allowed when converging to a solution. If SOLVGAS has not converged after NLOOP iterations, the execution is aborted but some results are still printed to help in debugging. NLOOP = 90 is a good number. Most cases are solved after 5 to 20 iterations (loops), although some might require more. Generally, a case not solved after 200 iterations will not converge.



NSUNK: If a value for UNACT, above, was specified, NSUNK must be input to identify which species has the activity given by UNACT. NSUNK is the sequence position of the selected gas in the list of component species in the GASTHERM data file. For example, NSUNK = 6 specifies HF.

IPRINT: If not zero, printing of extra output for closer inspection of the calculation progress will occur. Generally, this option is activated only for debugging purposes.

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, IPRINT 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 VI).

\* Records 9 and 10: skipped by SOLVGAS on input. Similar to records 3 and 4.

\* **Records 11 and beyond:** one record per component species (I5,1X, A8, 4X,2E16.9,F8.4): SAQ(i), NAME(i), MTOT(i), MTRY(i), GAMMA(i)

SAQ identifies an individual component species. Its values are those of the sequence positions of component species as listed near the top of the GASTHERM data file; i.e. the SAQ numbers are 1,2,3, etc., from the order of component species listed in GASTHERM (e.g., H<sub>2</sub> is 1, H<sub>2</sub>O is 2, CO<sub>2</sub> is 3, HBr is 7, etc.). SAQ, and not NAME, below, identifies which component species are used for the present calculation.

NAME contains the names of the selected component species identified by SAQ above. NAME here is a dummy marker variable which is skipped by SOLVGAS on input. It is part of the record only to improve the clarity of the GASRUN file; it can be left blank to no effect.

MTOT contains the total number of moles of component species SAQ in the system. MTOT defines the total composition of the chemical system, including any non-gaseous material that one may want to force into a gas phase for purposes of the calculation. MTOT values are generally positive, but can also be zero or negative if the system contains phases or derived species that are expressed in terms of a negative amount of a component species (e.g., SO<sub>2</sub> = H<sub>2</sub>S + 2 H<sub>2</sub>O - 3 H<sub>2</sub>, thus SO<sub>2</sub> contains negative H<sub>2</sub>). If fixing f(O<sub>2</sub>) (FO2LOG) or UNACT, it is not necessary to specify an MTOT value for H<sub>2</sub> or the NSUNK species, respectively.

MTRY contains the trial mole numbers of component species SAQ. These are initial estimates of the mole numbers of each individual component species for which SOLVGAS will solve (and which cannot be less than zero, in contrast to MTOT values). The closer these initial trial values are to the actual (unknown) mole numbers, the better are the chances for SOLVGAS to converge to a solution. MTRY values must be estimated (see chapter IV). It is generally better that they be on the small side.

GAMMA contains fugacity coefficients of component species as specified by SAQ. Default GAMMA values are 1.0 and these are used in most cases. Currently, SOLVGAS has no capability to compute gammas other than 1.0, but one can input the correct GAMMA values if known for a given chemical system.

\* **Next record:** MUST BE BLANK to indicate end of component species data.

### **The thermodynamic data file GASTHERM (IN2)**

Gastherm.dat contains all thermodynamic data for gas, solid, and liquid species. It is rarely modified by the user. A description of this file is provided in the appendix. The file is divided into four parts: the comment area (including data sources), the component species data, the derived gas species data, and the solid and liquid data.

Thermodynamic data in this file are described by Symonds and Reed (1993). The sources of these data include Anovitz et al. (1985), Barin and Knacke (1973), Barin et al. (1977), Berman (1988), Berman and Brown (1985), Chase et al. (1974,1975,1978,1982), Decock (1982), Helgeson et al. (1978), Pankratz (1982,1984), Pankratz et al. (1984,1987), Robie et al. (1978), and Stull and Prophet (1971).

### **The main output file (IOUT1): GASOUT.DAT**

The calculation results output file Gasout.dat is divided into three parts: the title block, the gas speciation, and saturation indexes for solids and liquids. The title block contains the title given in GASRUN, the number of iterations (loops) used to reach convergence, the pressure, temperature, and the total moles of gas at equilibrium. Always check to see whether the number of loops equals the specified loop limit. If it does, SOLVGAS stopped without converging on a solution, and you should ignore the results, except for how they may help with debugging.

The second part is the speciation of the gas phase. The data are in columns labeled (from left to right): MOLE NUMBER, MOLE FRACTION, PARTIAL PRESSURE, FUGACITY, LOG(F), and GAMMA. The values in the MOLE NUMBER column are the final solutions to the equations for equilibrium—values that converged to constants, starting from the MTRY's given GASRUN. The LOG(F) and GAMMA columns contain the log fugacities and fugacity coefficients, respectively. Other columns are self explanatory.

Oxygen fugacity is not output separately, but it can be read from the O<sub>2</sub> line, the first of the derived species in the listing. Derived species with mole numbers less than RAT (specified in the GASRUN input file) are not printed. Also, species with mole numbers less than 10<sup>-300</sup> are set to 10<sup>-300</sup> to avoid underflows (that limit can be changed by changing the variables, RMIN and RLOGMN, in the SOLVGAS code).

Following the speciation list, the characteristics of the component species are summarized. The MOLE NUMBER column contains the mole numbers of the component species. The TOTAL MOLES column defines the composition of the system and indicates the total moles of component species in the chemical system, as input in the GASRUN file or computed from input of f(O<sub>2</sub>) or an "nsunk" species. For each component species, the motot's are the sum of the molar amounts of all gas species containing that component species (as defined by the stoichiometries read in the GASTHERM data file). Total moles were input in the GASRUN file

as MTOT. A "CM" notation may appear after a value in the TOTAL MOLES column indicating the total molar amount of a component species (NSUNK) computed from input of its fugacity (UNACT), or for H<sub>2</sub>, from a specified f(O<sub>2</sub>). The PPM column refers to the mass (in ppm) of that component species in the gas; hence, for molybdenum it refers to the amount of H<sub>2</sub>MoO<sub>4</sub>---not elemental Mo---in the total gas. The MOLE FRACTION (TOTAL) column is equivalent to the TOTAL MOLES column divided by GASTOT.

The third part of the output is saturation indexes of solids and liquids, wherein a positive log (Q/K) indicates supersaturation and a negative value indicates undersaturation. Phases that are close to saturation may appear in either list.

If the IPRINT option is enabled in the GASRUN file, additional data is output for debugging purposes. This includes a dump, at the start of the output, of the component species read in GASRUN and of all derived species (gases, solids, liquids) read in GASTHERM with their log K's. A non-zero IPRINT also results in the output of the matrix of partial derivatives of mass-balance and mass-action equations after the first and second iterations, of gas speciation data after the second iteration, and, at each iteration, of the total moles of gas and the mole number of each component species, followed by a dump of the array containing the change in MTRY values from the previous iteration to the current one (these become very small as SOLVGAS converges). If the ITREF option in GASRUN is set non-zero, the residuals of the mass-balance and mass-action equations are also output.

### **The GASPLOT file (IOUT3)**

Gasplot.dat contains the log fugacities (or log mole fractions if NMOLF = 1) of gas species at each T-P step of the calculations, as illustrated in (Symonds et al, 1988). The file can be reordered using a sort program, if desired. The format of the plot file is given below.

\* Records 1 through 3 (10A8): Two title lines followed by a blank line

\* Next records, one record per gas species, blank line between incremental steps of calculations (A8, 5F10.5): name of gas species, log fugacity (or log mole fraction), temperature (in oC), pressure (in atmospheres), log(fO<sub>2</sub>), log of UNACT.

### **The SUBPLOT file (IOUT4)**

This file contains the list of saturation indexes (log (Q/K) values) for solids and liquids, at each temperature. This file can be reordered with a sort program for easier interpretation of the results, or can be directly used in plotting changes in saturation indexes versus temperature, pressure, log(fO<sub>2</sub>), or UNACT (Symonds et al, 1987). The format of the SUBPLOT file is given below.

\* Records 1 through 3 (10A8): Two title lines followed by a blank line

\* Next records, one record per gas species, blank line between incremental steps of calculations (A8, 5F10.5): name of solid or liquid species, log (Q/K), temperature, pressure, log(fO<sub>2</sub>), log of UNACT.

## CHAPTER IV. GETTING STARTED

This chapter addresses how to install SOLVGAS, how to recast gas compositions in terms of the component species, and how to set up GASRUN files. The first thing to do is to make sure that all input and output files are correctly assigned (see chapter III).

The software packet includes demonstration files for various types of SOLVGAS calculations. We suggest that you test and debug your installation of SOLVGAS using these files. These files also serve as templates to make your own GASRUN files.

### Installation

The SOLVGAS package comes with this manual and several files:

**SOLVGAS.EXE** The executable version of SOLVGAS. (The FORTRAN code is available on request.)

**GASTHERM.DAT** The main thermodynamic data file.

**GASTHERM.RST** A special shortened version of Gastherm.dat file used for restoring raw gas analyses.

**GASRUN.DM\*** Sample run files to demonstrate several applications of SOLVGAS.

**VOLCAL.EXE** The executable version of VOLCAL. (The FORTRAN code is available on request.)

**GAS.STO** A data file of derived-species stoichiometries cast in terms of component species. Used by VOLCAL to recast derived species, like SO<sub>2</sub> and CO, in terms of component species.

To install SOLVGAS on a personal computer, simply copy all the above files to a directory of your choice on the hard disk. Next, create a GASRUN.DAT from one of the GASRUN.DM\* files by using the DOS COPY command at the command prompt. A complete description of the demonstration files is given in chapter V. If you wish to use the GASTHERM.RST file (discussed below), simply rename it as the GASTHERM.DAT file (make sure to save the original GASTHERM.DAT file). Finally, type SOLVGAS and the program should be off and running (note that SOLVGAS.EXE, GASTHERM.DAT, and GASRUN.DAT must be in the same directory). If the program does not run, refer to chapter VI.

### Calculating MTOT values for thermodynamic components

The first step in any modeling with SOLVGAS is to recast the gas analysis in terms of moles of thermodynamic component species. This can be readily accomplished by running program

VOLCAL (see "The first run: setting the GASRUN file" below). This section describes how to calculate the moles of component species by hand to explain what VOLCAL does.

The basic procedure is to sum the amounts of all the appropriate species for each mass balance equation as constrained by the stoichiometry of the derived species expressions in GASTHERM. For modeling of volcanic gases, this consists of two steps: 1) recasting the amounts of the major and minor gas species, H<sub>2</sub>O, H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, SO<sub>2</sub>, H<sub>2</sub>S, S<sub>2</sub>, HCl, and HF in terms of moles of the major component species, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S, HCl, and HF; and 2) calculating the amounts of trace components in the gas from condensate or treated filter samples. MTOT values for the six main components are computed with the following equations:

$$\text{MTOT H}_2 = \text{H}_2 + \text{CO} - 3 \text{SO}_2 - 2 \text{S}_2 + 4 \text{CH}_4,$$

$$\text{MTOT H}_2\text{O} = \text{H}_2\text{O} - \text{CO} + 2 \text{SO}_2 - 2 \text{CH}_4,$$

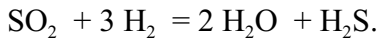
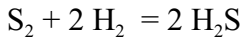
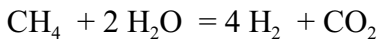
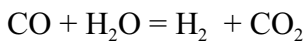
$$\text{MTOT CO}_2 = \text{CO}_2 + \text{CO} + \text{CH}_4,$$

$$\text{MTOT H}_2\text{S} = \text{H}_2\text{S} + \text{SO}_2 + 2\text{S}_2,$$

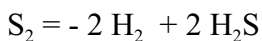
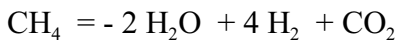
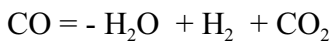
$$\text{MTOT HCl} = \text{HCl},$$

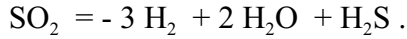
$$\text{MTOT HF} = \text{HF},$$

where concentrations are expressed as moles in the gas. These equations are the mass balance equations for the six major components in volcanic gases. Note that each equation contains a term for the component species itself. In addition, there are a number of terms for the derived species (additional derived species can be added as appropriate for a specific case). These terms are obtained from the derived-species expressions that are tabulated in GASTHERM. For the above case, there are four derived-species reactions:



These reactions can be rearranged as follows:





Finally, the derived species are added to the appropriate MTOT equation using the coefficients from the above reactions. For instance, the  $\text{S}_2$  equation contains the terms  $-2 \text{H}_2$  and  $+2 \text{H}_2\text{S}$  so a  $-2 \text{S}_2$  term must be added to the MTOT  $\text{H}_2$  equation and a  $+2 \text{S}_2$  term must be added to the MTOT  $\text{H}_2\text{S}$  equation.

For example, compute the MTOT values for the above components for the restored Dome-3 gas sample (Symonds et al., 1990) from Augustine volcano. By volume (mole %), this gas contains 83.91%  $\text{H}_2\text{O}$ , 6.04%  $\text{HCl}$ , 5.72%  $\text{SO}_2$ , 2.40%  $\text{CO}_2$ , 1.00%  $\text{H}_2\text{S}$ , 0.63%  $\text{H}_2$ , 0.20%  $\text{S}_2$ , 0.086%  $\text{HF}$ , and 0.020%  $\text{CO}$ . Converting to approximately one mole of total gas, the following MTOT values are computed:

$$\text{MTOT H}_2 = (0.63 + 0.020 - 3*5.72 - 2*0.20)/100 = -.1691\text{E}+00$$

$$\text{MTOT H}_2\text{O} = (83.91 - 0.020 + 2*5.72)/100 = 0.9533\text{E}+00$$

$$\text{MTOT CO}_2 = (2.40 + 0.020)/100 = 0.2420\text{E}-01$$

$$\text{MTOT H}_2\text{S} = (1.00 + 5.72 + 2*0.20)/100 = 0.7120\text{E}-01$$

$$\text{MTOT HCl} = (6.04)/100 = 0.6040\text{E}-01$$

$$\text{MTOT HF} = (0.086)/100 = 0.8600\text{E}-03$$

Concentrations of the trace components in volcanic gases can be estimated from analyses of condensed volcanic gas or condensates (Symonds et al., 1987), or from analyses of base-treated filters through which volcanic gas has been pumped (Finnegan et al., 1989). The basic equations is as follows:

$$C_i = R_i * M_r,$$

where  $C_i$  is the mole % of the trace component,  $i$ , in the gas;  $R_i$  is the molar ratio of  $i$  to the reference species,  $r$ , in the condensate or treated filter sample; and  $M_r$  is the mole % of  $r$  in the total gas. For condensates,  $\text{H}_2\text{O}$  is by far the best choice for the reference species because its concentration can be determined accurately in both the gas and condensate. For treated filter samples one can use total S or total Cl as the reference element.

To continue the above example, compute the trace element concentrations for the Dome-3 gas at Augustine. The average concentration of the Augustine dome condensates from Symonds et al. (1990) is as follows: 35 ppm Br, 20500 ppm Cl, 1050 ppm F, 2250 ppm sulfate, 470 ppb Al, 4800 ppb As, 33 ppb Bi, 1200 ppb Ca, 155 ppb Cd, 4 ppb Cr, 285 ppb Cu, 5700 ppb Fe, 22000 ppb K, 30 ppb Li, 75 ppb Mg, 61.5 ppb Mn, 1100 ppb Mo, 21500 ppb Na, 8.5 ppb Ni, 3200 ppb Pb, 300 ppb Sb, 150000 ppb Si, 3 ppb Sr, 20 ppb Ti, 5 ppb V and 2700 ppb Zn.

The first step is to calculate the amount of  $\text{H}_2\text{O}$  in the condensate. As an approximation, one can assume that the amount of  $\text{H}_2\text{O}$  is  $1 \times 10^6$  ppm. However, condensates are fairly salty

solutions so the amount of H<sub>2</sub>O is really less than 1x10<sup>6</sup> ppm. The amount of H<sub>2</sub>O in the condensates is calculated by the equation:

$$\text{H}_2\text{O (ppm)} = 1 \times 10^6 - (\text{total dissolved solids, in ppm}).$$

For the Dome-3 condensates, the total amount of dissolved solids is 24,049 ppm so the amount of H<sub>2</sub>O is 975,951 ppm.

Finally, the weight ratios of elements to H<sub>2</sub>O in the condensates are converted to Ri values, which are multiplied by 83.91, the appropriate Mr value for the Dome-3 sample. Dividing the Ci values by 100 (to convert to 1 mole of gas), the computed trace-element MTOT values are:

|                                 |                 |
|---------------------------------|-----------------|
| HBr                             | 0.678000000E-05 |
| NaCl                            | 0.145000000E-04 |
| KCl                             | 0.872000000E-05 |
| FeCl <sub>2</sub>               | 0.158000000E-05 |
| ZnCl <sub>2</sub>               | 0.640000000E-06 |
| Cd                              | 0.214000000E-07 |
| AlF <sub>3</sub>                | 0.270000000E-06 |
| CuCl                            | 0.695000000E-07 |
| BiCl <sub>3</sub>               | 0.245000000E-08 |
| PbCl <sub>2</sub>               | 0.239000000E-06 |
| H <sub>2</sub> MoO <sub>4</sub> | 0.178000000E-06 |
| AsCl <sub>3</sub>               | 0.992000000E-06 |
| SbCl <sub>3</sub>               | 0.382000000E-07 |
| SiF <sub>4</sub>                | 0.827000000E-04 |
| MgCl <sub>2</sub>               | 0.478000000E-07 |
| CaCl <sub>2</sub>               | 0.464000000E-06 |
| TiF <sub>4</sub>                | 0.647000000E-08 |
| CrCl <sub>4</sub>               | 0.119000000E-08 |
| NiCl <sub>2</sub>               | 0.224000000E-08 |
| MnCl <sub>2</sub>               | 0.173000000E-07 |
| VCl <sub>4</sub>                | 0.152000000E-08 |
| SrCl <sub>2</sub>               | 0.530000000E-09 |
| LiCl                            | 0.669000000E-07 |

Now it is necessary to adjust the MTOT values for HCl and HF. When analyzing volcanic gases, only total Cl and F, not HCl and HF, are measured directly (Symonds et al., 1988). Assuming that HCl and HF are the dominant species of Cl and F in the gas, total Cl and F are assigned to HCl and HF (Symonds et al., 1988). Therefore, published values of HCl and HF should be viewed as total Cl and F, including any metal halides in the gas. Since metal halides are used as component species, it is necessary to subtract the Cl and F in such component species (e.g., NaCl, AlF<sub>3</sub>) from the MTOT values for HCl and HF. In many cases it can be assumed that the abundances of trace components are small relative HCl and HF so that their effect on MTOT values of HCl and HF can be neglected. However, in rare cases such as the Na- and K-rich gases from Mount Etna (Le Guern, 1988), the trace components affect significantly the MTOT values

of HCl or HF. For the above case, the MTOT values of HCl and HF are recomputed using the equations:

$$\text{MTOT HCl} = \text{HCl} - \text{MTOT}(\text{NaCl}) - \text{MTOT}(\text{KCl}) - 2 * \text{MTOT}(\text{FeCl}_2) \\ - 2 * \text{MTOT}(\text{ZnCl}_2) \dots - \text{LiCl} = 0.6034\text{E-}01$$

$$\text{MTOT HF} = \text{HF} - 3 * \text{MTOT}(\text{AlF}_3) - 4 * \text{MTOT}(\text{SiF}_4) \\ - 4 * \text{MTOT}(\text{TiF}_4) = 0.5284\text{E-}03$$

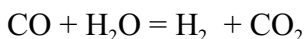
The file, GASRUN.DM1, illustrates a run that only includes the major components in the Dome-3 gas, whereas GASRUN.DM2 and GASRUN.DM3 are runs that also include the trace elements. These and other sample GASRUN files are described in chapter V.

### The first run: setting up the GASRUN file

The easiest way to set the GASRUN file is to run VOLCAL, or re-edit an old GASRUN file. To run VOLCAL, you will need the files, VOLCAL.EXE, GASTHERM.DAT, and GAS.STO, in the same directory. As discussed above, the GAS.STO file contains the stoichiometries of the derived species to be included in the input analysis. The first step in running VOLCAL is to edit the GAS.STO file to activate the appropriate derived species. The current version of the file looks like this:

|     |   |        |         |       |         |       |
|-----|---|--------|---------|-------|---------|-------|
| CO  | 4 | 1.000  | 1       | 1.000 | 3-1.000 | 2     |
| SO2 | 4 | -3.000 | 1       | 2.000 | 2       | 1.000 |
| CH4 | 4 | 4.000  | 1-2.000 | 2     | 1.000   | 3     |
| NH3 | 3 | 1.500  | 1       | 0.500 | 3       | 7     |
| S2  | 3 | -2.000 | 1       | 2.000 | 4       |       |
| O2  | 3 | -2.000 | 1       | 2.000 | 2       |       |
| H   | 2 | 0.500  | 1       |       |         |       |
| O   | 3 | -1.000 | 1       | 1.000 | 2       |       |
| C   | 4 | 2.000  | 1-2.000 | 2     | 1.000   | 3     |

where the first column in the species name, the second column is the number of species in the derived-species reaction including 1 for the derived species itself, and the last set of columns is for the moles and indexes of the component species in the reaction. Thus, the derived-species reaction for CO includes 1 mole of H<sub>2</sub> (component species #1 in GASTHERM) and 1 mole of CO<sub>2</sub> (component species #3), both on the right side of the reaction, and 1 mole of H<sub>2</sub>O (component species #2) on the left side of the reaction along with CO. Thus, the reaction looks like this:



Only the species above the first carriage return are activated. Thus, when using the above version of GAS.STO, you will only be asked for analytical data for CO and SO<sub>2</sub>. If you wish to activate other species, you will need to move them above the first carriage return. Note that several elements are included in the GAS.STO file. These are included so that one has the option



of inputting the elemental composition of a gas. Other species may be included in the GAS.STO file by adding the appropriate lines (stoichiometries of derived species can be obtained from the first line of each derived-species entry in GASTHERM).

Once the GAS.STO file is set, you are ready to run VOLCAL, which is activated by typing its name at the command prompt. Program VOLCAL is interactive and will ask you a series of questions. The questions are asked in the following order:

(1) Input the highest number of component species that will be used. The order of the component species are listed in GASTHERM and in the GASTHERM manual. Decide what components will be input and enter the number of the highest index here. For instance, if you only want to input data for the major gas species, HF included, input 6. On the other hand, if you want to input data for the major gases, Na, K, Cd, and As, input 19, which is the index for As.

(2) Input the title (two 80-character lines separated by a carriage return)

(3) Specify whether the gas data is in:

- 1) mole % for major gases and
- 2) mole % for all species
- 3) moles for all species  
ppm in condensate for trace elements,
- 4) moles for major gases and  
ppm in condensate for trace elements

If you choose option (1) or (2), the major and trace species will be input in the same units. Options (3) and (4) let you use condensate data for the trace elements. Options (1) and (3) always normalize the results to one mole of gas, whereas options (2) and (4) allow you to specify whether or not you want to normalize to one mole of gas.

(4) Input the compositional as prompted.

(5) Enter whether you want to create input files for SOLVGAS, GASWORKS, or QUIT. In this case, indicate that you want to create an input file for SOLVGAS. If you quit, the VOLOUT.DAT will be the only output.

(6) Enter the starting values for temperature, pressure, and LOGFO2. See discussions in Chapter 3 and below for setting these parameters.

(7) Modify other input parameters. Carefully select the desired options for each input parameter and make any necessary modifications from the default values here (see Chapter 3 and below for more discussion on each parameter). Generally, it best to use the default values for MTRY values as specified by VOLCAL (see below for detailed discussion on setting MTRY values).

The output from VOLCAL is given in the VOLOUT.DAT file and, if requested, in the appropriate GASRUN.DAT or WORKRUN.DAT file.

If you choose to edit an existing GASRUN file and one is not available, you will have to write the GASRUN file from scratch. Remember that GASRUN has extra records that contain format indicators and names of input variables. The extra records are used to facilitate editing, and are skipped by SOLVGAS (see chapter III). These extra records must always be present in the GASRUN file, or reading errors will result. If you are creating a file from scratch, leave these extra records blank. The formats and variables of all other records must be set carefully, according to the formats described in chapter III.

Select the desired options by giving appropriate values for input parameters in the GASRUN file as defined in chapter III. Chapter V contains details on how to set up particular calculations. For an initial calculation,  $f(\text{O}_2)$  will sometimes be specified, in which case  $\text{MTOT}(\text{H}_2)$  will be computed. Note that if the composition of the original gas includes large amounts of solids or liquids (that would form separate phases), attempting to calculate homogeneous equilibrium with SOLVGAS might fail; program GASWORKS might be needed instead to compute heterogeneous equilibrium.

MTRY values should be estimated carefully. For numerically difficult chemical systems, poor MTRY values may thwart convergence. If modeling a restored (or near-equilibrium) gas composition at its equilibrium (or vent) temperature, MTRY's for the major component species,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ , and  $\text{HF}$  are simply set equal to their analytical concentrations, and TEMPC is set to the equilibrium (or vent) temperature. This method will also work on disequilibrium mixtures if the analysis is sufficiently complete (i.e., if it includes detectable amounts  $\text{H}_2$  and  $\text{H}_2\text{S}$ ), and if TEMPC is set equal to the vent temperature.

For incomplete gas analyses or chemically difficult systems, it may be necessary to use another approach to estimate MTRY values. In this case, MTRY's for  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ , and  $\text{HF}$  may be set equal to their respective MTOT values. One notable exception is  $\text{H}_2\text{S}$ , whose MTRY value should be much less than MTOT if the gas mixture is highly oxidized (for example, if  $f\text{O}_2$  is above the hematite-magnetite oxygen buffer). A good MTRY value for  $\text{H}_2$  is  $10^{-3}$  if you are modeling a hot gas ( $> 600^\circ\text{C}$ ) with  $f(\text{O}_2)$  between NNO and QFM; lower MTRY ( $\text{H}_2$ ) values are required for cooler or more oxidized gases.

The MTRY's for trace component species,  $\text{NaCl}$ ,  $\text{KCl}$ , etc., are generally set equal to their respective MTOT values. However in halogen-poor volcanic gases, such as observed at Mount St. Helens in September 1981, some elements including  $\text{Sb}$ ,  $\text{As}$ , and  $\text{Pb}$  are transported as sulfides (Symonds and Reed, 1993); hence, the initial MTRY values of the chloride component species of these elements should be reduced accordingly.

Generally, MTRY values that are too small are better than ones that are too large. For simple chemical systems, you might choose to try running SOLVGAS without specifying MTRY values for the trace component species (e.g.,  $\text{NaCl}$ ,  $\text{H}_2\text{MoO}_4$ ,  $\text{H}_2\text{Se}$ ), in which case these are set at default values of  $10^{-10}$ .

Once all the parameters have been set in the GASRUN file, check that the GASRUN file meets all specifications given in chapter III, then run SOLVGAS. As SOLVGAS runs, the total moles of gas (GASTOT) after each iteration will appear on the screen. This value should converge to a constant value after 5 to 20 iterations. If the GASTOT converges but the iterations reach the loop limit, NLOOP, then ERPC may be too small.  $\text{ERPC} = 10^{-12}$  should work without problems. Smaller values are not recommended. (Note that in some cases, the GASTOT might converge, but SOLVGAS may still not converge, even if ERPC is set correctly).

After convergence is reached, SOLVGAS gives you the choice of changing temperature or  $f(\text{O}_2)$  (FO2LOG), or stopping. Pressure or UNACT may also be changed if NMOLF was set to 1 or if UNACT was specified, respectively, in the GASRUN file (see chapter III). If you change temperature,  $f(\text{O}_2)$  (FO2LOG), or UNACT make sure to take small incremental steps, or convergence might fail. Safe increments for  $f(\text{O}_2)$  (FO2LOG) or UNACT are typically between 1.0 and 0.5 log units (steps of 0.1 log units are required in some cases). Temperature is generally changed in intervals of  $100^\circ\text{C}$ , smaller if you want more detail in the computed results. If you are using pre-selected temperatures (TEMPC set to zero in GASRUN), input new values for NTEMP (1 through 13). To select other temperatures, input zero when the program asks for NTEMP, and SOLVGAS will let you input any temperature between  $25^\circ$  and  $1200^\circ\text{C}$ . If TEMPC was given in the GASRUN file, SOLVGAS will ask for any new temperature between  $25^\circ$  and  $1200^\circ\text{C}$ . In this case, if you desire to switch to preselected temperatures, input zero, and SOLVGAS will let you choose from the preselected temperatures. See Chapter VI if problems arise.

## **CHAPTER V. TYPES OF CALCULATIONS WITH SOLVGAS**

SOLVGAS is useful for a wide range of calculation types, which are addressed in this chapter. At the end of this chapter, we describe the test cases that are included with this software package. Chapter III contains a description of the input parameters discussed in this chapter.

### **Calculating equilibrium vapor pressures**

One use of SOLVGAS is to predict the molecular form of the major and trace components in volcanic gases at the equilibrium temperature (Symonds et al., 1992). Many studies have shown that volcanic gases stop reacting or quench at a temperature greater than or equal to the vent temperature (Gerlach, 1980a,b; Gerlach et al., 1986). This is called the last equilibrium temperature and it is the lowest temperature at which equilibrium was still maintained. To compute the distribution of species at the last equilibrium temperature, simply input the gas composition and run the calculations at the last equilibrium temperature. If metal contents in the gas are large, it may be necessary to fix  $f(\text{O}_2)$ . An example of this calculation type is given in GASRUN.DM2.

### **Temperature changes**

For many applications such as gas restorations, modeling the zonation of volcanic sublimates, or simply computing the gas speciation, it is useful to calculate the properties of the gas over a range of temperatures. Temperature changes are selected interactively in SOLVGAS. The user may select any temperatures between  $25^\circ$  and  $1200^\circ\text{C}$ , using TEMPC to specify the temperature. The NTEMP option for selecting discrete temperatures in 100-degree steps (NTEMP = 1 - 13) is disabled if a non-zero TEMPC is specified. To change from one option to the other during a SOLVGAS run, input zero when prompted for NTEMP or TEMPC. Avoid changing temperature by increments greater than  $100^\circ\text{C}$  to avoid convergence problems. Smaller temperature increments, ranging from  $50^\circ$  to  $1^\circ\text{C}$ , may be required for the calculations to

converge at temperatures below 400°C. If SOLVGAS converges easily on the first run or on the first several runs, but then fails to converge on successive runs, try changing the temperature by a smaller increment. Do not give up until you have tried temperature increments as small as 1°C; small increments might be necessary at temperatures below 100°C. Practice heating or cooling calculations with the GASRUN.DM1 file.

When computing speciation at various temperatures, SOLVGAS uses the method described by Symonds and Reed (1993) to compute  $f(\text{O}_2)$ . If one specifies  $\text{MTOT}(\text{H}_2)$ ,  $f(\text{O}_2)$  is computed at the specified temperature based on overall equilibrium. Alternatively,  $f(\text{O}_2)$  (FO2LOG) is input and SOLVGAS computes the total molar amount of component  $\text{H}_2$  in the gas that is required by overall equilibrium, including  $\text{O}_2$ - $\text{H}_2\text{O}$ - $\text{H}_2$  equilibrium. In either case, the value of  $\text{MTOT}(\text{H}_2)$  does not change with temperature, and is subsequently used to compute  $f(\text{O}_2)$  at other temperatures. The basis for this calculation is directly analogous to that used to compute pH at all temperatures in hydrothermal waters, as described by Reed and Spycher (1984).

When specifying  $f(\text{O}_2)$ , the value is generally known or can be estimated by assuming equilibrium with a solid buffer (e.g., NNO, QFM). It is essential to know a specific temperature to which the specified  $f(\text{O}_2)$  applies; run SOLVGAS at this temperature initially using a specified  $f(\text{O}_2)$ . You can then interactively change the temperature and compute the  $f(\text{O}_2)$  at other desired temperatures. Once SOLVGAS has computed  $\text{MTOT}(\text{H}_2)$ , you will probably want to input  $\text{MTOT}(\text{H}_2)$  and set FO2LOG to zero in the GASRUN file.

In the above examples, it is assumed that  $f(\text{O}_2)$  is buffered by the gas itself as temperature changes. It is also possible that  $f(\text{O}_2)$  is buffered by the rock, in which case it may be necessary to specify  $f(\text{O}_2)$  at each temperature increment as done by Symonds et al. (1992). Buffered heating or cooling is accomplished in the following steps: (1) run SOLVGAS at the starting temperature, fixing  $f(\text{O}_2)$  or  $\text{MTOT}(\text{H}_2)$ , (2) change the temperature, (3) change  $f(\text{O}_2)$  to the appropriate value for the new temperature, and (4) repeat steps 2 and 3. The GASRUN.DM2 file illustrates a buffered heating calculation.

### **Pressure changes**

When modeling the speciation of volcanic gases discharging from magmas, it is instructive to compute the distribution of species as a function of pressure (Symonds et al., 1992). Pressure can be changed interactively in SOLVGAS. To increment pressure, set the NMOLF option to 1 in the GASRUN file. After SOLVGAS converges, it will prompt you for a new pressure. At this point, you may change pressure once or repeatedly after successive re-equilibration calculations, or you may stop.

When incrementing pressure, you may fix  $f(\text{O}_2)$  for the first run. After the first equilibration, however,  $f(\text{O}_2)$  changes as pressure is incremented. The file, GASRUN.DM3, is set up for incrementing pressure.

### **Oxygen fugacity changes**

The oxygen fugacity is an important parameter in volcanic gases, and incrementing  $f(\text{O}_2)$  will allow one to study its effect on species distribution (Bernard et al., 1990). The  $f(\text{O}_2)$ , just as temperature or pressure, can be changed interactively when running SOLVGAS. In this case, the

total molar amount of the hydrogen gas component (MTOT(H<sub>2</sub>)) is recomputed for each run. We recommend that the f(O<sub>2</sub>) not be change by more than 1.0 log unit per step and, if convergence problems arise, one should use an even smaller step (0.5 to 0.1 log units). GASRUN.DM4 is a sample file set up for incrementing f(O<sub>2</sub>).

### **Changing the fugacities of gas species**

When modeling the distribution of species or the saturation of solid phases in volcanic gases, it is often useful to study the effect of varying the fugacities of component species such as H<sub>2</sub>S, HCl, or HF (Symonds et al., 1988; Bernard et al., 1990). To do this, one must specify the starting fugacity (UNACT) of the species to be varied and its SAQ number (NSUNK). One should also fix f(O<sub>2</sub>) when selecting this option if one is varying a species like H<sub>2</sub>S that affect f(O<sub>2</sub>). As with pressure, SOLVGAS will prompt for each UNACT change. GASRUN.DM5 illustrates this type of calculation.

### **Restoring gas samples**

One of the major uses of SOLVGAS is to process samples of the main volcanic gases H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, HCl, HF, CO, S<sub>2</sub>, CH<sub>4</sub>). The goals of such calculations are to test whether the samples are equilibrium mixtures, elucidate the cause(s) of disequilibrium if the samples are not equilibrium mixtures, and to restore nonequilibrium mixtures to their original equilibrium state. For a complete discussion of gas restoration procedures, the reader is referred to the papers by Terry Gerlach (Gerlach 1980a,b; Le Guern et al., 1982; Gerlach and Casadevall, 1986). Specific examples of samples restored with SOLVGAS are discussed by Symonds et al. (1990) and Kodosky et al. (1991).

One of the most useful ways to evaluate equilibrium in volcanic gas samples is to calculate correspondence temperatures (CTs). CTs are the temperature at which the analytical concentration is equal to the calculated fugacity. If the CTs for all gas species agree at a reasonable temperature, that is good evidence that the gas is an equilibrium mixture (Le Guern et al., 1982; Gerlach and Casadevall, 1986). If the CTs do not agree, then the specific way in which they disagree may help diagnose the reason(s) for disequilibrium in the sample (Gerlach 1980a,b; Le Guern et al., 1982; Gerlach and Casadevall, 1986).

To compute CTs with SOLVGAS, follow the ensuing procedure:

(1) Copy the GASTHERM.RST file, a special version of GASTHERM used for restoring volcanic gases, into GASTHERM.DAT. Make sure to save the original GASTHERM.DAT file. Modify the new GASTHERM file so that it only includes the analytically determined or otherwise abundant species. Thus, one should always include H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, and CO. If reported in the original analysis, HCl, HF, COS, CH<sub>4</sub>, and other species should also be included. The species S<sub>2</sub> is generally not reported in volcanic gas analyses, but probably should be included in the calculation of CTs and in the ensuing restoration procedure if the sample contains more than 2% total S (S<sub>2</sub> can be neglected if total S is < 2%).

(2) Compute the MTOT values for the component species, excluding atmospheric N<sub>2</sub>, Ar, and O<sub>2</sub>. If primary, N<sub>2</sub> and the noble gases can be incorporated in the input composition with no effect on the CTs, although GASTHERM currently lacks noble-gas component species. To

compute the MTOT values, input the mole numbers of the requisite species (mole% data can be treated as mole numbers if molar quantities are unavailable). When using mole% data, it is not necessary to renormalize the composition to 100% before computing MTOT values.

(3) Create a GASRUN file and set TEMPC to some high temperature, normally 1200°C.

(4) Run SOLVGAS and decrease temperature at 100°C increments until reaching 100°C (smaller increments, often as low as 1°C, can be used on successive runs to avoid interpolation). From the output, interpolate between data at different temperatures to determine the CTs, the temperature at which the computed mole numbers equal the input mole numbers.

If all the CTs agree, then the gas is an equilibrium mixture that stopped reacting at the CT. Round off the fugacities to the number of significant figures given in the original analysis and report the equilibrium temperature and corresponding  $f(\text{O}_2)$ .

In many cases, however, the CTs do not agree. If the CTs do not agree, one must diagnose the reason(s) for the deviation(s) and, if possible, restore the gas composition. Listed below are some of the most common deviant patterns for CTs and possible restoration procedures.

| <u>Diagnostic Pattern</u>                                                                                                           | <u>Possible Cause and Solution</u>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|-------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Very low CT for CH <sub>4</sub>                                                                                                     | 1) Addition of hydrothermal CH <sub>4</sub> to the volcanic gas or generation of CH <sub>4</sub> at low-temperatures in the sample bottle. In either case, remove CH <sub>4</sub> , renormalize to 100%, and recompute the CT's. See Gerlach and Casadevall (1986) and Kodosky et al. (1991).                                                                                                                                                                                                                                                                |
| Low CT's for H <sub>2</sub> , H <sub>2</sub> O, SO <sub>2</sub> , and H <sub>2</sub> S relative to CT's for CO <sub>2</sub> and CO. | 1) Water addition to sample without overall equilibration of the gas. Remove an increment of H <sub>2</sub> O from the original analysis, renormalize the adjusted analysis, and recalculate CTs. Repeat procedure until all CT's converge. See Gerlach (1980a,b).<br>2) Nonequilibrium oxidation of H <sub>2</sub> to H <sub>2</sub> O. Convert an increment of H <sub>2</sub> O to H <sub>2</sub> in the original analysis, renormalize the adjusted analysis, and recalculate CT's. Repeat procedure until all CT's converge. See Le Guern et al. (1982). |
| High CT's for H <sub>2</sub> , H <sub>2</sub> O, SO <sub>2</sub> , and H <sub>2</sub> S relative to CT's CO <sub>2</sub> and CO.    | 1) Water loss from sample without overall equilibration of the gas. Add an increment of H <sub>2</sub> O to the original analysis, renormalize the adjusted analysis, and recalculate CT's. Repeat procedure until all CT's converge. See Gerlach (1980b) and Symonds et al. (1990).<br>2) Oxidation of CO to CO <sub>2</sub> . Convert an increment of CO to CO <sub>2</sub> in the original analysis, renormalize the adjusted analysis, and recalculate CT's. Repeat procedure until all CT's converge.                                                   |

The above list is by no means comprehensive and only serves as a guide to get the user started. Some volcanic gas samples have been modified by several processes and identification of these alterations and the ensuing restoration procedures are much more complex. GASRUN.DM7 illustrates the computation of CT's and a simple gas restoration procedure.

## Computing saturation indexes of sublimates

SOLVGAS can also be used to model the zoning of sublimates around volcanic fumaroles (Symonds et al., 1987; Bernard et al., 1990). The basic technique is to calculate the temperature at which the volcanic gas saturates with a particular phase by computing saturation indexes,  $\log(Q/K)$  values, over a range of temperatures as has been done for geothermal waters (Reed and Spycher, 1984; Palandri and Reed, 2001). In this expression,  $K$  is the equilibrium constant and  $Q$  is the activity quotient. When  $\log(Q/K)$  for a phase is zero, the gas is saturated with that phase. When  $\log(Q/K)$  is greater or less than zero, the gas is oversaturated or undersaturated, respectively.

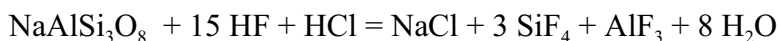
To produce data for a  $\log(Q/K)$  plot, simply start the calculations at some arbitrary but hot temperature and then decrease temperature by 100°C increments (smaller steps can be used for more detailed results). The effects of variable major gas compositions or metal contents can be studied by varying UNACT (e.g.,  $f_{H_2S}$ ) or MTOT values (e.g., for Mo) in the input file as was done by Bernard et al., (1990). The GASRUN.DM6 file is set up for computing  $Q/K$ 's for sublimates in the Merapi volcanic gas.

## Volatility calculations

For some calculations, such as determining metal volatilities (Symonds, et al, 1987) in gases where the concentrations of the major gases ( $H_2O$ ,  $HCl$ ,  $HF$ , etc.) are known, the procedure is to add arbitrary quantities of the metal components to the gas phase to approach saturation of the gas with certain minerals (e.g., assume equilibrium with sillimanite and quartz to compute the volatilized amounts of Al and Si). For such calculations the values of MTOT of the components species must be appropriately adjusted to reflect that addition of solid to the system.

For example, to add 0.01 mole of albite to a gas:

- 1) Write the equilibrium expression for albite in terms of the component species:



- 2) Using the coefficients indicated in the reaction, compute new values of MTOT for  $HF$ ,  $HCl$ ,  $NaCl$ ,  $SiF_4$ ,  $AlF_3$  and  $H_2O$ , for example:

$$MTOT(HF), \text{ new} = MTOT(HF), \text{ old} - 0.01 * 15.0$$

$$MTOT(AlF_3), \text{ new} = MTOT(AlF_3), \text{ old} + 0.01 * 1.0$$

- 3) Using the re-adjusted values for total composition, run SOLVGAS to distribute species, then check  $\log(Q/K)$  to determine the proximity to actual equilibrium.

Another, more efficient approach to volatility calculations is to use program GASWORKS, and compute the mineral saturations directly for heterogeneous equilibrium.

## Forcing equilibrium with specified solids and liquids

Forced equilibration with non-gas phases is not yet incorporated into SOLVGAS as it is in SOLVEQ. The following is provided in anticipation of this capability.

If the concentration of a gas component is unknown, but you wish to compute an amount assuming equilibration with a given solid, liquid, or gas, EQNAM and IEQ must be specified at the bottom of the GASRUN file. You can specify as many species as you want, as long as you do not violate the phase rule. Each species for which you wish to compute a total molar amount (species IEQ) must be listed among the SAQ series in the GASRUN file. MTOT values input for these species need not be specified, but you must input MTRY values. For numerical reasons, this option might cause convergence problems. In many instances, these problems are avoided if MTRY values for IEQ species are set small, typically 1.E-10. Generally, we recommend first computing equilibrium without this option, thus leaving out the species for which concentrations are unknown. You can thus obtain a set of good MTRY values for the species for which concentrations are known. Then, you can run SOLVGAS specifying EQNAM and IEQ. Remember that some cases might never converge simply because the constraints of  $f(\text{O}_2)$  and composition are such that forced equilibration with a given species is thermodynamically impossible.

### Test cases and examples of GASRUN files

The rest of this chapter describes the demonstration files included with the software. These test cases facilitate learning to run SOLVGAS and illustrate several applications of the program. The files also serve as examples of how to compute the MTOT values for component species from gas and condensate analyses. All of the examples are taken from the literature, and the reader is referred to the specific reference for each case.

AUGUSTINE DOME-3 SAMPLE (SYMONDS ET AL., 1990). NO TRACE ELEMENTS IN THIS RUN. GASRUN DEMONSTRATION 1.

```
< ERPC >< FO2LOG >< UACT >< GASTOT >< TEMPC >< PF >< RAT >
.10000E-110.0000E+00.00000E+00.10000E+01.87000E+03.10000E+01-.3000E+03
```

```
BSTO NTEM NMTT NMOL IGAM NLOO NSUN IPRI ITRE
 42    0    1    0    0   90    0    0    0
```

```
<saq> < name >    <   mtot   ><   mtry   ><  gamma >
 1 H2              -.169100000E+00 0.500000000E-02 1.0000
 2 H2O             0.953300000E+00 0.800000000E+00 1.0000
 3 CO2             0.242000000E-01 0.200000000E-01 1.0000
 4 H2S             0.712000000E-01 0.100000000E-01 1.0000
 5 HCL             0.604000000E-01 0.600000000E-01 1.0000
 6 HF              0.860000000E-03 0.800000000E-03 1.0000
```

File: GASRUN.DM1. Example showing how the distribution of species and  $f\text{O}_2$  are computed from a gas analysis. At 870°C, the computed  $\log(f\text{O}_2)$  should be -12.60 for this gas composition. Try heating and cooling the gas to see how the distribution of species varies with temperature. This example is for the restored Dome-3 gas sample from Augustine volcano (Symonds et al., 1990) and is described in chapter IV. The complete gas composition with metals is given in the GASRUN.DM2 file.



AUGUSTINE DOME-3 SAMPLE (SYMONDS ET AL., 1992). COMPUTE SPECIATION AT 870 C AND 1 ATM IN THIS RUN. GASRUN DEMONSTRATION 2.

< ERPC >< FO2LOG >< UNACT >< GASTOT >< TEMPC >< PF >< RAT >  
 .10000E-110.0000E+00.00000E+00.10000E+01.87000E+03.10000E+01-.3000E+03

BSTO NTEM NMTT NMOL IGAM NLOO NSUN IPRI ITRE  
 42 0 1 0 0 90 0 0 0

| <saq> | < name > | < mtot >        | >< mtry >       | >< gamma > |
|-------|----------|-----------------|-----------------|------------|
| 1     | H2       | -.169100000E+00 | 0.500000000E-02 | 1.0000     |
| 2     | H2O      | 0.953300000E+00 | 0.800000000E+00 | 1.0000     |
| 3     | CO2      | 0.242000000E-01 | 0.200000000E-01 | 1.0000     |
| 4     | H2S      | 0.712000000E-01 | 0.100000000E-01 | 1.0000     |
| 5     | HCL      | 0.603400000E-01 | 0.600000000E-01 | 1.0000     |
| 6     | HF       | 0.528400000E-03 | 0.800000000E-02 | 1.0000     |
| 7     | HBR      | 0.678000000E-05 | 0.100000000E-04 | 1.0000     |
| 8     | NACL     | 0.145000000E-04 | 0.100000000E-04 | 1.0000     |
| 9     | KCL      | 0.872000000E-05 | 0.100000000E-05 | 1.0000     |
| 10    | FECL2    | 0.158000000E-05 | 0.100000000E-05 | 1.0000     |
| 11    | ZNCL2    | 0.640000000E-06 | 0.100000000E-06 | 1.0000     |
| 12    | CD       | 0.214000000E-07 | 0.100000000E-07 | 1.0000     |
| 13    | ALF3     | 0.270000000E-06 | 0.100000000E-09 | 1.0000     |
| 14    | CUCL     | 0.695000000E-07 | 0.100000000E-07 | 1.0000     |
| 15    | BICL3    | 0.245000000E-08 | 0.100000000E-08 | 1.0000     |
| 16    | PBCL2    | 0.239000000E-06 | 0.100000000E-06 | 1.0000     |
| 17    | H2MOO4   | 0.178000000E-06 | 0.100000000E-06 | 1.0000     |
| 19    | ASCL3    | 0.992000000E-06 | 0.100000000E-06 | 1.0000     |
| 20    | SBCL3    | 0.382000000E-07 | 0.100000000E-07 | 1.0000     |
| 21    | SIF4     | 0.827000000E-04 | 0.100000000E-04 | 1.0000     |
| 22    | MGCL2    | 0.478000000E-07 | 0.100000000E-07 | 1.0000     |
| 23    | CACL2    | 0.464000000E-06 | 0.100000000E-06 | 1.0000     |
| 24    | TIF4     | 0.647000000E-08 | 0.100000000E-09 | 1.0000     |
| 25    | CRCL4    | 0.119000000E-08 | 0.100000000E-08 | 1.0000     |
| 27    | NICL2    | 0.224000000E-08 | 0.100000000E-08 | 1.0000     |
| 28    | MNCL2    | 0.173000000E-07 | 0.100000000E-07 | 1.0000     |
| 29    | VCL4     | 0.152000000E-08 | 0.100000000E-09 | 1.0000     |
| 30    | SRCL2    | 0.530000000E-09 | 0.100000000E-09 | 1.0000     |
| 32    | LICL     | 0.669000000E-07 | 0.100000990E-07 | 1.0000     |

File: GASRUN.DM2. Demonstrates the calculation of equilibrium vapor pressures and buffered heating calculations as described by Symonds et al. (1992). Try a run at the vent temperature of 870oC to calculate the trace-element species (see Table 1 for results). Then try their buffered heating calculation, whereby the gas is heated from 870o to 1050oC at 0.07 log units below the Ni-NiO buffer. Do this calculations in the following steps: (1) complete the first calculation at 870oC, (2) increase temperature by 20oC steps until reaching 1050oC, adjusting the log fO2 at each step to Ni-NiO - 0.07 (e.g., -12.22 at 890oC, -11.87 at 910oC, -11.52 at 930oC, -11.19 at 950oC, -10.87 at 970oC, -10.56 at 990oC, -10.26 at 1010oC, -9.97 at 1030oC, -9.68 at 1050oC). Results shown in Fig. 1.

Table 1. Calculated distribution of gas species for the Augustine volcanic gas at 870o and 1 atm pressure. Computed with the GASRUN.DM2 file. After Symonds et al. (1992).Figure 1. Calculated distribution of gas species for the Augustine volcanic gas at 870o to 1050oC and 1 atm pressure. Computed with the GASRUN.DM2 file. After Symonds et al. (1992).

|                                  |                      |                                  |                       |                                   |                                   |                                 |                                   |                                   |                                   |                                   |                                 |                                   |
|----------------------------------|----------------------|----------------------------------|-----------------------|-----------------------------------|-----------------------------------|---------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|---------------------------------|-----------------------------------|
| H <sub>2</sub> O                 | 8.4x10 <sup>-1</sup> | S                                | 7.9x10 <sup>-9</sup>  | <1x10 <sup>-11</sup>              | AlF <sub>3</sub>                  | TiO <sub>2</sub>                | (NaOH) <sub>2</sub>               | MoCl <sub>5</sub>                 | TiBr <sub>4</sub>                 | (SbS) <sub>4</sub>                | <1x10 <sup>-40</sup>            |                                   |
| HCl                              | 6.0x10 <sup>-2</sup> | SIF <sub>3</sub>                 | 7.3x10 <sup>-9</sup>  | LiOH                              | SF                                | SSF <sub>2</sub>                | AlOH                              | SrF                               | C <sub>2</sub> H <sub>2</sub>     | MoF <sub>2</sub>                  | F <sub>2</sub> O                |                                   |
| SO <sub>2</sub>                  | 5.7x10 <sup>-2</sup> | TiCl <sub>4</sub>                | 6.3x10 <sup>-9</sup>  | AsH <sub>3</sub>                  | MoO <sub>3</sub>                  | AlF <sub>2</sub>                | (KF) <sub>2</sub>                 | BiBr <sub>3</sub>                 | AlO                               | (MgBr <sub>2</sub> ) <sub>2</sub> | SiC                             |                                   |
| CO <sub>2</sub>                  | 2.4x10 <sup>-2</sup> | AsCl <sub>3</sub>                | 6.1x10 <sup>-9</sup>  | BiCl <sub>3</sub>                 | (MgCl <sub>2</sub> ) <sub>2</sub> | MgOH                            | Mg                                | (TiCl <sub>3</sub> ) <sub>2</sub> | SiH <sub>3</sub>                  | CF                                | MoF <sub>6</sub>                |                                   |
| H <sub>2</sub> S                 | 1.0x10 <sup>-3</sup> | S <sub>4</sub>                   | 6.0x10 <sup>-9</sup>  | (HF) <sub>2</sub>                 | Sb <sub>2</sub>                   | Li <sub>2</sub> ClF             | MgS                               | MgH                               | (CuBr) <sub>3</sub>               | <1x10 <sup>-24</sup>              | TiBr                            |                                   |
| H <sub>2</sub>                   | 6.2x10 <sup>-3</sup> | H                                | 5.1x10 <sup>-9</sup>  | Na                                | AlOCl                             | CaCl                            | NaO                               | (CuBr) <sub>3</sub>               | <1x10 <sup>-21</sup>              | TiCl                              | CCl <sub>4</sub>                |                                   |
| S <sub>2</sub>                   | 1.9x10 <sup>-3</sup> | SiO <sub>2</sub>                 | 4.1x10 <sup>-9</sup>  | SrCl                              | Br <sub>2</sub>                   | Cr                              | SF <sub>2</sub>                   | <1x10 <sup>-21</sup>              | TiCl                              | O <sub>3</sub>                    | CCl <sub>2</sub>                |                                   |
| HF                               | 5.4x10 <sup>-4</sup> | OH                               | 4.1x10 <sup>-9</sup>  | BrCl                              | Br <sub>2</sub>                   | Cr                              | SF <sub>2</sub>                   | <1x10 <sup>-21</sup>              | TiCl                              | O <sub>3</sub>                    | CCl <sub>2</sub>                |                                   |
| CO                               | 2.0x10 <sup>-4</sup> | Br                               | 3.3x10 <sup>-9</sup>  | AlF <sub>3</sub>                  | NiBr                              | As <sub>4</sub> O <sub>6</sub>  | CaF                               | SiH <sub>2</sub> Br               | CH <sub>2</sub>                   | CCl                               | C <sub>2</sub>                  |                                   |
| SIF <sub>4</sub>                 | 8.0x10 <sup>-5</sup> | NiCl <sub>2</sub>                | 2.2x10 <sup>-9</sup>  | Cu                                | PBF                               | SbF <sub>3</sub>                | CH <sub>3</sub>                   | SrBr                              | CaO                               | CH                                | Si <sub>2</sub> C               |                                   |
| S <sub>2</sub> O                 | 2.3x10 <sup>-5</sup> | FeCl <sub>3</sub>                | 1.6x10 <sup>-9</sup>  | CdS                               | CS                                | SrBr <sub>2</sub>               | Mn                                | LiO                               | TiF                               | MoF <sub>4</sub>                  | C <sub>2</sub> F <sub>2</sub>   |                                   |
| SO                               | 2.1x10 <sup>-5</sup> | BiCl                             | 1.6x10 <sup>-9</sup>  | (FeCl <sub>2</sub> ) <sub>2</sub> | S <sub>7</sub>                    | LiAlF <sub>4</sub>              | SiCH <sub>3</sub> F <sub>3</sub>  | (LiF) <sub>3</sub>                | MoBr <sub>4</sub>                 | (AlBr <sub>3</sub> ) <sub>2</sub> |                                 |                                   |
| H <sub>2</sub> S <sub>2</sub>    | 1.6x10 <sup>-5</sup> | VOC1 <sub>3</sub>                | 1.5x10 <sup>-9</sup>  | Ca(OH) <sub>2</sub>               | CuF                               | <1x10 <sup>-18</sup>            | AlBr <sub>3</sub>                 | LiNaO                             | MoF                               |                                   |                                 |                                   |
| CO <sub>S</sub>                  | 1.4x10 <sup>-5</sup> | SiC <sub>3</sub>                 | 1.2x10 <sup>-9</sup>  | VC1 <sub>4</sub>                  | <1x10 <sup>-14</sup>              | As <sub>4</sub> S <sub>4</sub>  | SrCl                              | Pb <sub>2</sub>                   | C <sub>2</sub> H <sub>4</sub>     | SrH                               | <1x10 <sup>-45</sup>            |                                   |
| NaCl                             | 1.4x10 <sup>-5</sup> | As <sub>2</sub>                  | 1.1x10 <sup>-9</sup>  | CuH                               | HCO                               | COClF                           | NiH                               | TiBr <sub>3</sub>                 | LiClO                             | CCl <sub>3</sub> F                | Fe(CO) <sub>5</sub>             |                                   |
| HS                               | 8.9x10 <sup>-6</sup> | SiHCl <sub>3</sub>               | 1.1x10 <sup>-9</sup>  | VO <sub>2</sub>                   | Na <sub>2</sub> SO <sub>4</sub>   |                                 | BrF                               | SiH <sub>2</sub> Br <sub>2</sub>  | (FeBr <sub>2</sub> ) <sub>2</sub> | F <sub>2</sub>                    | BrF <sub>3</sub>                |                                   |
| KCl                              | 8.7x10 <sup>-6</sup> | CrO <sub>2</sub> Cl <sub>2</sub> | 1.1x10 <sup>-9</sup>  | SiH <sub>2</sub> F <sub>2</sub>   | NiS                               | <1x10 <sup>-16</sup>            | (FeCl <sub>3</sub> ) <sub>2</sub> | SiH <sub>4</sub>                  | MoBr <sub>2</sub>                 | Mo                                | Ca <sub>2</sub>                 |                                   |
| HBr                              | 6.8x10 <sup>-6</sup> | AlCl <sub>3</sub>                | 1.0x10 <sup>-9</sup>  | S <sub>6</sub>                    | CHFO                              | (NaF) <sub>2</sub>              | VO                                | SiH <sub>2</sub>                  |                                   | (AlO) <sub>2</sub>                | C <sub>3</sub>                  |                                   |
| S <sub>3</sub>                   | 4.1x10 <sup>-6</sup> | CS <sub>2</sub>                  | 1.0x10 <sup>-9</sup>  | (CuCl) <sub>3</sub>               | FeF <sub>3</sub>                  | MnF <sub>2</sub>                | AsBr <sub>3</sub>                 | AlBr                              | <1x10 <sup>-25</sup>              | AlH <sub>2</sub>                  | AlC                             |                                   |
| SiOF <sub>2</sub>                | 7.8x10 <sup>-6</sup> | BiS                              | 7.8x10 <sup>-10</sup> | S <sub>2</sub> Cl <sub>2</sub>    | (KBr) <sub>2</sub>                | CH <sub>3</sub> Cl              | FS <sub>2</sub> F                 | K <sub>2</sub> S                  | Sr                                |                                   | SF <sub>5</sub>                 |                                   |
| FeCl <sub>2</sub>                | 1.6x10 <sup>-6</sup> | Zn                               | 7.2x10 <sup>-10</sup> | CH <sub>2</sub> O                 | MgBr <sub>2</sub>                 | HO <sub>2</sub>                 | TiOF                              | SbCl <sub>5</sub>                 | Li <sub>2</sub> O                 | <1x10 <sup>-30</sup>              | CF <sub>3</sub> OF              |                                   |
| AsS                              | 9.8x10 <sup>-7</sup> | Fe(OH) <sub>2</sub>              | 7.0x10 <sup>-10</sup> | PbBr                              | AlO <sub>2</sub> Hi               | Fe                              | COF                               | TiO                               | CHCl <sub>2</sub> F               | MoCl <sub>6</sub>                 | CF <sub>3</sub>                 |                                   |
| ZnCl <sub>2</sub>                | 6.4x10 <sup>-7</sup> | SrCl <sub>2</sub>                | 5.3x10 <sup>-10</sup> | NaAlF <sub>4</sub>                | PbH                               | SO <sub>2</sub> Cl <sub>2</sub> | LiH                               | (AlF <sub>3</sub> ) <sub>2</sub>  | C1O <sub>2</sub>                  | C <sub>2</sub> H <sub>4</sub> O   | (HF) <sub>7</sub>               |                                   |
| SiCl <sub>4</sub>                | 5.3x10 <sup>-7</sup> | SiS                              | 4.6x10 <sup>-10</sup> |                                   | HSO <sub>3</sub> F                | SiH <sub>3</sub> F              | SiBr <sub>2</sub>                 | PbF <sub>4</sub>                  | SrO                               | FO <sub>2</sub>                   | C <sub>2</sub> F <sub>4</sub>   |                                   |
| CaCl <sub>2</sub>                | 4.6x10 <sup>-7</sup> | AlCl <sub>2</sub> F              | 4.0x10 <sup>-10</sup> |                                   | <1x10 <sup>-12</sup>              | AlClF                           | S <sub>8</sub>                    | Sb <sub>3</sub> S <sub>2</sub>    | MgO                               | FO                                | CCl <sub>2</sub> F <sub>2</sub> |                                   |
| (NaCl) <sub>2</sub>              | 2.9x10 <sup>-7</sup> | NaOH                             | 3.3x10 <sup>-10</sup> |                                   | (LiCl) <sub>2</sub>               | H <sub>2</sub> O <sub>2</sub>   | SbH <sub>3</sub>                  | SO <sub>2</sub> F <sub>2</sub>    | (MgF <sub>2</sub> ) <sub>2</sub>  | CCl <sub>2</sub>                  | Li <sub>2</sub> O <sub>2</sub>  | <1x10 <sup>-50</sup>              |
| ClSiF <sub>3</sub>               | 2.8x10 <sup>-7</sup> | Cl <sub>2</sub>                  | 3.0x10 <sup>-10</sup> |                                   | CaF <sub>2</sub>                  | CrO <sub>3</sub>                | SrF <sub>2</sub>                  | (BiS) <sub>2</sub>                | SiBr <sub>3</sub>                 | CHCl                              | CBr                             | ClO <sub>3</sub> F                |
| AlF <sub>2</sub> O               | 2.7x10 <sup>-7</sup> | S <sub>5</sub>                   | 2.7x10 <sup>-10</sup> |                                   | Sif <sub>2</sub>                  | MnBr <sub>2</sub>               | AlF                               | (LiBr) <sub>2</sub>               | BiF <sub>3</sub>                  | K <sub>2</sub>                    | VF <sub>5</sub>                 | Si <sub>3</sub>                   |
| PbCl <sub>2</sub>                | 2.7x10 <sup>-7</sup> | Se <sub>1</sub>                  | 2.3x10 <sup>-10</sup> |                                   | NiCl                              | MoCl <sub>4</sub>               | BiF                               | (KOH) <sub>2</sub>                | SiHBr <sub>3</sub>                | TiS                               | C <sub>2</sub> Cl <sub>2</sub>  | C <sub>2</sub> Cl <sub>6</sub>    |
| MoO <sub>2</sub> Cl <sub>2</sub> | 1.1x10 <sup>-7</sup> | MgClF                            | 1.6x10 <sup>-10</sup> |                                   | FeBr <sub>2</sub>                 | CrO                             | Ni                                | CuF <sub>2</sub>                  | CH <sub>2</sub> ClF               | CHF                               | CCl <sub>3</sub> F              | SCl <sub>5</sub>                  |
| PbCl <sub>4</sub>                | 8.6x10 <sup>-8</sup> | TiCl <sub>3</sub>                | 1.5x10 <sup>-10</sup> |                                   | K                                 | O                               | Bi <sub>2</sub>                   | SiCl                              | CHClF <sub>2</sub>                | LifO                              | ClF <sub>5</sub>                |                                   |
| CuCl                             | 6.9x10 <sup>-8</sup> | KOH                              | 1.3x10 <sup>-10</sup> |                                   | ZnBr <sub>2</sub>                 | TiOF <sub>2</sub>               | MgF                               |                                   | <1x10 <sup>-22</sup>              | CaH                               | Ti                              | SF <sub>6</sub>                   |
| LiCl                             | 6.7x10 <sup>-8</sup> | NaF                              | 1.2x10 <sup>-10</sup> |                                   | CrO <sub>2</sub>                  | Sb <sub>2</sub> S <sub>4</sub>  | Li                                | <1x10 <sup>-19</sup>              | Ca                                | (HF) <sub>4</sub>                 | C                               | BrSF <sub>5</sub>                 |
| H <sub>2</sub> MoO <sub>4</sub>  | 6.5x10 <sup>-8</sup> | SCl <sub>2</sub>                 | 1.0x10 <sup>-10</sup> |                                   | As <sub>4</sub>                   | FeS                             | SiH <sub>3</sub> Cl               | NiF                               | SiBr                              | MoF <sub>3</sub>                  | CF <sub>4</sub>                 | C <sub>2</sub> F <sub>6</sub>     |
| MgCl <sub>2</sub>                | 4.8x10 <sup>-8</sup> | CuBr                             | 9.6x10 <sup>-11</sup> |                                   | SiH <sub>2</sub> Cl <sub>2</sub>  | (SbS) <sub>2</sub>              | FeF                               | (HF) <sub>3</sub>                 | SiCH <sub>3</sub> Cl <sub>3</sub> | V                                 | Li <sub>2</sub>                 |                                   |
| Cl                               | 4.3x10 <sup>-8</sup> | Bi                               | 9.1x10 <sup>-11</sup> |                                   | MgF <sub>2</sub>                  | NaH                             | S <sub>2</sub> Br <sub>2</sub>    | KO                                | AlO <sub>2</sub>                  | C <sub>3</sub> O <sub>2</sub>     | Ni(CO) <sub>4</sub>             | <1x10 <sup>-60</sup>              |
| SiS <sub>2</sub>                 | 3.4x10 <sup>-8</sup> | CrCl <sub>4</sub>                | 8.9x10 <sup>-11</sup> |                                   | O <sub>2</sub>                    | TiOCl                           | CaBr                              | Sb <sub>4</sub> O <sub>6</sub>    | Sb <sub>4</sub> S <sub>3</sub>    | CF <sub>3</sub>                   | C <sub>4</sub>                  |                                   |
| FSiCl <sub>3</sub>               | 3.3x10 <sup>-8</sup> | Pb                               | 8.7x10 <sup>-11</sup> |                                   | PbO                               | <1x10 <sup>-15</sup>            | AlCl                              | Bi <sub>2</sub> S <sub>3</sub>    | Cl <sub>2</sub> O                 | MoBr <sub>3</sub>                 | AlH <sub>3</sub>                | C <sub>6</sub> H <sub>6</sub>     |
| SbCl <sub>3</sub>                | 2.6x10 <sup>-8</sup> | KF                               | 5.4x10 <sup>-11</sup> |                                   | As <sub>3</sub>                   | ClO                             | MgBr                              | (LiOH) <sub>2</sub>               | MoO                               | Al                                | Al <sub>2</sub> O               | Si(CH <sub>3</sub> ) <sub>4</sub> |
| PbS                              | 2.5x10 <sup>-8</sup> | AlClF <sub>2</sub>               | 5.4x10 <sup>-11</sup> |                                   | COCl                              | K <sub>2</sub> SO <sub>4</sub>  | KH                                | SIF                               | Na <sub>2</sub>                   | MoOF <sub>4</sub>                 | C <sub>2</sub> HF               | C <sub>5</sub>                    |
| S <sub>2</sub> Cl                | 2.4x10 <sup>-8</sup> | As                               | 4.7x10 <sup>-11</sup> |                                   | ZnS                               | MgCl                            | COF <sub>2</sub>                  | Li <sub>2</sub> SO <sub>4</sub>   | SrS                               |                                   | AsF <sub>5</sub>                |                                   |
| Cd                               | 2.1x10 <sup>-8</sup> | HClO                             | 4.0x10 <sup>-11</sup> |                                   | TiF <sub>4</sub>                  | TiF <sub>2</sub>                |                                   | CH <sub>2</sub> Cl <sub>2</sub>   | CrBr <sub>4</sub>                 | <1x10 <sup>-27</sup>              | (HF) <sub>5</sub>               | <1x10 <sup>-70</sup>              |
| MnCl <sub>2</sub>                | 1.7x10 <sup>-8</sup> | LiBr                             | 3.3x10 <sup>-11</sup> |                                   | PbBr <sub>2</sub>                 | CuO                             | <1x10 <sup>-17</sup>              | CH <sub>3</sub> F                 |                                   | C <sub>2</sub> HCl                | SF <sub>4</sub>                 | CSF <sub>8</sub>                  |
| (KCl) <sub>2</sub>               | 1.7x10 <sup>-8</sup> | SiCl <sub>2</sub>                | 2.9x10 <sup>-11</sup> |                                   | Sb <sub>2</sub> S <sub>3</sub>    | NiBr <sub>2</sub>               | SOF <sub>2</sub>                  | NiO                               | <1x10 <sup>-23</sup>              | CF <sub>2</sub>                   | BrF <sub>5</sub>                |                                   |
| SiHF <sub>3</sub>                | 1.6x10 <sup>-8</sup> | TiOCl <sub>2</sub>               | 2.9x10 <sup>-11</sup> |                                   | TiCl <sub>2</sub>                 | CaOH                            | (AlCl <sub>3</sub> ) <sub>2</sub> | SiBr <sub>4</sub>                 | HAIO                              | <1x10 <sup>-35</sup>              |                                 |                                   |
| NaBr                             | 1.6x10 <sup>-8</sup> | TiF <sub>3</sub>                 | 2.5x10 <sup>-11</sup> |                                   | <1x10 <sup>-13</sup>              | AsF <sub>3</sub>                | (LiF) <sub>2</sub>                | (SbS) <sub>3</sub>                | AlH                               | MoF <sub>5</sub>                  | <1x10 <sup>-80</sup>            |                                   |
| SiO                              | 1.3x10 <sup>-8</sup> | CaBr <sub>2</sub>                | 2.4x10 <sup>-11</sup> |                                   | CaBr <sub>2</sub>                 | COCl <sub>2</sub>               | PbBr <sub>4</sub>                 | CaS                               | SiH                               | CCl <sub>3</sub>                  | CBrF <sub>3</sub>               | ClF <sub>5</sub>                  |
| SbS                              | 1.2x10 <sup>-8</sup> | LiF                              | 1.3x10 <sup>-11</sup> |                                   | CH <sub>4</sub>                   | Sr(OH) <sub>2</sub>             | ClF                               |                                   | Sb <sub>4</sub>                   | C <sub>2</sub> H <sub>6</sub>     | Mg <sub>2</sub>                 |                                   |
| SO <sub>3</sub>                  | 1.2x10 <sup>-8</sup> | Mg(OH) <sub>2</sub>              | 1.2x10 <sup>-11</sup> |                                   | (NaBr) <sub>2</sub>               | FeF <sub>2</sub>                | SO <sub>2</sub> ClF               | <1x10 <sup>-20</sup>              | Si                                | VBr <sub>4</sub>                  | C <sub>2</sub> Cl <sub>4</sub>  | <1x10 <sup>-90</sup>              |
| KBr                              | 9.3x10 <sup>-9</sup> | H <sub>2</sub> SO <sub>4</sub>   | 1.2x10 <sup>-11</sup> |                                   | KS                                | FeCl                            | SbBr <sub>3</sub>                 | SrOH                              | AlS                               | SF <sub>3</sub>                   | Si <sub>2</sub>                 | S <sub>2</sub> F <sub>10</sub>    |
| PbCl                             | 9.0x10 <sup>-9</sup> |                                  |                       |                                   | SBr <sub>2</sub>                  | F                               | NiF <sub>2</sub>                  | TiBr <sub>2</sub>                 | CHCl <sub>3</sub>                 | CHF <sub>3</sub>                  | (AlS) <sub>2</sub>              |                                   |

AUGUSTINE DOME-3 SAMPLE (SYMONDS ET AL., 1992). VARYING PRESSURE AT 1050 C IN THIS RUN. FO2 FIXED FOR FIRST STEP. GASRUN DEMONSTRATION 3

< ERPC >< FO2LOG >< UNACT >< GASTOT >< TEMPC >< PF >< RAT >  
 .10000E-11-.9680E+01.00000E+00.10000E+01.10500E+04.10000E+01-.3000E+03

BSTO NTEM NMTT NMOL IGAM NLOO NSUN IPRI ITRE  
 42 0 1 1 0 90 0 0 0

| <saq> | < name > | < mtot          | >< mtry         | >< gamma > |
|-------|----------|-----------------|-----------------|------------|
| 1     | H2       | 0.0             | 0.500000000E-02 | 1.0000     |
| 2     | H2O      | 0.953320000E+00 | 0.800000000E+00 | 1.0000     |
| 3     | CO2      | 0.242000000E-01 | 0.200000000E-01 | 1.0000     |
| 4     | H2S      | 0.712600000E-01 | 0.100000000E-01 | 1.0000     |
| 5     | HCL      | 0.603400000E-01 | 0.600000000E-01 | 1.0000     |
| 6     | HF       | 0.528400000E-03 | 0.800000000E-02 | 1.0000     |
| 7     | HBR      | 0.678000000E-05 | 0.100000000E-04 | 1.0000     |
| 8     | NACL     | 0.145000000E-04 | 0.100000000E-04 | 1.0000     |
| 9     | KCL      | 0.872000000E-05 | 0.100000000E-05 | 1.0000     |
| 10    | FECL2    | 0.158000000E-05 | 0.100000000E-05 | 1.0000     |
| 11    | ZNCL2    | 0.640000000E-06 | 0.100000000E-06 | 1.0000     |
| 12    | CD       | 0.214000000E-07 | 0.100000000E-07 | 1.0000     |
| 13    | ALF3     | 0.270000000E-06 | 0.100000000E-09 | 1.0000     |
| 14    | CUCL     | 0.695000000E-07 | 0.100000000E-07 | 1.0000     |
| 15    | BICL3    | 0.245000000E-08 | 0.100000000E-08 | 1.0000     |
| 16    | PBCL2    | 0.239000000E-06 | 0.100000000E-06 | 1.0000     |
| 17    | H2MOO4   | 0.178000000E-06 | 0.100000000E-06 | 1.0000     |
| 19    | ASCL3    | 0.992000000E-06 | 0.100000000E-06 | 1.0000     |
| 20    | SBCL3    | 0.382000000E-07 | 0.100000000E-07 | 1.0000     |
| 21    | SIF4     | 0.827000000E-04 | 0.100000000E-04 | 1.0000     |
| 22    | MGCL2    | 0.478000000E-07 | 0.100000000E-07 | 1.0000     |
| 23    | CACL2    | 0.464000000E-06 | 0.100000000E-06 | 1.0000     |
| 24    | TIF4     | 0.647000000E-08 | 0.100000000E-09 | 1.0000     |
| 25    | CRCL4    | 0.119000000E-08 | 0.100000000E-08 | 1.0000     |
| 27    | NICL2    | 0.224000000E-08 | 0.100000000E-08 | 1.0000     |
| 28    | MNCL2    | 0.173000000E-07 | 0.100000000E-07 | 1.0000     |
| 29    | VCL4     | 0.152000000E-08 | 0.100000000E-09 | 1.0000     |
| 30    | SRCL24   | 0.530000000E-09 | 0.100000000E-09 | 1.0000     |
| 32    | LICL     | 0.669000000E-07 | 0.100000000E-07 | 1.0000     |

File: GASRUN.DM3. Example file showing how to compute the distribution of gas species as a function of pressure. This particular case is for the Augustine volcanic gas, and is described by Symonds et al. (1992). Following their assumptions, fix log fO2 at -9.68 (0.07 units below the Ni-NiO buffer), for the first equilibration at 1050oC and 1 atmosphere pressure. Then, increase pressure in small steps from 1 to 100 atmospheres, letting SOLVGAS compute fO2 at pressures above 1 atmosphere. Results of this calculation are shown in Fig. 2.

Figure 2. Calculated distribution of gas species for the Augustine volcanic gas at 1050oC and at pressures from 1 to 100 atmospheres. Computed with the GASRUN.DM3 file. After Symonds et al. (1992).

Figure 2 omitted here

SEPTEMBER 1981 GAS MOUNT ST. HELENS. GAS DATA MODIFIED FROM BERNARD ET AL. (1990). VARY OXYGEN FUGACITY IN THIS RUN. GASRUN DEMONSTRATION 4.

< ERPC >< FO2LOG >< UNACT >< GASTOT >< TEMPC >< PF >< RAT >  
 .10000E-11-.9500E+01.00000E-00.10000E+01.10500E+04.10000E+01-.3000E+03

BSTO NTEM NMTT NMOL IGAM NLOO NSUN IPRI ITRE  
 42 0 1 0 0 90 0 0 0

| <saq> | < name > | < mtot >        | < mtry >        | < gamma > |
|-------|----------|-----------------|-----------------|-----------|
| 1     | H2       | 0.191300000E-02 | 0.700000000E-02 | 1.0000    |
| 2     | H2O      | 0.987317000E+00 | 0.980000000E+00 | 1.0000    |
| 3     | CO2      | 0.888300000E-02 | 0.800000000E-02 | 1.0000    |
| 4     | H2S      | 0.166000000E-02 | 0.100000000E-04 | 1.0000    |
| 5     | HCL      | 0.760000000E-03 | 0.760000000E-03 | 1.0000    |
| 6     | HF       | 0.300000000E-03 | 0.300000000E-03 | 1.0000    |
| 7     | HBR      | 0.670000000E-08 | 0.670000000E-08 | 1.0000    |
| 17    | H2MOO4   | 0.180000000E-07 | 0.100000000E-07 | 1.0000    |
| 18    | H2WO4    | 0.290000000E-09 | 0.200000000E-09 | 1.0000    |

File: GASRUN.DM4. Example file for computing the speciation of Mo and W in the Mount St. Helens gas as a function of fO2 as discussed by Bernard et al. (1990). Try varying log fO2 from -9.5 to -4.5 and see how the distribution of Mo and W gas species changes. The results of these calculations are shown in Fig. 3. The gas composition from Bernard et al. (1990) is as follows: 98.6% H2O, 0.39% H2, 0.886% CO2, 0.0023% CO, 0.067% SO2, 0.099% H2S, 0.076% HCl, and 0.03% HF. The condensates contain 95 ppb Mo, 30 ppb Br, and 3 ppb W (modified from Bernard et al., 1990). It is assumed that the condensates contain approximately 1\*106 ppm H2O.

Figure 3 omitted here

Figure 3. Log fugacities of selected volatile species of Mo and W as a function of (A) oxygen fugacity and (B) HCl fugacity for the Mount St. Helens gas at 1050oC. Computed with the GASRUN.DM4 and GASRUN DM5 files. After Bernard et al. (1990).

SEPTEMBER 1981 GAS FROM MOUNT ST. HELENS. GAS DATA MODIFIED FROM BERNARD ET AL (1990). VARY HCL FUGACITY RUN. GASRUN DEMONSTRATION 5.

< ERPC >< FO2LOG >< UNACT >< GASTOT >< TEMPC >< PF >< RAT >  
 .10000E-110.0000E+00.10000E-03.10000E+01.10500E+04.10000E+01-.3000E+03

BSTO NTEM NMTT NMOL IGAM NLOO NSUN IPRI ITRE  
 42 0 1 0 0 90 5 0 0

| <saq> | < name > | < mtot >        | >< mtry >       | >< gamma > |
|-------|----------|-----------------|-----------------|------------|
| 1     | H2       | 0.191300000E-02 | 0.700000000E-02 | 1.0000     |
| 2     | H2O      | 0.987317000E+00 | 0.980000000E+00 | 1.0000     |
| 3     | CO2      | 0.888300000E-02 | 0.800000000E-02 | 1.0000     |
| 4     | H2S      | 0.166000000E-02 | 0.100000000E-04 | 1.0000     |
| 5     | HCL      | 0.760000000E-03 | 0.760000000E-03 | 1.0000     |
| 6     | HF       | 0.300000000E-03 | 0.300000000E-03 | 1.0000     |
| 7     | HBR      | 0.670000000E-08 | 0.670000000E-08 | 1.0000     |
| 17    | H2MOO4   | 0.180000000E-07 | 0.100000000E-07 | 1.0000     |
| 18    | H2WO4    | 0.290000000E-09 | 0.200000000E-09 | 1.0000     |

File: GASRUN.DM5. Example file for computing the speciation of Mo and W in the Mount St. Helens gas as a function of HCl fugacity as discussed by Bernard et al. (1990). Try varying log fHCl from -4.0 to -1.0 and see how the distribution of Mo and W gas species changes. The results of these calculations are shown in Fig. 3. Note that fO2 does not change significantly over the course of the calculations and therefore it is not necessary to fix FO2LOG. The gas composition for this run is given in the GASRUN.DM4 example.

MERAPI SAMPLE 79-2 FROM LE GUERN ET AL. (1982). MEAN CONDENSATE ANALYSIS FROM SYMONDS ET AL, 1987. COMPUTE Q/K RUN. GASRUN DEMO 6

< ERPC >< FO2LOG >< UNACT >< GASTOT >< TEMPC >< PF >< RAT >  
 .10000E-110.0000E+00.10000E+00.10000E+01.91500E+03.10000E+01-.3000E+03

BSTO NTEM NMTT NMOL IGAM NLOO NSUN IPRI ITRE  
 42 0 1 0 0 90 0 0 0

| <saq> | < name > | < mtot >        | >< mtry >       | >< gamma > |
|-------|----------|-----------------|-----------------|------------|
| 1     | H2       | -.191000000E-01 | 0.100000000E-01 | 1.0000     |
| 2     | H2O      | 0.910100000E+00 | 0.890000000E+00 | 1.0000     |
| 3     | CO2      | 0.723000000E-01 | 0.700000000E-01 | 1.0000     |
| 4     | H2S      | 0.243000000E-01 | 0.110000000E-01 | 1.0000     |
| 5     | HCL      | 0.588000000E-02 | 0.590000000E-02 | 1.0000     |
| 6     | HF       | 0.327000000E-03 | 0.300000000E-03 | 1.0000     |
| 7     | HBR      | 0.322000000E-05 | 0.300000000E-05 | 1.0000     |
| 9     | KCL      | 0.288000000E-05 | 0.100000000E-05 | 1.0000     |
| 10    | FECL2    | 0.259000000E-05 | 0.100000000E-05 | 1.0000     |
| 11    | ZNCL2    | 0.246000000E-05 | 0.100000000E-05 | 1.0000     |
| 12    | CD       | 0.286000000E-08 | 0.100000000E-08 | 1.0000     |
| 13    | ALF3     | 0.244000000E-04 | 0.100000000E-05 | 1.0000     |
| 14    | CUCL     | 0.228000000E-07 | 0.100000000E-07 | 1.0000     |
| 15    | BICL3    | 0.462000000E-08 | 0.100000000E-14 | 1.0000     |
| 16    | PBCL2    | 0.621000000E-07 | 0.100000000E-07 | 1.0000     |

|    |        |                 |                 |        |
|----|--------|-----------------|-----------------|--------|
| 17 | H2MOO4 | 0.325000000E-07 | 0.100000000E-07 | 1.0000 |
| 18 | H2WO4  | 0.114000000E-07 | 0.100000000E-07 | 1.0000 |
| 19 | ASCL3  | 0.114000000E-06 | 0.100000000E-12 | 1.0000 |
| 20 | SBCL3  | 0.793000000E-08 | 0.100000000E-11 | 1.0000 |
| 22 | MGCL2  | 0.397000000E-05 | 0.100000000E-05 | 1.0000 |
| 25 | CRCL4  | 0.247000000E-07 | 0.100000000E-07 | 1.0000 |
| 26 | COCL2  | 0.546000000E-09 | 0.100000000E-09 | 1.0000 |
| 27 | NICL2  | 0.274000000E-07 | 0.100000000E-07 | 1.0000 |
| 28 | MNCL2  | 0.527000000E-07 | 0.100000000E-07 | 1.0000 |
| 29 | VCL4   | 0.537000000E-07 | 0.100000000E-12 | 1.0000 |
| 30 | SRCL2  | 0.220000000E-07 | 0.100000000E-07 | 1.0000 |
| 31 | GACL3  | 0.185000000E-07 | 0.100000000E-07 | 1.0000 |
| 32 | LICL   | 0.255000000E-07 | 0.100000990E-07 | 1.0000 |

File: GASRUN.DM6. Sample file for computing log (Q/K) values for the Merapi sublimates (after Symonds et al., 1987). To compute log (Q/K) values, decrease temperature at 100oC steps from 915o to 100oC (use smaller increments for more detail). Compare the results with Fig. 4. The gas composition from Le Guern et al. (1982) is as follows: 88.87% H2O, 1.54% H2, 7.07% CO2, 0.16% CO, 1.15% SO2, 1.12% H2S, 0.08% S2, 0.59% HCl, and 0.04% HF. The condensates contain 7 ppm K, 9 ppm Fe, 10 ppm Zn, 20 ppb Cd, 41 ppm Al, 90 ppb Cu, 60 ppb Bi, 800 ppb Pb, 200 ppb Mo, 130 ppb W, 530 ppb As, 60 ppb Sb, 6 ppm Mg, 80 ppb Cr, 2 ppb Co, 100 ppb Ni, 180 ppb Mn, 170 ppb V, 120 ppb Sr, 80 ppb Ga, 11 ppb Li, 3500 ppm Cl, 770 ppm SO4, 170 ppm F, and 16 ppm Br (after Symonds et al., 1987).

Figure 4 omitted

Figure 4. Plot of log (Q/K) values for sublimate minerals from Merapi volcano, Indonesia. Computed with the GASRUN.DM6 file. After Symonds et al. (1987).

16 SEPT. 1981 GAS ANALYSIS FROM MT. ST. HELENS (GERLACH AND CASADEVALL (1986). COMPUTE CTS IN THIS RUN. GASRUN DEMONSTRATION 7.

```
< ERPC >> FO2LOG >> UNACT >> GASTOT >> TEMPC >> PF >> RAT >
.10000E-110.0000E+000.0000E+00.10000E+02.67000E+03.10000E+01-.3000E+03
```

```
BSTO NTEM NMTT NMOL IGAM NLOO NSUN IPRI ITRE
 42    0    1    0    0    90    0    0    0
```

```
saq> < name >      <      mtot      >>      mtry      >>      gamma >
  1 H2              0.263840000E-01 0.100000000E-01 1.0000
  2 H2O             0.986446580E+02 0.890000000E+00 1.0000
  3 CO2             0.914321000E+00 0.700000000E-00 1.0000
  4 H2S             0.210000000E+00 0.110000000E-00 1.0000
  5 HCL             0.890000000E-01 0.590000000E-01 1.0000
```

GASRUN.DM7. Sample file demonstrating how to compute CTs and how to restore a gas analysis (taken from Gerlach and Casadevall 1986, p. 115-116). The raw gas analysis is as follows: 98.50% H<sub>2</sub>O, 0.244% H<sub>2</sub>, 0.913% CO<sub>2</sub>, 0.0013% CO, 0.073% SO<sub>2</sub>, 0.137% H<sub>2</sub>S, 0.089% HCl, and 0.000021% CH<sub>4</sub>. To calculate CTs, follow the procedure in the text and only activate the species, H<sub>2</sub>O, H<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub>, CO, HCl, and CH<sub>4</sub> in the GASTHERM file. The CTs for this analysis are 655oC for H<sub>2</sub>O, H<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S; 670oC for CO<sub>2</sub>; 669oC for CO; and 183oC for CH<sub>4</sub> (the concentration of HCl does not change with temperature so a CT for HCl is meaningless). As discussed by Gerlach and Casadevall (1986), the gas can be restored by removing CH<sub>4</sub> from the original analysis and converting trial amounts of H<sub>2</sub>O to H<sub>2</sub>. For the restoration, only activate the species, H<sub>2</sub>O, H<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub>, and CO in the GASTHERM file. As shown in Table 2, all the CTs converge at 665.7oC after converting 0.0275 moles of H<sub>2</sub>O to H<sub>2</sub> in the original analysis. This is an overdetermination of the data to illustrate the restoration procedure. Normally, one would stop the restoration at 666oC after converting 0.027 moles of H<sub>2</sub>O to H<sub>2</sub>. The small discrepancies between the SOLVGAS results and those from Gerlach and Casadevall (1986) are probably due to differences in the thermochemical data.

Table 2. The GASOUT file for the restored 16 Sept. 1981 gas analysis from Mount St. Helens. The unrestored analysis is given in the GASRUN.DM7 file.

RAW GAS ANALYSIS FROM MT. ST. HELENS COLLECTED BY E. CORAZZA ON 16 SEPT. 1981.  
 REPORTED ON P. 115 OF GERLACH AND CASADEVALL (1986). COMPUTE CTS IN THIS RUN.  
 ++++++  
 NO. OF LOOPS USED = 5 LOOP LIMIT = 90

TEMPERATURE: 665.7 DEGREES CENTIGRADE  
 PRESSURE: 1.000 ATM  
 TOTAL MOLES OF GAS = .9995731E+02

| SPECIES  | MOLE NUMBER | MOLE FRACTION | PARTIAL PRESSURE | FUGACITY    | LOG(F)   | GAMMA   |
|----------|-------------|---------------|------------------|-------------|----------|---------|
| 1 H2     | 0.27152E+00 | 0.27163E-02   | 0.27163E-02      | 0.27163E-02 | -2.5660  | 1.00000 |
| 2 H2O    | 0.98472E+02 | 0.98515E+00   | 0.98515E+00      | 0.98515E+00 | -0.0065  | 1.00000 |
| 3 CO2    | 0.91300E+00 | 0.91339E-02   | 0.91339E-02      | 0.91339E-02 | -2.0393  | 1.00000 |
| 4 H2S(G) | 0.13699E+00 | 0.13705E-02   | 0.13705E-02      | 0.13705E-02 | -2.8631  | 1.00000 |
| 5 HCL    | 0.89000E-01 | 0.89038E-03   | 0.89038E-03      | 0.89038E-03 | -3.0504  | 1.00000 |
| 6 O2     | 0.20419E-14 | 0.20427E-16   | 0.20427E-16      | 0.20427E-16 | -16.6898 | 1.00000 |
| 7 CO     | 0.13007E-02 | 0.13012E-04   | 0.13012E-04      | 0.13012E-04 | -4.8856  | 1.00000 |
| 8 SO2    | 0.73007E-01 | 0.73038E-03   | 0.73038E-03      | 0.73038E-03 | -3.1365  | 1.00000 |

SPECIES WHOSE LOG(MOLES) = -300.00 IS ACTUALLY LESS ABUNDANT THAN THAT  
 SPECIES WITH LOG FUGACITY LESS THAN -300.0 IS NOT PRINTED

| COMPONENT | MOLE NUMBER    | TOTAL MOLES    | PPM            | MOLE FRACTION (TOTAL) |
|-----------|----------------|----------------|----------------|-----------------------|
| 1 H2      | 0.27151902E+00 | 0.53800000E-01 | 0.59348059E+02 | 0.53822979E-03        |
| 2 H2O     | 0.98472488E+02 | 0.98617200E+02 | 0.97222898E+06 | 0.98659321E+00        |
| 3 CO2     | 0.91299932E+00 | 0.91430000E+00 | 0.22019879E+05 | 0.91469051E-02        |
| 4 H2S(G)  | 0.13699344E+00 | 0.21000000E+00 | 0.39159953E+04 | 0.21008969E-02        |
| 5 HCL     | 0.89000000E-01 | 0.89000000E-01 | 0.17758006E+04 | 0.89038013E-03        |



## CHAPTER VI. PROBLEMS AND ERRORS: HELPFUL TIPS

SOLVGAS generally runs easily. If all input data are set correctly, and the chemical system is not too persnickety, problems are rare. In this chapter, we review the most common problems encountered with SOLVGAS. These problems can be divided into three categories: "clean stops", which are execution stops and error messages built into SOLVGAS, and that are not related to other system errors, "bombs" (execution abortions) related to input/output errors, and "bombs" resulting from convergence problems. Most "bombs" are related to simple problems, such as mistakes in the input data and formats, and are easily corrected. More serious "bombs" relate to numerical problems and machine precision, and might require more effort to solve.

### Clean stops and built-in error messages

All execution stops built into SOLVGAS 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 GASRUN EXCEEDS THE CURRENT ARRAY DIMENSION (\_\_\_). CHECK GASRUN DATA FILE.

From routine: MAIN. Execution stop: YES

Self explanatory. SOLVGAS accepts only up to a certain number of component species (current limit is 50). This message might also occur if there is no blank line after the component species data in the GASRUN 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 SOLVGAS (current limit is 50). Check for format mistakes in the GASRUN file, or for an invalid SAQ number.

NUMBER OF SPECIES READ IN GASTHERM EXCEEDS MAXIMUM OF \_\_\_\_ . LAST NAME READ IS: \_\_\_\_\_ (NS = \_\_\_\_).

From routine: MAIN. Execution stop: YES

The total number of gaseous species read in GASTHERM cannot exceed the dimension of arrays specified in SOLVGAS. The current limit is 999 species, including the component species. Reduce the number of components in your chemical system, or increase the array dimensions in SOLVGAS. Note that NS in this message should equal the current allowed maximum value.

SPECIES \_\_\_\_\_ IN GASTHERM HAS TOO MANY COMPONENTS. ITOT FOR THAT SPECIES IS \_\_\_\_; MAXIMUM IS \_\_\_\_

From routine: MAIN. Execution stop: YES

Derived-species reactions in the GASTHERM data file are limited to a certain amount of stoichiometric components (current limit is 8). The number of stoichiometric components to be read is indicated for each reaction by the integer ITOT in the GASTHERM data file (see appendix). If ITOT is too large, or improperly aligned, this message will occur.

\*\* WARNING ! MOLE NUMBER OF \_\_\_\_\_ LESS THAN \_\_\_\_\_

From routine: MAIN. Execution stop: NO

This message is printed if, during the iteration process, the mole number of a component species reaches the lowest value allowed by the computer without underflow errors (the current lowest limit is 10-300). Note that convergence will most likely fail if this occurs (even though GASTOT might converge to a constant value).

\*\*\*\* 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, SOLVGAS will stop. If the GASTOT values printed on the screen after each iteration seem to converge, ERPC might be too small. Generally, an ERPC of 10-12 should work, but some runs may require slightly larger ERPC values. If the error is encountered on the first run, check all input data and readjust MTRY to better estimates. If the error occurs after the first equilibration, repeat the calculation with a smaller step size. If the above methods do not work, then you have a convergence problem (see chapter VI).

NUMBER OF SOLIDS AND LIQUIDS READ IN GASTHERM EXCEEDS MAXIMUM OF \_\_\_\_.  
LAST SPECIES READ IS: \_\_\_\_\_

From routine: MINSAT. Execution stop: YES

The total number of solids and liquids read in GASTHERM cannot exceed the dimension of arrays specified in SOLVGAS. The current limit is a total of 900 solids and liquids. Reduce the number of components in your chemical system, or increase the array dimensions in SOLVGAS.

SPECIES \_\_\_\_\_ IN GASTHERM HAS TOO MANY COMPONENTS. ITOT FOR THAT  
SOLID OR LIQUID IS \_\_\_\_; MAXIMUM IS \_\_\_\_

From routine: MINSAT. Execution stop: YES

Derived-species reactions in the GASTHERM data file are limited to a certain amount of stoichiometric components (current limit is 8). The number of stoichiometric components to be read is indicated for each reaction by the integer ITOT in the GASTHERM data file (see appendix). 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 will occur if the system is overdetermined (i.e., if a component species can be expressed in terms of other component species, or if two component species in the matrix are similar). Check to see if, by mistake, similar solids or liquids are specified when forcing equilibration, or if one or more component species repeat in GASRUN.

---

Future error messages

Unlike SOLVEQ, SOLVGAS does not currently have the ability to force equilibration with solids or liquids. When it does the following clean stop error messages will be programmed in.

IEQ FOR \_\_\_\_\_ IS NOT CORRECTLY SPECIFIED (=\_\_\_\_) CHECK INPUT FORMAT.

From routine: MAIN. Execution stop: NO

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

FOLLOWING GIVEN MINERAL NOT FOUND IN GASTHERM: \_\_\_\_\_

From routine: MAIN. Execution stop: YES

EQNAM names specified in the GASRUN file must spell exactly as in the GASTHERM data file. A spelling mistake will cause a mismatch. Also, this message will occur if you specify a solid or liquid which has its suppression flag enabled (SUP not blank or 'G') in the GASTHERM data file (see appendix).

GIVEN MINERAL \_\_\_\_\_ DOES NOT CONTAIN \_\_\_\_\_

From routine: MAIN. Execution stop: YES

If forcing equilibrium with a solid or liquid (EQNAM in gasrun 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 liquid.

---

### **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

These errors commonly occurs when files are not assigned correctly. Because SOLVGAS does not incorporate file assignment statements, you have to 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 GASRUN file is within format specifications. The GASTHERM data file needs one blank line at the bottom of the solid and liquid data. Check to see if there is enough disk space for output files.

#### - ILLEGAL DECIMAL CHARACTERS

This will happen anytime SOLVGAS reads something that it is not expected to read. Check all input file formats. The GASTHERM data file needs a blank line after the gas data and after the solid and liquid data. The input file GASRUN needs blank lines between the different sections (see chapter III). Also, make sure that BSTOT is set to the correct value: currently 42.

### **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, but it is not necessarily so. A convergence problem causes SOLVGAS to reach the loop limit (NLOOP) without converging, or to "bomb" before that limit is reached. Typical convergence "bombs" consist of OVERFLOWS and UNDERFLOWS, as well as wrong types of arguments for logarithm and exponential functions. If you encounter convergence problems, the first thing to do is to check that all the previously discussed problems are taken care of (this will take care of 90% of the problems).

If starting an original run, convergence problems generally result from poor guesses for MTRY values (see chapter III). Specifying MTRY values that are too small seems to be better than specifying ones that are too large. If a convergence problem occurs after changing temperature, pressure,  $f(\text{O}_2)$ , or UNACT try to restart the calculation and change the variable by a smaller increment. Convergence problems can also be related to the composition of the gas phase. SOLVGAS brackets all mole numbers of derived species between  $10^{-300}$  and a value of  $10 * \text{GASTOT}$  to avoid over and underflow problems on most computer systems. However, it might happen that the mole number of a component species becomes very small, and that convergence problems result.

Convergence problems may also occur if the component species becomes much less abundance than its derived species. The best example of such a problem is running an oxygenated gas wherein  $\text{H}_2\text{S}$ , the component species for sulfur, is much less than  $\text{SO}_2$ , the main derived sulfur species for oxygenated gases. The speciation calculations with an oxygenated gas will have a difficult time converging on the correct MTRY value for  $\text{H}_2\text{S}$ ; better estimates of the MTRY ( $\text{H}_2\text{S}$ ) values may be required. Similar problems may also arise with the trace component species (e.g.,  $\text{SbCl}_3$ ,  $\text{AsCl}_3$ ) if one is modeling a halogen-poor gas composition.

In some cases, it might be easy to obtain convergence for the major components ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{HF}$ ), but difficult to reach convergence for the entire gas composition with trace

elements. In this case, run the major gas composition first, and put the solved MTRY values for the major species into GASRUN. Then, adding trace components one at a time, adjust the MTRY value for the newly-added species until convergence is reached. After each step, the solved MTRY values should be put in GASRUN.

If the discussion above did not help your problems, 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 problem(s). If convergence is not reached, but there are no obvious reasons as for why, there might be numerical difficulties with the Newton-Raphson convergence process itself, and you need a piece of dark chocolate. There is an option in SOLVGAS to improve convergence, ITREF. ITREF will generally not help unless there are precision limit problems with the computer, but such problems are rare with modern computers and compilers. In any case, ITREF is a last resort option. If ITREF does 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.

## APPENDIX

### A. MORE ABOUT THE GASTHERM DATA FILE

The GASTHERM file contains all thermodynamic data for gas, solid, and liquid species. This file generally does not have to be modified by the user. GASTHERM is divided into four parts: the comment area, the component species data, the derived gas species data, the solid and liquid data, and optional miscellaneous data.

#### The comment area

The comment area is skipped by SOLVGAS, 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 GASTHERM, 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: "\*" in 8 or more first columns

#### The component species data

These data immediately follow the line of 8 or more stars, and consist of one record per component species, as follows:

\* Each record (A8,5X,F9.4): NAME, W

where, for each component species, NAME is the name and W the molecular weight.

The order of these records should not be changed. For the stoichiometries of derived gas species, solids, and liquids described in the next sections, each component species is identified by its position in the component species data area (H<sub>2</sub> is 1, H<sub>2</sub>O is 2, HBr is 7, etc), and the order of component species in this area is critical. The total number of component species in GASTHERM may vary, but must be consistent with the array dimensions specified in the programs reading this file. To insure proper reading of this file, the total number of component species, BSTOT, in GASTHERM, must be given in the input file specific to each calculation (e.g., WORKRUN or GASRUN). As of this writing, the component species listed in GASTHERM number 42.

#### The derived species data

This area contains data for gaseous derived species, and immediately follows the component species data area. The data for each derived species is given by 4 records, which are the following:

\* 1st record (A8,7X,A1,I1,7(F6.3,I2),F5,3,I2): NAME, SUP, ITOT, COEF(i) and SPEC(i) i = 1 to ITOT

where NAME is the name of the derived species. If not blank (i.e., if a "\$" is here), SUP will cause the species to be suppressed from the calculations. ITOT is the number of component species in the derived species, plus one. 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<sub>2</sub>, 7 for HBr, etc.). The i = 1 position is left blank. If a derived species contains H<sub>2</sub>, H<sub>2</sub> must be entered in the i = 2 position.

\* 2nd record (A8,8F8.3)

\* 3rd record (A8,8F8.3)

\* 4th record (A8,5E14.7)

The 2nd and 3rd records contains log K data for the derived-species stoichiometry at 25°, 100°, 200°, 300°, 400°, 500°, 600°, 700°, 800°, 900°, 1000°, 1100°, and 1200°C. The end of the 2nd record also contains a reference code for the data, with the exact reference given in the comment area and in the GASTHERM manual. The 4th record contains regression coefficients a, b, c, d, and e to calculate log K as a function of temperature, such that  $\log K = a + b/T + c \cdot T + d/T^2 + e \cdot \log_{10}(T)$ , with T in K, from 298.15 to 1473.15 K (25° to 1200°C).

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

\* Last record: must be BLANK.

#### The mineral and liquid data

The data for solids and liquids immediately follows the derived gas data. The data for each solid and liquid are given by 4 records, which are as follows:

\* 1st record (A8,A1,1X,F7.2,I2,1X,7(F6.3,I2),F4.3,/,I2,  
F6.3, I2, F6.3): MIN, SUP, XMOLW, ITOT, COEFM(i) and SPECM(i) i = 1 to ITOT, B,  
JSOLS

MIN is the name of the solid or liquid species. If SUP is not blank, the solid or liquid will be suppressed from the calculation. XMOLW is the molecular weight. ITOT is the number of component species in the solid or liquid. COEFM(i) contains the stoichiometric coefficient for species SPECM(i) in the solid or liquid. SPECM(i) identifies the component species in the solid or liquid, and corresponds to the position of component species in the component species area (e.g., SPECM = 1 for H<sub>2</sub>, 7 for HBr, etc.). B and JSOLS are non zero for solid or liquid solutions.

If a solid or liquid stoichiometry is long (ITOT>6), the 1st record will spread on a second line, resulting in a total of five records for some species (e.g., for alunite and KAl<sub>2</sub>SO<sub>4</sub>). For solid or liquid solutions, B represents the exponent for solid or liquid end-members to be used to calculate activity using ideal multi-site mixing, and JSOLS identifies the index of the solid or liquid solution (if any) to which this solid or liquid belongs. See the comment area in GASTHERM to check the current solid solutions and their JSOLS indexes.

\* 2nd record (A8,8F8.3)

\* 3rd record (A8,8F8.3)

\* 4th record (A8,5E14.7)

The 2nd, 3rd, and 4th records for solids and liquids are similar to the 2nd, 3rd, and 4th records for derived species (see derived species section). In the future, the 4th record will also contain one more variable which is the density of the solid or liquid in g/cm<sup>3</sup> for volume calculations. If density is not given (as is the current case), SOLVGAS will assume a density of 2.5.

The total number of solid and liquid solutions and of their end- members must be consistent with the array dimensions specified in the program. The total number of solids and liquids in GASTHERM may vary, but must also be consistent with array dimensions. To insure proper reading of GASTHERM, a blank line has to be inserted after the data for the last solid or liquid species:

\* Last record: must be BLANK.

#### Optional miscellaneous data

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

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