

WANG Yanzhe, HU Jiawen, GUO Tao, WANG Xianghui and JIN Lihua, 2014. Examination of Some Commonly Used Equations of State for Supercritical Water. *Acta Geologica Sinica* (English Edition), 88(supp. 2): 1163-1164.

Examination of Some Commonly Used Equations of State for Supercritical Water

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1 Statistical Results of Examination

Since 1970, many equations of state have been developed for supercritical water. Meanwhile, a huge number of experimental data have been obtained for the pressure-volume-temperature (*PVT*) properties of water. Based on the data published before 1990, Wagner and Pruss (2002) established a very accurate thermodynamic model for water, i.e. IAPWS-95 (273.15–1273.15 K, 0–10 kbar). Recently, Zhang and Duan (2005) obtained many accurate *PVT* data of water using molecular dynamics simulations (523.15–4273.15 K, 1–500 kbar). These data and the IAPWS-95 model are used here to examine some commonly used equations of state for supercritical water (Table 1).

2 Some Supplemental Explanations

Although some equations are also valid for subcritical water, they are only examined at $T \geq T_C$, where T_C is the critical temperature (647.096 K); while other equations are all examined in the applicable *P-T* range claimed by the original author(s). Since the deviations of each equation usually differ significantly in different *P-T* regions, it is necessary to give some explanations for the corresponding details: (1) Equation of Holloway (1977). At T_C –723 K and 0–10 kbar, its average and maximum volume deviations (AD and MD) are 3.09% and 59.1%, respectively, and all large deviations occur at 0.1–1 kbar. (2) Equation of Kerrick and Jacobs (1981). Compared with IAPWS-95, its volume deviations between 2% and 5% appear at 180–450 bar, where the MD appears near the critical point; at $T \geq 700$ K, its volume deviations are all within 3%. (3) Equation of Halbach and Chatterjee (1982). Above 800.15 K, its volume deviations from IAPWS-95 are all less than 2%. (4) Fugacity equation of Powell and Holland (1985). Compared with IAPWS-95, its volume deviations greater than 10% are all within 3 kbar; Above 3

kbar, its AD and MD are 1.32% and 8.73%, respectively. (5) Fugacity equation of Holland and Powell (1990). Compared with IAPWS-95, its MD and AD below 3 kbar are 750% and 43.1%, respectively; At $P \geq 3$ kbar, its AD and MD are 1.07% and 2.62%, respectively. (6) Equation of Duan et al. (1992). At T_C –723.15 K, its AD and MD from IAPWS-95 are 0.43% and 28.41%, respectively.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos 41172118, 90914010), the Natural Science Foundation of Hebei Province (Grant No.D2012403010), and the support

Table 1 Applicable *P-T* ranges and deviations of equations of state for H₂O

Authors	<i>T-P</i> range	AD(%)	MD(%)
Holloway (1977)	723–2073 K 0.5–40 kbar	1.41 (8.79)	10.5 (19.6)
Kerrick and Jacobs (1981)	573–1323 K 0–20 kbar	0.585 (1.95)	58.2 (3.33)
Halbach and Chatterjee (1982)	373.15–1273.15 K 0–200 kbar	1.12 (1.41)	74.1 (3.56)
Powell and Holland (1985)	600–1400 K 1–30 kbar	6.67 (2.37)	65.6 (4.58)
Holland and Powell (1990)	573.15–1473.15 K 0.1–40 kbar	19.4 (3.34)	750 (7.08)
Holland and Powell (1991)	373.15–1673.15 K 0.001–50 kbar	1.75 (1.54)	61.3 (4.08)
Belonoshko and Saxena (1991)	700–4000 K 5–1000 kbar	1.33 (3.33)	2.11 (22.7)
Belonoshko and Saxena (1992)	700–4000 K 5–1000 kbar	0.99 (4.39)	6.24 (30.5)
Duan et al. (1992)	273.15–1273.15 K 0–8 kbar	0.406	28.4
Pitzer and Sterner (1994)	273.15–2000 K 0–100 kbar	0.26 (2.04)	4.01 (11.1)
Duan et al. (1996)	1.37 T_C –2000 K 0–25 kbar	0.79 (2.49)	11.02 (4.85)
Zhang and Duan (2005)	273.15–2000 K 1–200 kbar	0.34 (0.22)	2.69 (0.98)
Duan and Zhang (2006)	673.15–2573.15 K 0–100 kbar	0.09 (0.34)	1.2 (2.77)

Note : In the AD and MD columns, the numbers in brackets are the deviations from the data simulated by Zhang and Duan (2005), and those not bracketed are those from IAPWS-95.

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program (II) of a Hundred Outstanding Innovative Talents in Universities of Hebei Province (Grant No. BR2-109).

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