

Recalibration of the 5-parameter MRK equation of state for C-O-H fluids under upper mantle conditions and some experimental tests

Taylor, W.R.¹, and Matveev, S.²

¹R.S.E.S., Australian National University, Canberra, A.C.T. 0200, Australia
²Institut für Mineralogie und Geochemie, Universität zu Köln, Zùlpicher Str. 49b, 50674 Köln, Germany (formerly Max Planck Institute, Mainz, Germany)

An extensive series of experiments in the system C-O-H fluid + graphite at 2.4 GPa and 1000°C was undertaken by Matveev et. al. (1997). The fluids were either unbuffered or were buffered by various metal-oxide oxygen buffers and fluid analyses were undertaken by a capsule piercing-gas chromatography technique. Numerous experimental tests showed that the fluid analyses reflected those of high-P,T equilibrium, i.e. quench modification processes were generally not significant provided maximum quench rates were employed. One goal of these experiments was to develop an equation of state (EOS), or modify an existing EOS, for supercritical C-O-H fluids in order to better estimate species activities and distributions under upper mantle P, T, fO₂ conditions.

We have compared a number of equations of state for supercritical C-O-H fluids and found that the 5-parameter Modified-Redlich-Kwong (5PMRK) EOS of Taylor (1989), using standard mixing rules, provides the best fit to the experimental data. The 5PMRK EOS has the form:

$$P = [R \cdot T \cdot (1 + y + y^2 - y^3)] / [V_m \cdot (1 - y)^3] - [(a_1 + a_2/V_m + a_3/V_m^2)] / [T^{1/2} \cdot V_m \cdot (V_m + b)]$$

b = b₁ + b₂/T V_m = molar volume (cm³mol⁻¹) T = temperature (K)
y = b / 4V_m P = pressure (bar) R = 83.143 cm³barK⁻¹mol⁻¹
a = 3-term attractive MRK parameter b = 2-term repulsive MRK parameter

Although good agreement was found for major fluid species such as H₂O and CH₄, calculated abundances for the minor species H₂ and C₂H₆ were found to be too low by ~25%. In an attempt to achieve better agreement with the experimental data, but by a method independent of the experiments, the MRK parameters for both H₂ and C₂H₆ were refitted using molar volume constraints for the pure fluids provided by shock wave data and molecular dynamics simulations. This data was not available at the time of the original calibration of the 5PMRK. The recalibration was performed using an iterative Monte Carlo fitting routine and yielded the following results:

TABLE 1. 5PMRK Parameters

Species	b ₁	b ₂	a ₁ /10 ⁷	a ₂ /10 ⁸	a ₃ /10 ⁹
H ₂ O	21.34	5420	13.29	25.41	19.15
CO ₂	45.53	10730	12.87	11.22	444.3
CO	40.11	3769	3.869	6.45	8.008
H ₂	12.18	2825	0.0664	0.0814	0.1045
CH ₄	43.38	7409	6.742	28.93	97.49
C ₂ H ₆	74.38	7520	21.1	61.5	163.0

Species distributions were then calculated with the Fortran77 program ‘GFLUID6’ (available from the authors on request). For the most robust experiments buffered at IW, and for a number of unbuffered experiments, agreement was found to be excellent (Table 2). Good agreement was also obtained with the lower P, T experiments of Jakobsson and Oskarsson

(1990). Of the various MRK equations available in the literature, the recalibrated 5PMRK gives the best agreement with experiment for CH₄-H₂O-rich fluids and should be suitable for extrapolation to pressure of at least 5 GPa.

TABLE 2. Comparison of Experimental and Calculated C-O-H (+graphite) Fluids†

	expt ^a	1σ	calc.	expt ^a	1σ	calc.	expt ^b	1σ	calc.
P(GPa)	2.4		2.4	2.4		2.4	1.5		1.5
T(K)	1273		1273	1273		1273	1473		1473
log(fO ₂)	IW		-13.75	none		-12.0	IW		-11.34
no. analyses	n=5			n=2			n=4		
H ₂ O	11.7	.9	11.5	88.3	2.3	88.4	21.8	1.1	20.7
CO ₂	bdl		<0.1	0.17	.01	0.16	0.11	.02	0.14
CO	bdl		<0.1	bdl		<0.1	0.38	.05	0.25
H ₂	5.1	.4	4.9	1.8	.1	1.8	11.3	1.0	11.2
CH ₄	81.4	.8	81.7	9.7	2.2	9.6	65.3	1.5	66.3
C ₂ H ₆	1.9	.2	1.9	0.12	.03	0.05	1.03	.06	1.42

† Fluid compositions in mole%; bdl = below detection limit.

a Matveev et al., 1997, and unpubl. experimental data.

b Jakobsson and Oskarsson (1990)

References

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