The assemblage WO₂ + H₂O as a steady-state hydrogen source in moderately reduced hydrothermal experiments

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ABSTRACT

The values of f_{H_2} for the assemblage $WO_2 + WO_{2.72} + H_2O$ (designated as WO) have been measured in sealed Au capsules under an external pressure of 2 kbar CH_4 and between 650 and 800 °C using Ag-AgBr-HBr sensors of f_{H_2}. The f_{H_2} values obtained can be represented by the equation

$$\log(f_{H_2}^{WO})_{2kbar,T}(\pm 0.06) = \frac{-1924.9}{T, \text{K}} + 4.06$$

and are found to be slightly greater than those associated with the previously calibrated C-CH₄ buffer. The value at 2 kbar and 650 °C is approximately an order of magnitude lower than the theoretical value of the wüstite-magnetite-H₂O buffer. The assemblage has been found to generate reproducible steady-state f_{H_2} values at fixed P-T conditions. However, at the relatively high H_2 pressures developed by this assemblage, H_2 leakage through the Au capsule was unavoidable. This leakage can be mitigated by decreasing the f_{H_2} gradient across the Au capsule wall, but it is strongly recommended that f_{H_2} sensors be employed to monitor the actual redox conditions in experiments using buffers or assemblages that generate f_{H_2} values equivalent to the Co-CoO-H₂O buffer or greater. The $WO_2 + WO_{2.72} + H_2O$ assemblage can still be used as a redox buffer even though the system's H_2 consumption is accomplished by H_2 leakage rather than chemical reaction.

INTRODUCTION

Measurements of the steady-state values of f_{H_2} imposed by the C-CH₄ buffer in cold-seal pressure vessels at 2 kbar and between 600 and 800 °C (Chou, 1987a) show that the f_{H_2} values are only ¼ to ⅓ of those calculated from thermochemical data as given by Eugster and Skippen (1967). Furthermore, reproducible f_{H_2} values cannot be obtained at temperatures lower than 650 °C because of kinetic problems. Therefore, it is useful to find suitable redox buffers that can control the redox states of hydrothermal experimental systems at levels equivalent to the theoretical C-CH₄ buffer. For this reason, the assemblage of $WO_2 + WO_3 + H_2O$, first studied by King et al. (1960), is considered. We report here on the measured f_{H_2} values imposed by the assemblage $WO_2 + WO_3 + H_2O$ at 2 kbar and between 550 and 800 °C; preliminary results were presented earlier (Cygan and Chou, 1987). In addition, since a significant influence is exerted by the pressure medium upon the f_{H_2} values that can be attained in hydrothermal experiments contained in Au capsules (Chou and Cygan, 1987, 1989, 1990), the measurements of f_{H_2} for the assemblage $WO_2 + WO_3 + H_2O$ were performed using three pressure media, CH_4, Ar, and H_2O, to assess these effects.

This buffer assemblage has been used to obtain reducing conditions in other hydrothermal experiments (Tacker and Candela, 1987; Wood and Vlassopoulos, 1989) even though it is not a stable assemblage at the P-T con-

ditions at which those studies took place (discussion follows). The assemblage $WO_2 + H_2O$ was used as the starting assemblage in the latter part of this study to avoid the problem of metastability. In this way, the assemblage was used only as a source of H, rather than a true buffer, through the reaction

$$WO_{2(s)} + xH_2O = WO_{2+x(s)} + xH_{2(g)} \qquad (1)$$
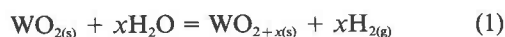
where $x = 0.72$ or 0.90, s = solid, and g = gas. Even under the external pressure of CH_4, the most reducing pressure medium employed in this study, the high leakage rate of H through the Au capsule walls impedes H build-up in the charge to the levels predicted by the equilibrium constant of Reaction 1.

In other words, in our experiments, Reaction 1 always proceeds to the right, and the f_{H_2} levels of the system are always below the equilibrium values. Steady-state f_{H_2} values can be maintained in the system, however, when the rate of H_2 production by means of Reaction 1 is countered by the rate of H_2 leakage out of the capsule. For hydrothermal experiments involving quantitative redox control, where the actual redox state is monitored by an f_{H_2} sensor, it does not matter whether the redox control is achieved by a buffering equilibrium or by a steady-state process. What is important is that the redox state of the system is fixed at certain known values at P and T during the experiment.

In this study, the steady-state values of f_{H_2} for the H-generating assemblage $WO_2 + H_2O$ contained in a Au
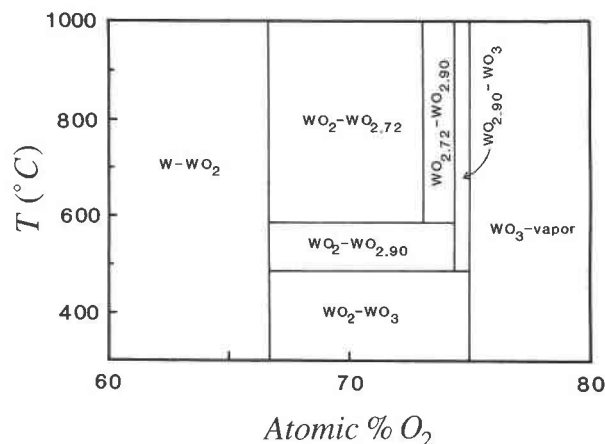
Fig. 1. A portion of the W-O system showing phase relations for the pertinent species in this study, at 1 atm pressure, in atomic percent O$_2$. Adapted from Phillips and Chang (1964).

capsule under an external pressure of 2 kbar CH$_4$ were measured between 650 and 800 °C. Results were compared with those obtained for the metastable assemblage WO$_2$ + WO$_3$ + H$_2$O described above. The technique used in this study is similar to that employed for calibrating the C-CH$_4$ buffer using Co-CoO-H$_2$O as a reference buffer and the Ag-AgBr-(H$_2$O, HBr) H sensor (Chou, 1987a).

PHASE RELATIONS IN THE W-O SYSTEM

The W-O system contains several stable oxide phases intermediate to the end-members. Past experiments have established the existence of at least four oxides, WO$_2$, WO$_{2.72}$, WO$_{2.90}$, and WO$_3$ (St. Pierre et al., 1962; Phillips and Chang, 1964; Bousquet and Perachen, 1964). Figure 1 shows the temperature-composition relations at 1 atm for a portion of the binary relevant to this study.

King et al. (1960) presented thermodynamic data, including measured low and high temperature heat capacity and free energy data for WO$_2$ and WO$_3$. Unfortunately, their measurements were made for the metastable assemblage WO$_2$ + WO$_3$, and the stable intermediate oxide species in the W-O system were not considered. Figure 2 gives the stabilities of the intermediate species for this study as calculated from the data in JANAF (1971). At least two intermediate oxides, WO$_{2.72}$ and WO$_{2.90}$, are formed before further oxidation of WO$_2$ to WO$_3$ at $T >$ 585 °C. There appears to be confusion as to whether an intervening higher oxide, WO$_{2.75}$, will form from the reduction of WO$_3$ to WO$_{2.72}$; however, recent high resolution electron microscopy has shown that only an amorphous intermediate step appears prior to the stable stoichiometric WO$_{2.72}$ phase (Sahle, 1982).

EXPERIMENTAL PROCEDURE

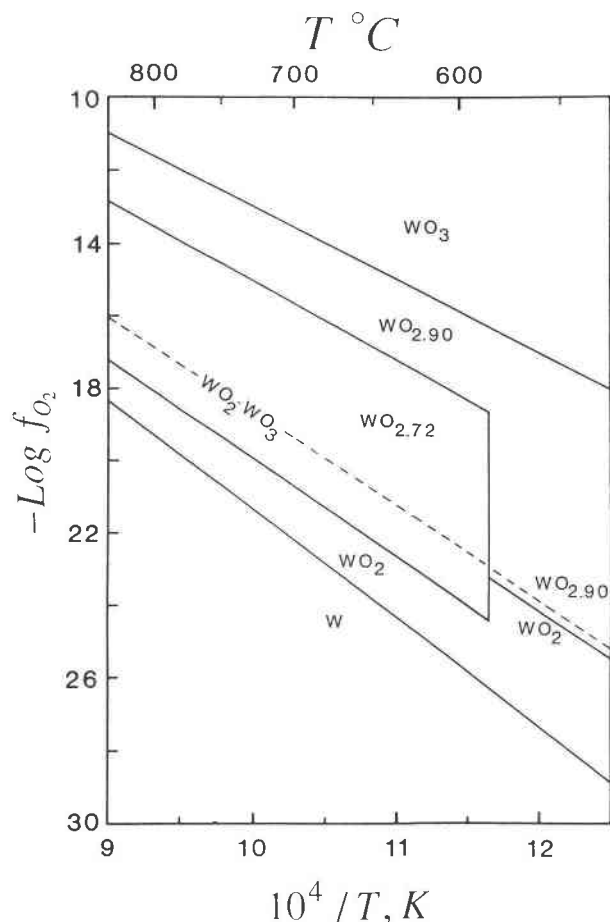Starting materials consisted of commercially available WO$_2$ (Alfa Products,[1] lot #102036) and WO$_3$ (Fisher Sci-

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[1] Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Fig. 2. Log f_{O_2}-T diagram for the pertinent W-O system species at 1 atm using data from JANAF (1971). Solid lines are stable phase boundaries and the dashed line represents the experimentally produced values for the metastable WO$_2$ + WO$_3$ assemblage as determined by King et al. (1960).

entific, lot #732211). WO$_2$ as purchased contains <1.5% "other oxide" not identified on the bottle; however, X-ray analysis determined only minor W to be present. The f_{H_2} sensors were sealed Pt capsules (1.85 mm od, 1.54 mm id and 19 mm long) containing 8 to 15 mg of either distilled, deionized H$_2$O (sensor A) or 1.5 M HBr (sensor B), and approximately 50 mg of a 1/1 mix of Ag and AgBr (both from Fisher Scientific; lot #771462 and #751585, respectively). Either one or both of these sensors, depending upon the available space in the Au capsule, were then sealed inside a cleaned Au outer capsule (4.4 mm od, 4.0 mm id and 25.4 mm long), which contained 0.4 to 0.6 g of WO$_2$ + WO$_3$ and approximately 20 to 40 μL H$_2$O, or solely WO$_2$ + H$_2$O. If two sensors were placed in the capsule, complementary sensors A and B were used to demonstrate reversals in H$_2$ transfer. Multiple experiments with single sensors were conducted at higher temperatures when space in the Au capsule presented a problem. Further details of the charge configuration are in Chou (1987b).

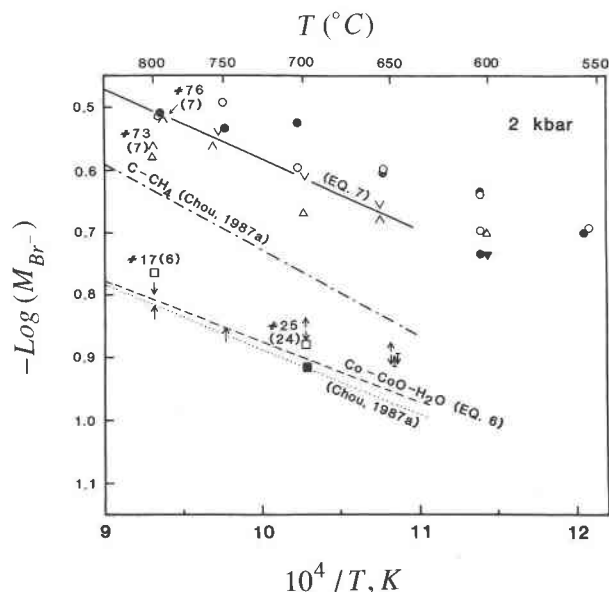Cold-seal pressure vessels made of stellite 25 (a Co-

$T\ (^\circ C)$

Fig. 3. Experimental data of $-\log M_{Br^-}$ in the f_{H_2} sensors at 2-kbar pressure using Ar, H$_2$O, and CH$_4$ pressure media. Symbol definitions are presented as (sensor A/sensor B), where sensor A approaches osmotic equilibrium from below or undersaturation, whereas sensor B approaches from above. Experiments using initial assemblage WO$_2$ + H$_2$O and employing CH$_4$ external pressure ($\wedge/\vee$); experiments with an initial assemblage of WO$_2$ + WO$_3$ + H$_2$O and CH$_4$ (O/●) Ar (△/▼) H$_2$O (□/■) external pressure; and those using an initial assemblage of Co + CoO + H$_2$O plus Ar (↑/↓) or CH$_4$ (↑/↓) external pressure. Uncertainties are about the size of the symbols (± 0.01 in log M_{Br^-} and ± 3 °C). The heavy solid line is a regressed line through measurements represented by the chevrons (Eq. 7). The Co + CoO + H$_2$O assemblage was used as a reference in this study; the dashed line represents Equation 6, and the dotted line is from Chou (1987a). The calibrated log M_{Br^-} values for the C + CH$_4$ assemblage determined by Chou (1987a) are depicted by the dash-dot line. Numbers in parentheses represent experiment durations (in hours) for those experiments. Note that experiments made under H$_2$O external pressure, numbers 17 and 25, plot near the Co + CoO + H$_2$O line, well beneath the experiments exposed to CH$_4$ and Ar external pressure. See text for discussion.

TABLE 1. Measured Br$^-$ concentrations in the Ag-AgBr f_{H_2} sensors equilibrated with the Co-CoO-H$_2$O assemblage under 2-kbar Ar external pressure

Experiment no.	Temperature (°C)	Experiment duration (h)	$(M_{Br^-})_{1\ atm,\ 25\ °C}$ in sensors*		$-\log(M_{Br^-})$ in sensors	
			A	B	A	B
21	800	8	0.1509	—	0.8212	—
23	800	8	—	0.1585	—	0.7999
22	752	16	0.1407	—	0.8517	—
19	700	68	—	0.1342	—	0.8722
24a	701	52	0.1454	—	0.8375	—
26	651	96	0.1329	0.1228	0.8763	0.9107
28**	650	120	0.1263	0.1227	0.8985	0.9113

* Sensor A contains an initial assemblage of Ag + AgBr + H$_2$O, whereas sensor B contains Ag + AgBr + 1.5 *M* HBr.
** Conducted under CH$_4$ external pressure.

pecially at high temperatures. The maximum decrease in pressure was approximately 35 bars.

The experiments were quenched using compressed air with temperatures below 200 °C attained in about 1–1.5 min, followed by immersion in cold H$_2$O. The recovered capsules were cleaned and weighed to check for leaks. Occasionally it was necessary to determine the weight loss or gain of H$_2$O in the outer capsule resulting from H$_2$ diffusion. In this case, the capsules were first cleaned, weighed, and punctured with a stainless steel needle, dried at 100 °C in a vacuum oven for 15–20 min, and then reweighed to ± 50 μg. The outer encapsulation was then removed and the H sensor recovered and cleaned. The sensor's solution was recovered for analysis using 3, 5, or 10 μL microcapacity disposable pipets with uncertainties of $\pm 1\%$. Bromide concentrations in the sensors were measured on a Buchler chloridometer with uncertainties of $\pm 1\%$. In addition, all solid products were examined optically and by X-ray diffraction methods.

EXPERIMENTAL RESULTS AND DISCUSSION

It has been shown (Chou, 1987a) that the reaction governing the H sensors used in this study is

$$Ag_{(s)} + HBr_{(aq)} = AgBr_{(s\ or\ l)} + \tfrac{1}{2}H_{2(g)} \qquad (2)$$

where (aq) is aqueous and (l) is liquid. For pure solids and liquid, the equilibrium constant of this reaction can be represented by

$$K_2 = f_{H_2}^{0.5}/f_{HBr}. \qquad (3)$$

From Equation 3, and for the dilute HBr solutions generated in the sensors under the P-T conditions of this investigation,

$$(f_{H_2})_{P,T} = K'(m_{HBr})_{P,T}^2 \approx K'(M_{Br^-})_{1\ atm,\ 25\ °C}^2, \qquad (4)$$

where K$'$ is a constant and m_i and M_i are molality and molarity of i, respectively. Therefore, by measuring Br$^-$ concentrations in the H sensors exposed to the WO$_2$-H$_2$O system, the f_{H_2} of the system can be related to that of the previously calibrated Co-CoO-H$_2$O system through

$$(f_{H_2}^{WO})_{P,T} = (f_{H_2}^{CoO})_{P,T}(M_{Br^-}^{WO}/M_{Br^-}^{CoO})_{1\ atm,\ 25\ °C}^2, \qquad (5)$$

based on) alloy) with a 3.18-cm od, a 20.32-cm length, and a 6.35-mm id were used. The pressure media used were CH$_4$, Ar, and H$_2$O; when CH$_4$ (99.99% pure, supplied by Matheson) was used, a pure graphite bar was inserted as a filler rod, and when Ar or H$_2$O was used, a stainless steel bar was employed. Occasionally, when H$_2$O was used to transmit pressure, the intrinsic f_{H_2} of the pressure vessel was monitored by f_{H_2} sensors.

All experiments were made using horizontal Pt-wound furnaces with conventional temperature proportional controllers. Temperatures were monitored by calibrated chromel-alumel type thermocouples sheathed in inconel with an accuracy of ± 3 °C. Pressures were monitored by Heise gauges with an accuracy of ± 30 bars for the Ar and H$_2$O pressure media. Experiments performed with CH$_4$ as the pressure medium required periodic recharging because of H$_2$ leakage through the pressure vessel wall,

TABLE 2. Measured Br$^-$ concentrations in the Ag-AgBr f_{H_2} sensors from experiments made at 2-kbar total pressure of various pressure media

| Experiment no. | Temperature (°C) | External pressure | Experiment duration (h) | $-\log(M_{Br^-})$ in sensors* | | Final phase products** |
				A	B	
(a)			WO$_2$ + H$_2$O starting assemblage			
76†	793	CH$_4$	7	0.5111	—	in: 1,2; out: 1,2,4
73††	801	CH$_4$	7	0.5596	—	1,2,(3)
67	758	CH$_4$	8	0.5568	—	1,2,(3)
71	754	CH$_4$	8	—	0.5427	1,2
63	700	CH$_4$	46	—	0.6148	1,2,(3)
72	656	CH$_4$	143	0.6749	0.6564	1,2,(3)
(b)			WO$_2$ + WO$_3$ + H$_2$O starting assemblage			
52	794	CH$_4$	20	—	0.5098	1,2,4
42	793	CH$_4$	18	0.5114	—	1,2,(3),4
51	751	CH$_4$	27	—	0.4940	1,2,(3),4
47	750	CH$_4$	27	0.5351	—	1,2,(3),4
31	704	CH$_4$	46	0.5965	0.5253	1,2,4
44	654	CH$_4$	120	0.5989	0.6062	1,2,(3),4
45	605	CH$_4$	168	0.6400	0.6415	1,2,3,4
54	802	Ar	8	0.5833	—	1,2,4
55	699	Ar	50	0.6720	—	1,2,(3),4
56	604	Ar	168	0.6969	0.7433	1,2,3,4
62	554	Ar	120	0.6938	0.7018	1,3,4
17	800	H$_2$O	6	0.7707	—	1,2,4
25	700	H$_2$O	24	0.8788	0.9194	1,2,(3),4

* Sensor A contains Ag + AgBr + H$_2$O; sensor B contains Ag + AgBr + 1.5 *M* HBr.
** 1 = WO$_2$; 2 = WO$_{2.72}$; 3 = WO$_{2.90}$; 4 = WO$_3$; ( ) indicates trace amounts, probably formed upon quench.
† Triple capsule experiment. In and out refer to Au capsule positions in the triple capsule configuration. For details, see text.
‡ Not used in regression because of excessive H$_2$ leakage.

where the superscripts WO and CoO represent the assemblages WO$_2$ + WO$_{2.72}$ + H$_2$O and Co + CoO + H$_2$O, respectively. The bromide measurements used to compute the f_{H_2} values are given in Tables 1 and 2 and shown in Figure 3.

The Br$^-$ concentrations in the sensors equilibrated with the Co-CoO-H$_2$O buffer under an external pressure of 2 kbar CH$_4$ obtained by Chou (1987a) are shown in Figure 3 by the dotted line. Results of the additional experiments conducted under Ar external pressure given in Table 1 are shown in Figure 3 by the arrows. The agreement of these two sets of data is excellent at $T \geq 750$ °C, but some discrepancies exist at lower temperatures. The dashed line represents the least-squares fit of all available data, which can be described by the equation

$$\log M_{Br^-} = \frac{-1003.7}{T, \text{K}} + 0.134 \qquad (r^2 = 0.819). \qquad (6)$$

Experimental results for two initial external assemblages, (a) WO$_2$ + H$_2$O and (b) WO$_2$ + WO$_3$ + H$_2$O, are given in Table 2. Analysis of the quenched solid phases indicates that the initial assemblage (a) produces the stable solid assemblage WO$_2$ + WO$_{2.72}$, whereas the initial assemblage (b) consistently produces metastable solid assemblages WO$_2$ + WO$_{2+x}$ + WO$_3$ (depending on temperature, $x = 0.72$, 0.90, or both; see Fig. 1 and Table 2). Most X-ray diffractograms produced a few broad, small peaks, suggesting the presence of a poorly crystallized WO$_{2.90}$ phase at temperatures much higher than the stability field would indicate (see Fig. 1). We interpret these peaks to represent a metastable phase formed upon quench. Experiments on assemblage (a) were performed

under CH$_4$ external pressure only (chevrons in Fig. 3), whereas three pressure media were used for assemblage (b): CH$_4$ (circles), Ar (triangles), and H$_2$O (squares). Under CH$_4$ external pressure, the assemblages (a) and (b) yield about the same Br$^-$ concentrations, indicating that the presence or absence of WO$_3$ in the external assemblage does not significantly affect the level of f_{H_2} that can be maintained in the Au capsules in this particular experimental setup. At the highest temperatures of this study, we were initially unable to maintain a steady-state condition in the experiment, and H$_2$ leakage occurred (see experiment 73). We attempted to mitigate the leakage through a modified capsule configuration represented by experiment 76, which we term a triple capsule technique. This arrangement essentially seals the sample configuration of experiment 73 inside a second, thicker-walled Au capsule (0.25 mm) that is also loaded with WO$_2$ + H$_2$O. This arrangement effectively provides an additional H$_2$ source and Au shield between the internal Au tube plus H sensor and the external pressure medium. The H$_2$O content of the two nested Au tubes was measured at the conclusion of the experiment; 19.6 mg ($\approx$50%) of H$_2$O was lost from the outer Au tube assembly, whereas only 9.7 mg ($\approx$20%) was lost from the inner Au tube. In addition, solid phases produced at the conclusion of the experiment indicate oxidation of WO$_2$ to WO$_3$ in the outer capsule, although the inner capsule maintained an effective steady-state f_{H_2} condition represented by quenched experimental products of WO$_2$ + WO$_{2.72}$ + H$_2$O and an f_{H_2} value of about 0.5 log units greater than that in experiment 73.

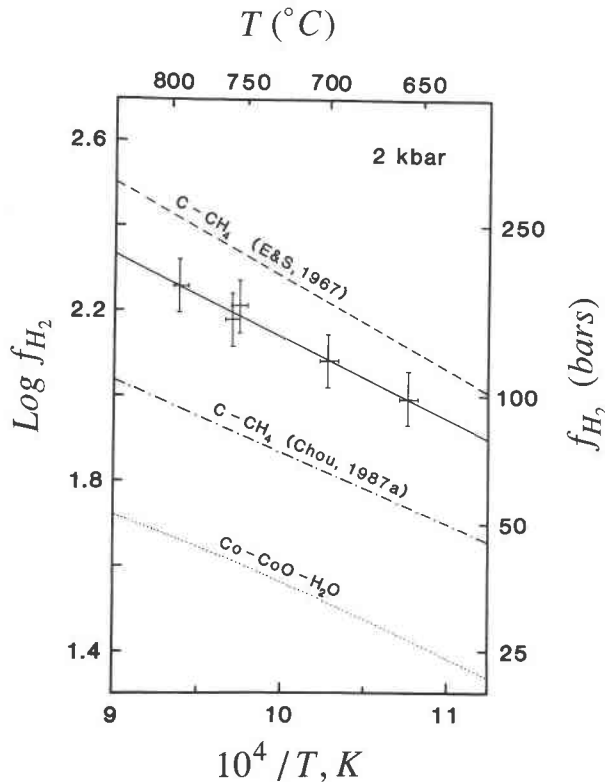The results for assemblage (b) under different pressure

Fig. 4. Calculated results of log f_{H_2} at 2 kbar using measured M_{Br^-} data presented in Table 2 employing WO$_2$ + H$_2$O as the initial assemblage under CH$_4$ external pressure. Also shown are the calculated f_{H_2}-T relations for the C-CH$_4$ buffer from Eugster and Skippen (1967; dashed line) and the calibrated values from Chou (1987a; dash-dot line). Values for the Co-CoO-H$_2$O buffer used in the calculation of $(f_{H_2}^{WO})_{2kbar,T}$ are given as a dotted line. Uncertainties are shown as vertical and horizontal bars at each data point.

media indicate that the pressure medium has a significant effect on the level of f_{H_2} that can be maintained in the Au capsules. Experiments made under Ar external pressure approached the minimum log (M_{Br^-}) values of those experiments conducted under CH$_4$ external pressure; however, enough H$_2$ loss has occurred to upset the steady-

state balance of Equation 1 on the basis of the monitored H$_2$O content before and after the experiment. H$_2$ loss is even greater in experiments 17 and 25 that use H$_2$O for external pressure. These charges generate log(M_{Br^-}) values at or very near to the intrinsic f_{H_2} values of the pressure medium in the Co-based pressure vessel [log(M_{Br^-}) $\propto f_{H_2}$, see Eq. 4]. Even though durations of the experiments (in hours, given in parentheses in Fig. 3) are similar to those of experiments made under CH$_4$ external pressure, massive H$_2$ loss to the pressure medium has occurred at a high rate. We have discussed this effect extensively (Chou and Cygan, 1987, 1989, 1990), and the current results further strengthen our previous conclusion that H$_2$O is a poor pressure medium for hydrothermal experiments involving redox control at the f_{H_2} levels equivalent to the Co-CoO-H$_2$O buffer or higher.

The following discussion will be restricted to the experimental results obtained from the stable assemblage produced by the initial assemblage (a). The $(f_{H_2}^{WO})_{2kbar,T}$ values calculated from Equation 5 using the $M_{Br^-}^{WO}$ values given in Table 2 and $M_{Br^-}^{CoO}$ values given in Table 3 are plotted in Figure 4. Linear least-squares fit of the data between 793 and 656 °C gives

$$\log(f_{H_2}^{WO})_{2kbar,T}(\pm 0.06) = \frac{-1924.9}{T,\ K} + 4.06$$

$$(r^2 = 0.985) \qquad (7)$$

which is shown in Figure 4 by the heavy solid line. Also shown in Figure 4 are the f_{H_2} values for the C-CH$_4$ buffer calculated from thermochemical data (Eugster and Skippen, 1967) and those calibrated by Chou (1987a). The f_{H_2} values for the Co-CoO-H$_2$O buffer used in Equation 5 to obtain $(f_{H_2}^{WO})_{2kbar,T}$ values for this study are listed in Table 3 and shown in Figure 4 (dotted line).

It should be emphasized that the f_{H_2} values described by Equation 7 (solid line in Fig. 4) are not necessarily the equilibrium values for the assemblage WO$_2$ + WO$_{2.72}$ + H$_2$O at P-T conditions. These f_{H_2} values measured by the f_{H_2} sensors simply reflect the actual f_{H_2} levels maintained in the Au capsules just before quench. Two competing processes determine these f_{H_2} levels: (1) the generation of H$_2$ through WO$_2$ oxidation, represented by Reaction 1

TABLE 3. Calculation of $(f_{H_2})_{P,T}$ values for the WO$_2$ + WO$_{2.72}$ + H$_2$O assemblage in Au capsules under 2-kbar CH$_4$ external pressure

Experiment no.	T (°C)	$\log(f_{O_2}^{CoO})_{P,T}$[A]	log K_w[B]	$\log(f_{H_2O})_{P,T}$[C]	$\log(f_{H_2}^{CoO})_{P,T}$[D]	$\log(M_{Br^-}^{CoO})_{1\ atm,\ 25\ °C}$[E]	$\log(M_{Br^-}^{WO})_{1\ atm,\ 25\ °C}$[E]	$\log(f_{H_2}^{WO})_{P,T}$[F]	$\log(f_{O_2}^{WO})_{P,T}$[G]
76	793	−15.4391	9.2494	3.193	1.663	−0.8078	−0.5110	2.257	−16.627
67	758	−16.2078	9.6626	3.173	1.614	−0.8398	−0.5568	2.180	−17.339
71	754	−16.2990	9.7116	3.170	1.608	−0.8436	−0.5427	2.210	−17.503
63	700	−17.6034	10.4134	3.128	1.516	−0.8978	−0.6148	2.082	−18.735
72	656	−18.7784	11.0451	3.086	1.430	−0.9467	−0.6656	1.992	−19.902

[A] $(f_{O_2}^{CoO}) = -24242.6/T + 7.205 + 0.052(P - 1)T$; T in K and P in bar (Chou, 1987b).
[B] K_w for the reaction H$_2$ + ½O$_2$ = H$_2$O; data from Robie et al. (1979).
[C] Data from Burnham et al. (1969).
[D] Calculated from the equation $\log f_{H_2}^{CoO} = \log f_{H_2O} - \log K_w - \frac{1}{2} \log f_{O_2}$.
[E] Calculated from Equation 6.
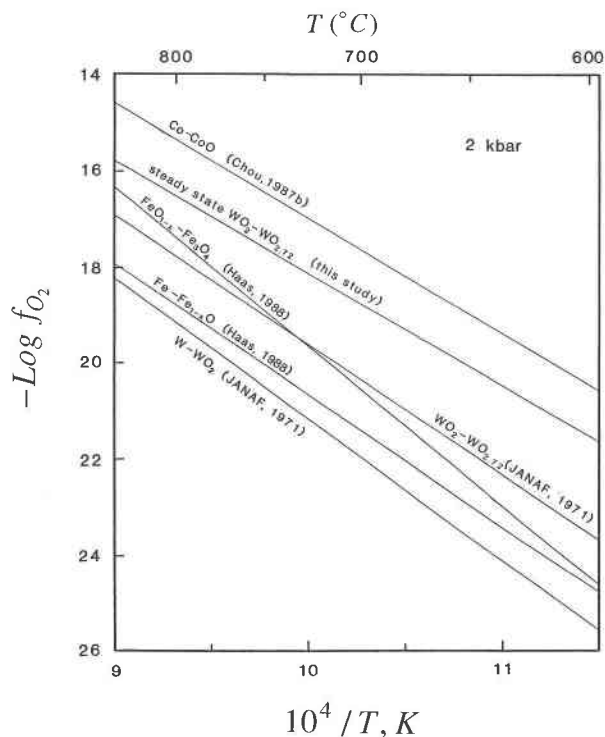[F] Calculated from Equation 5.
[G] Calculated from Equations 5 and 9.

Fig. 5. Diagram of log f_{O_2} vs. 1/T at 2 kbar based on the data given in Table 3. The data for WO$_2$-WO$_{2.72}$ and W-WO$_2$ equilibria were from JANAF (1971). Those for WM (wüstite-magnetite) and IW (iron-wüstite) were from Haas (1988). All calculations were corrected to 2-kbar pressure using the molar volume data of Robie et al. (1979) or were estimated using molar volumes of the WO$_2$ and WO$_3$ end-members. Note that the steady-state f_{O_2} values obtained in this study for the assemblage WO$_2$ + WO$_{2.72}$ + H$_2$O are about one to two orders of magnitude more oxidizing than the equilibrium values.

proceeding to the right, and (2) the loss of H$_2$ through the Au capsule wall to the external pressure medium, CH$_4$ in this case. If the first process dominates, the f_{H_2} levels in the system may build sufficiently to closely approach the equilibrium values. If the second process prevails, there will not be an f_{H_2} increase in the system, and the f_{H_2} levels will tend to approach the external f_{H_2} conditions of the pressure vessel + pressure medium. However, if these two processes counterbalance each other during the run, steady-state f_{H_2} levels can be maintained in the system. The apparent linear trend of our experimental data shown in Figure 4 indicates that reproducible steady-state f_{H_2} values can be obtained in our particular experimental system, even though the time dependency of the f_{H_2} level at each P-T condition was not determined in this study. Of course, the actual f_{H_2} levels that can be obtained in this type of experimental system are system dependent. However, the important controlling factors are the nature of the container (i.e., the size and wall thickness of the Au or Ag capsules), the nature of the external pressure medium (see Fig. 3 and previous discussion), and the kinetics of the H$_2$-generating reaction used in the experiment.

The measured f_{H_2} values in Au capsules containing the initial assemblage WO$_2$ + H$_2$O under an external pressure of 2 kbar CH$_4$ were recalculated to $(f_{O_2}^{WO})_{2kbar,T}$ values through the following relations:

$$H_2 + \tfrac{1}{2}O_2 = H_2O \qquad (8)$$

and

$$K_w = f_{H_2O}/f_{H_2} \cdot f_{O_2}^{1/2}. \qquad (9)$$

The K_w data from Robie et al. (1979) and the f_{H_2O} data from Burnham et al. (1969) are used in this calculation. We have considered the effect of H$_2$ partial pressure on f_{H_2O} in the binary system H$_2$O-H$_2$ but found it to be negligible at the P-T-f_{O_2} conditions of this investigation. For example, we used PVT data from Presnall (1969), Shaw and Wones (1964), and Shaw (1967) to calculate the activity coefficient of H$_2$, γ_{H_2}, in our mixture H$_2$ + H$_2$O, which was then incorporated into our computations of log $f_{H_2}^{WO}$. That value was then converted to log $f_{O_2}^{WO}$ through Relations 8 and 9 and compared to log $f_{O_2}^{WO}$ values, not including $\gamma_{H_2}^{mixture}$; differences of ±0.02 log units were obtained, and therefore the activity coefficients of H$_2$ are not considered further.

The steady-state f_{O_2} values obtained for the initial assemblage WO$_2$ + H$_2$O at 2 kbar are listed in Table 3 and shown in Figure 5. Also shown in Figure 5 for comparison are the f_{O_2} values for the assemblages Co + CoO (Chou, 1987b), WO$_2$ + WO$_{2.72}$ (JANAF, 1971), W + WO$_2$ (JANAF, 1971), wüstite-magnetite, and iron-wüstite (WM and IW, respectively; Haas, 1988). The steady-state f_{O_2} values for the assemblage WO$_2$ + WO$_{2.72}$ + H$_2$O obtained in this study under an external pressure of 2 kbar CH$_4$ are about one to two orders of magnitude higher than the equilibrium values calculated from JANAF (1971). This difference demonstrates the danger of assuming equilibrium redox control of the buffer assemblage in the hydrothermal experiments using the O$_2$-buffer technique (see Chou and Cygan, 1989, 1990). As pointed out previously (Chou, 1987b), the presence of the buffer assemblage examined after quench (WO$_2$ + WO$_{2.72}$ + H$_2$O in this case) is a necessary, but not a sufficient, condition for equilibrium redox control.

For quantitative redox control in hydrothermal experiments, it has been suggested that an f_{H_2} sensor be incorporated into the experimental system to determine its true redox condition (Chou, 1988; Chou and Cygan, 1989, 1990). This practice is particularly important for systems that are employing the assemblage Co + CoO + H$_2$O or assemblages that are more reducing (see Fig. 5). In addition, H$_2$O should not be used as a pressure medium at these relatively reducing conditions. A recent example demonstrating the utility of f_{H_2} sensors can be found in the hydrothermal phase-equilibrium study of Moecher and Chou (1990) who employed a wide range of buffers including the WO$_2$ + H$_2$O assemblage. The f_{H_2} sensors were used to obtain isobaric reversals of equilibria that are f_{O_2}-T dependent at constant T rather than the traditional T reversal along an f_{O_2} buffer curve.

The use of the WO$_2$ + H$_2$O assemblage for steady-state redox control in hydrothermal systems differs from conventional redox buffers in two ways: (1) the actual redox state of the system is not governed by the chemical equilibrium of the buffer assemblage but rather by the dynamic balance between the rate of H$_2$ production and the rate of H$_2$ leakage and (2) the consumption of H$_2$ in the system is not achieved through the buffer reaction but rather through H$_2$ leakage through the capsule wall. Therefore, the presence or absence of WO$_{2.72}$ in the initial experimental assemblage has no effect on the redox state of the system, and the f_{H_2} of the system can never attain the level that allows Reaction 1 to proceed to the left and achieve values approaching those predicted through thermochemical calculations.

CONCLUSIONS

The f_{H_2} values for the H$_2$-generating assemblage WO$_2$ + H$_2$O contained in Au capsules were measured between 650 and 793 °C, under an external pressure of 2 kbar CH$_4$ using the previously calibrated Co-CoO-H$_2$O buffer as a reference. H$_2$ containment in the experimental sample has been demonstrated to be a problem at the H$_2$ levels produced by the WO$_2$ + H$_2$O assemblage. However, the use of this type of assemblage to generate a reproducible reducing environment, albeit steady state, can be successful in hydrothermal experiments if precautions are taken. These consist of the use of quantitative redox control techniques to measure the f_{H_2} at the experimental conditions, monitoring the H$_2$O content to reveal the degree of reaction, and lowering the f_{H_2} gradient across the capsule wall by using appropriate pressure media. The assemblage WO$_2$ + H$_2$O as a source of H$_2$ appears to be a useful addition to the available redox buffers, and its application can be extended to temperatures below 650 °C, the applicable low temperature limit of the C-CH$_4$ buffer (Chou, 1987a).

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