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Short note

GFluid: An Excel spreadsheet for investigating C–O–H fluid composition under high temperatures and pressures ☆

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1. Introduction

Carbon (C), Oxygen (O) and Hydrogen (H) are major elements in most geological fluid systems. Through chemical reactions, these elements form fluids composed of H_2O, CO_2, CH_4, H_2, O_2, CO, C_2H_6 and their mixtures, and these fluids play a key role in many geologic processes. Presented is an easy-to-use Microsoft Excel spreadsheet to calculate the compositions and the thermodynamic properties (pressure–volume–temperature relationship (*PVT*), fugacity coefficient, chemical potential, enthalpy, etc.) of the C–O–H system at temperature and pressure (*TP*) conditions up to 2573 K and 10 GPa under specific geological conditions with defined oxygen fugacity (f_{O_2}) or atomic fraction of oxygen X_o, where $X_o = n_o/(n_o + n_H)$, and n_o and n_H are the moles of oxygen and hydrogen atoms, respectively.

The spreadsheet is a reliable tool to investigate C–O–H fluid in the Earth's upper mantle. Compared with previous programs like GEOFLUID (Larsen, 1993) and C–O–H (Huizenga, 2001, 2005), it adds a new global free energy minimization mode combined with an improved equation of state (EOS), which omits the ideal mixing assumption when handling fluid mixture and improves the accuracy and reliability, especially under high *TP* conditions. The introduction of ethane in the calculation results in some interesting aspects which were ignored in previous studies. The program is available at the author's website (http://www.geochem-model.org/programs.htm).

2. Basic principles in calculation

The maximum number of species that can be obtained in the C–O–H system are H_2O, CO_2, CH_4, H_2, O_2, CO, and C_2H_6 in a fluid phase, and either graphite or diamond in a solid phase. When the solid carbon phase presents, the fluid phase is carbon saturated and the degrees of freedom are reduced to three; we need only to define one more variable besides temperature and pressure to determine the composition of fluid. Otherwise, the carbon activity must be given for the system to be determined if carbon is undersaturated.

The equilibrium composition corresponds to the minimum of system's Gibbs free energy or the sum of chemical potentials of all species. For any fluid species in a mixture, the chemical potential of species *i* can be expressed as

$$\mu_i = \mu_i^0(T) + RT\ln\frac{f_i}{P^0} \quad (1)$$

where

$$f_i = x_i P\hat{\phi}_i = n_i P\hat{\phi}_i/n_t \quad (2)$$

μ_i^0 is the standard state chemical potential. n_i, x_i, $\hat{\phi}_i$ and f_i are the number of moles, molar fraction, fugacity coefficient and fugacity of specie *i*, respectively. n_t is the total molar number and P^0 is the pressure at standard state (0.1 MPa).

☆ Code available from server at http://www.iamg.org/CGEditor/index.htm

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The first part of Eq. (1), μ_i^0 relies on temperature (T, in Kelvin) only. According to statistical mechanics, it can be calculated as

$$\mu^0(T) = -RT\ln(qkT/V) + RT\ln P^0 \tag{3}$$

where k is Boltzmann constant, and q is the total partition function calculated from statistical mechanics. The molecular constants for each species can be found in the publications of Huber and Herzberg (1979) and Shimanouchi (1972).

As indicated by Eq. (2), the contribution of pressure can be evaluated by the fugacity coefficient, which is the integral of partial volume $\bar{V}_i$ with specific EOS

$$\ln\hat{\phi}_i = -\frac{1}{RT}\int\left(\frac{RT}{P} - \bar{V}_i\right)dP. \tag{4}$$

For the solid carbon phase, the explicit Gibbs free energy equation of state for graphite/diamond proposed by Fried and Howard (2000) is adopted. Its chemical potential is expressed as

$$\mu_C = \mu_C^*(T,P) + RT\ln a_C \tag{5}$$

where $\mu_C^*(T,P)$ is the chemical potential of graphite/diamond at T and P and a_C denotes the carbon activity.

3. EOS for fluid mixtures up to 2573 K, 10 GPa

EOS for fluid mixtures plays a key role in studying the equilibrium composition in the C–O–H system. However, accurate EOS, especially for mixtures valid up to high TP conditions, are rare. Thus many former studies use EOS for pure species instead, and adopt ideal mixing, which assumes the fugacity coefficients of each species in mixture are the same as their pure state. Experimental studies have shown substantial deviation from ideal behavior in a higher TP region, therefore, considering efficiency and accuracy, we recommend the use of the EOS of Zhang and Duan (2009) to calculate non-ideal fluid fugacities for species H_2O, CO_2, CH_4, H_2, O_2, CO, and C_2H_6 and their mixtures. The formulation of that EOS is based on both experimental and molecular simulation data up to 2573 K and 10 GPa, and it takes the form

$$\begin{aligned}Z = \frac{P_mV_m}{RT_m} &= 1 + \frac{a_1 + a_2/T_m^2 + a_3/T_m^3}{V_m} + \frac{a_4 + a_5/T_m^2 + a_6/T_m^3}{V_m^2} \\ &+ \frac{a_7 + a_8/T_m^2 + a_9/T_m^3}{V_m^4} + \frac{a_{10} + a_{11}/T_m^2 + a_{12}/T_m^3}{V_m^5} \\ &+ \frac{a_{13}}{T_m^3V_m^2}\left(a_{14} + \frac{a_{15}}{V_m^2}\right)\exp\left(-\frac{a_{15}}{V_m^2}\right)\end{aligned} \tag{6}$$

$$P_m = \frac{3.0636\sigma^3P}{\varepsilon} \tag{7}$$

$$T_m = \frac{154T}{\varepsilon} \tag{8}$$

$$V = 1000V_m\left(\frac{\sigma}{3.691}\right)^3 \tag{9}$$

$$\varepsilon = \sum_{i=1}^{n}\sum_{j=1}^{n}x_ix_jk_{1,ij}\sqrt{\varepsilon_i\varepsilon_j} \tag{10}$$

$$\sigma = \sum_{i=1}^{n}\sum_{j=1}^{n}x_ix_jk_{2,ij}(\sigma_i+\sigma_j)/2 \tag{11}$$

where Z denotes the compress factor, and the parameters $a_1 - a_{15}$ and the Lenard–Jones potential parameters $\varepsilon_i$and σ_i for different species can be found in Zhang and Duan (2009).

The implementation of other EOS's, like MRK EOS (Holloway, 1977, 1981) and KJ EOS (Jacobs and Kerrick, 1981; Kerrick and Jacobs, 1981), is also provided in the program.

4. Implementation details

The main program comprises an Excel spreadsheet with five visible worksheets and a FORTRAN dynamic link library (DLL), in which all iteration procedures are packaged to improve the efficiency. In fact, the Excel spreadsheet is a user-friendly shell to call functions in the DLL. The information in each worksheet is organized in blocks and different colors to distinguish the input, optional input, output and comments regions. An option button is added on the upper right corner of the worksheet for switching between "Easy Mode" and "Advanced Mode". In the Easy Mode, the program presents only necessary items and all options are automatically set to default values. In the Advanced Mode, users take full control of all variables as needed. This is designed to balance the simplicity and flexibility.

The worksheet "Index" shows a short guide for users to access other worksheets. The "ThermoProperities" worksheet helps users to get the standard thermodynamic properties under a specific TP with the statistical mechanism mentioned in Eq. (3). The "EOS" worksheet can be used to calculate PVT properties, and fugacity coefficient and enthalpy at a given TP and composition. The last two worksheets, "Speciation—EquConstant" and "Speciation—MinGibbs" implement the equilibrium constant method and free energy minimization method to calculate the equilibrium compositions of C–O–H fluid systems under different geological environments, respectively.

4.1. Equilibrium constants method

When the system reaches its minimum of Gibbs free energy, all chemical reactions in the system must be in an equilibrium state. We can write five independent reactions for this system,

$$C + O_2 \Leftrightarrow CO_2 \tag{12}$$

$$C + \tfrac{1}{2}O_2 \Leftrightarrow CO \tag{13}$$

$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O \tag{14}$$

$$C + 2H_2 \Leftrightarrow CH_4 \tag{15}$$

$$2C + 3H_2 \Leftrightarrow C_2H_6 \tag{16}$$

By adopting Eqs. (1)–(5), we define equilibrium constants K_1–K_5 as

$$K_1 : \exp\left(\frac{(\mu_C^* + \mu_{O_2}^0 - \mu_{CO_2}^0)}{RT}\right) \tag{17}$$

$$K_2 : \exp\left(\frac{(\mu_C^* + 0.5\mu_{O_2}^0 - \mu_{CO}^0)}{RT}\right)(p^0)^{0.5} \tag{18}$$

$$K_3 : \exp\left(\frac{(\mu_{H_2}^0 + 0.5\mu_{O_2}^0 - \mu_{H_2O}^0)}{RT}\right)(p^0)^{-0.5} \tag{19}$$

$$K_4 : \exp\left(\frac{(\mu_C^* + 2\mu_{H_2}^0 - \mu_{CH_4}^0)}{RT}\right)(p^0)^{-1} \tag{20}$$

$$K_5 : \exp\left(\frac{(2\mu_C^* + 3\mu_{H_2}^0 - \mu_{C_2H_6}^0)}{RT}\right)(p^0)^{-2} \quad (21)$$

If f_{O_2} is chosen as a controlling variable, we can get the molar fractions of CO_2 and CO directly.

$$X_{CO_2} = \frac{a_C K_1}{\phi_{CO_2} P} f_{O_2} \quad (22)$$

$$X_{CO} = \frac{a_C K_2}{\phi_{CO} P} f_{O_2}^{0.5} \quad (23)$$

Considering the normalization constraint, we have

$$\frac{a_C \phi_{H_2}^3 P^2 K_5}{\phi_{C_2H_6}} X_{H_2}^3 + \frac{a_C \phi_{H_2}^2 P K_4}{\phi_{CH_4}} X_{H_2}^2 + \left(\frac{\phi_{H_2} K_3 f_{O_2}^{0.5}}{\phi_{H_2O}} + 1\right) X_{H_2} = 1 - X_{CO_2} - X_{CO}. \quad (24)$$

Solve this cubic equation we get X_{H_2}, then all other species' molar ratio are known

$$X_{C_2H_6} = \frac{a_C \phi_{H_2}^3 P^2 K_5}{\phi_{C_2H_6}} X_{H_2}^3 \quad (25)$$

$$X_{CH_4} = \frac{a_C \phi_{H_2}^2 P K_4}{\phi_{CH_4}} X_{H_2}^2 \quad (26)$$

$$X_{H_2O} = \frac{\phi_{H_2} K_3 f_{O_2}^{0.5}}{\phi_{H_2O}} X_{H_2} \quad (27)$$

Naturally, the highest f_{O_2} in the system is

$$1 - X_{CO_2} - X_{CO} = 1 - \frac{a_C K_1}{\phi_{CO_2} P} f_{O_2} - \frac{a_C K_2}{\phi_{CO} P^{0.5}} f_{O_2}^{0.5} = 0. \quad (28)$$

If we choose X_O as the control variable, we use the iterative method to find the corresponding f_{O_2}. The maximum f_{O_2} is used as a starting point which corresponds to X_O=1. The benefit of the iterative method is that it does not need the assumption that X_{H_2} and X_{CO} are small and can be ignored (Huizenga, 2005). Thus, we can extend our calculation to extreme conditions encountered in the deep part of the Earth's interior.

4.2. Free energy minimization method

In this method, we turn the speciation equilibrium problem into searching the minimum value of total free energy under a mass balance constraint. By introducing the Lagrange multiplier λ_j, we have

$$\varsigma(n,\lambda) = \sum_i^{N_s+N_m} n_i \mu_i + \sum_j^{M} \lambda_j \Big(b_j - \sum_i^{N_s+N_m} a_{ji} n_i\Big) \quad (29)$$

where N_m represents the number of species in the fluid phase,$N_s = 1$ stands for the solid phase such as graphite or diamond, M represents the number of elements and a_{ji} is the subscript to the jth element in the molecular formula of species i.

When the system is at equilibrium, it meets

$$\frac{\partial \varsigma}{\partial n_k} = \mu_k - \sum_j^{M} a_{jk} \lambda_j = 0, \quad k = 1,2,\ldots,N_s + N_m \quad (30)$$

$$\frac{\partial \varsigma}{\partial \lambda_j} = b_j - \sum_i^{N_s+N_m} a_{ji} n_i = 0, \quad j = 1,2,\ldots,M \quad (31)$$

Following the RAND algorithm proposed by Smith and Missen (1982), substituting Eq. (1) into the linear formulas group produced by Newton–Raphson method we get

$$\sum_{i=1}^{M} \sum_{k=1}^{N_s+N_m} a_{ik} a_{jk} n_k' \frac{\delta\lambda_i}{RT} + \sum_{\alpha=1}^{N_s+N_m} b_{j\alpha}' u_\alpha = \sum_{k=1}^{N_s+N_m} a_{jk} n_k' \frac{\mu_k'}{RT} + b_j - b_j', \quad j = 1,2,\ldots,M \quad (32)$$

$$\sum_{i=1}^{M} b_{i\alpha}' \frac{\delta\lambda_i}{RT} = \sum_{k=1}^{N_s+N_m} n_{k\alpha}' \frac{\mu_{k\alpha}'}{RT}, \quad \alpha = 1,2,\ldots,\pi_s + \pi_m \quad (33)$$

where

$$u = \sum_i \delta n_i \Big/ \sum_i n_i \quad (34)$$

δn and $\delta\lambda$ are the steps of the numbers of moles and the Lagrange multipliers, respectively. $b_j' = \sum_{i=1}^{N} a_{ji} n_i'$ represents the element abundance in each iteration.

To omit the assumption of ideal mixing, which takes fugacity coefficients of pure species instead of the corresponding value in the mixture, we added an outer loop to update the fugacity coefficients of each species in the mixture, based on reliable EOS after the original RAND algorithm gets molar fraction with given coefficients. The fugacity coefficients of pure species are used as an initial guess and the procedure repeats until all fugacity coefficients are self-consistent. This helps us to improve the accuracy in the high pressure region.

5. Examples

5.1. Composition of carbon saturated fluid under 1273 K, 2.4 GPa with f_{O_2} buffered by iron–wüstite (IW)

Matveev et al. (1997) investigated the fluid composition under 1273 K, 2.4 GPa with different buffers. We take some of their experimental points and use the worksheet "Speciation—EquConstants" to calculate the equilibrium fluid compositions. The input and output are listed in Table 1 and the calculated results are close to the experimental data.

5.2. Composition of carbon saturated fluid under 1693 K, 5.7 GPa

Sokol et al. (2004) investigated diamond genesis from C–O–H fluid under 1693 K, 5.7 GPa. Considering the uncertainty of experimentally measured species fraction, we sum measured species fraction up and take the total X_O as the control variable. The calculation of the worksheet "Speciation—MinGibbs" with a given X_O is summarized in Table 2. The results reveal that the maximum carbon fraction in the fluid with X_O=0.2672 (correspond to their experimental point 3) is 4.90%, which is closed to 5.98% as determined in experiments where diamonds are precipitated. The similarity between experimental results and calculated values is also found in all other experimental points.

Table 1

Input		Output		Exp.[a]
T (K)	1273	X_{H_2O}	0.1169	(0.1172)
P (MPa)	2400	X_{CO_2}	< 0.0001	–
Carbon activity	1	X_{CH_4}	0.8152	(0.8136)
Method for Kp	1—Statistical mechanism	X_{H_2}	0.0359	(0.0538)
EOS	1—This study	X_{CO}	0.0001	–
Including Ethane	1—Yes	$X_{C_2H_6}$	0.0319	(0.0184)
Control Variable	1—f_{O_2}			
$\Delta \mathrm{Log}_{10} f_{O_2}$(QFM)	−4.5	X_O	0.0302s	

[a] Average value from all five experimental runs buffered by iron–wüstite (IW).

Table 2

Input		Output		Exp.[a]
T (K)	1693	X_{H_2O}	0.8478	
P (MPa)	5700	X_{CO_2}	0.0002	
Initial speciation	1—Automatic	X_{CH_4}	0.1393	
Method for free energy	1—Statistical mechanism	X_{H_2}	0.0005	
EOS	1—This study	X_{CO}	<0.0001	
Including ethane	1—Yes	$X_{C_2H_6}$	0.0121	–
Control variable	2—X_O			
X_O	0.2672	$\text{Log}_{10} f_{O_2}$	-16.57	
		n_C (%)	4.90	5.98
		n_H (%)	69.69	68.89
		n_O (%)	25.41	25.12

[a] Experimental Point 3 of Sokol et al. (2004) with diamond precipitated.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cageo.2009.05.008.

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