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Pressure-Volume-Temperature Measurements on Hydrogen from 200° to 600°C and up to 1800 Atmospheres

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Experimental pressure-volume-temperature (*P-V-T*) measurements on hydrogen have been made over the range 200°–600°C and 0–1800 atmospheres; from these data, fugacity coefficients have been calculated over this same temperature range and up to 2000 atmospheres. These data provide a basis for accurate calculation of oxygen fugacities in H_2-H_2O gas mixtures as long as the oxygen fugacities are higher than those of the wüstite-iron buffer assemblage.

INTRODUCTION

For hydrothermal experiments at high pressures, oxygen fugacity is frequently controlled by using an assemblage of solid phases that has a fixed oxygen fugacity at a given temperature [*Eugster*, 1957; *Eugster and Wones*, 1962]. By using a variety of mineral assemblages, it is possible to obtain different oxygen fugacities, but the method has the disadvantage that the oxygen fugacity cannot be varied continuously. *Shaw* [1963, 1967] developed a method that permits a continuous range of oxygen fugacities to be obtained, but the effective use of this method requires compressibility data on hydrogen over a wide range of temperature and pressure. Also, data on hydrogen at high temperatures and pressures will become increasingly important as experimental studies are extended to reactions with multicomponent gas phases [*Eugster and Skippen*, 1967].

Previously, reliable data for hydrogen have not extended above 300°C, and, for temperatures above 150°C, they have not extended above 1000 atmospheres. *Shaw and Wones* [1964] fitted an empirical equation to the low-temperature data and used this equation to calculate extrapolated fugacity coefficients up to 1000°C and 3000 atmospheres. However, it is desirable to have experimental data on hydrogen at these higher pressures and temperatures. *P-V-T* data on hydrogen are presented here for temperatures from 200° to 600°C and pressures up to 1800 atmospheres.

APPARATUS AND EXPERIMENTAL METHOD

The high-pressure part of the apparatus (Figure 1) consists of a bomb with an internal volume of about 15 cm^3, a nichrome-wound resistance furnace, an Aminco diaphragm-type compressor (model no. 46-14021), a cold trap, and two Heise bourdon-tube pressure gages. To avoid brittle failure of the bourdon tubes by contact with hydrogen, the gages were filled with oil and separated from the hydrogen by a U tube filled with mercury. The cold trap was used to remove any traces of grease or oil that might have entered the gas from the valve fittings or the pump. The low-pressure part of the apparatus consists of a 10-liter bottle attached to a mercury manometer and a vacuum pump. A cold trap on the vacuum side of the manometer helped prevent mercury vapor from entering the vacuum pump.

The volume of the 10-liter bottle plus connective glass tubing was measured as 9748 ± 2 cm^3 (average deviation) by expanding air at 1 atmosphere from a 3-liter flask of carefully measured volume into the previously evacuated 10-liter bottle.

To determine the volume of the bomb, it was filled with hydrogen at room temperature and at various pressures up to 1000 atmospheres. The amount of hydrogen was measured by expelling the gas into the 10-liter bottle, and the volume was then calculated using

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the data of *Michels et al.* [1959]. Replicate determinations of the volume yielded an average deviation of 0.1%. Volume determinations using hydrogen agreed within experimental error with check determinations using argon and nitrogen based on the data of *Michels et al.* [1951*a*, *b*]. The measured volume of the bomb consists of not only the volume of the bomb chamber but also the volume of a capillary stem and a valve block at the end of the stem (Figure 2). The calculated volume due to the stem and valve block was 0.64% of the volume of the bomb. At high temperatures and pressures, the bomb volume was corrected for thermal expansion and elastic stretch, using the data in Table 1. The elastic stretch correction was computed from the equation given by *Kennedy* [1954, p. 232]. The correction for thermal expansion varied from 0.64% at 200°C to 2.1% at 600°C; the maximum correction for elastic stretch was 0.31%.

Temperatures were measured with sheathed chromel-alumel thermocouples. These were calibrated by comparison against a chromel-alumel thermocouple standardized by the National Bureau of Standards. Recalibration of the chromel-alumel thermocouples following the *P-V-T* measurements showed some drift in the calibration curves, and taking this drift into account, the temperature measurements are believed to have a maximum possible error of 4°C. All emf measurements were made with a Leeds and Northrop White potentiometer.

The temperature inside the bomb chamber and closure stem was calibrated at each working temperature by replacing the capillary tube

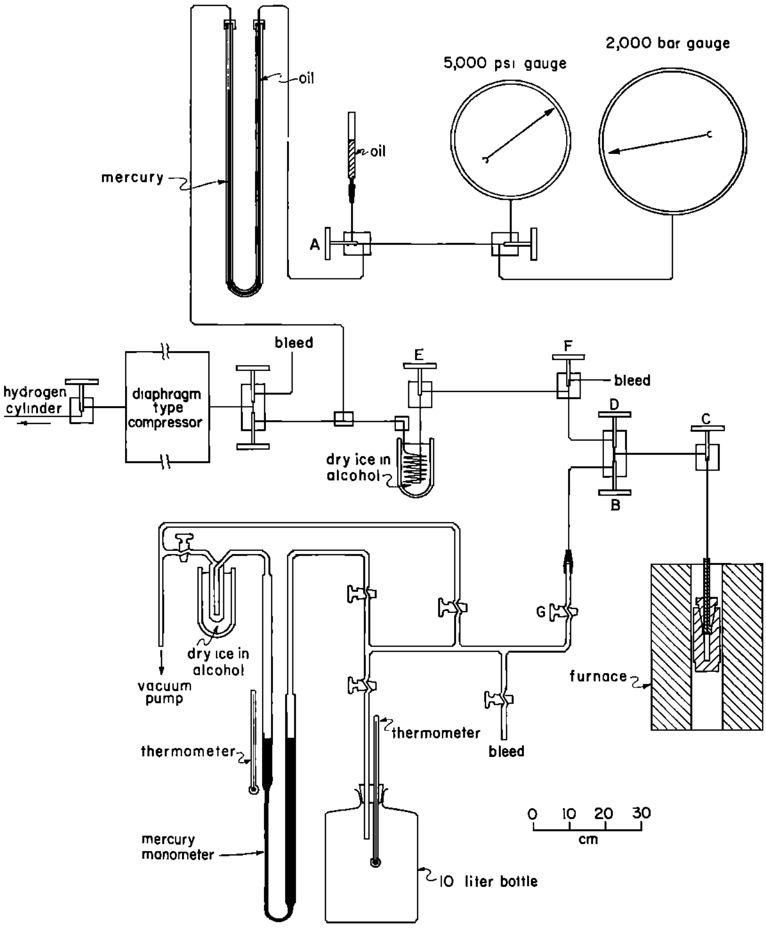

Fig. 1. Experimental apparatus for *P-V-T* measurements on hydrogen.

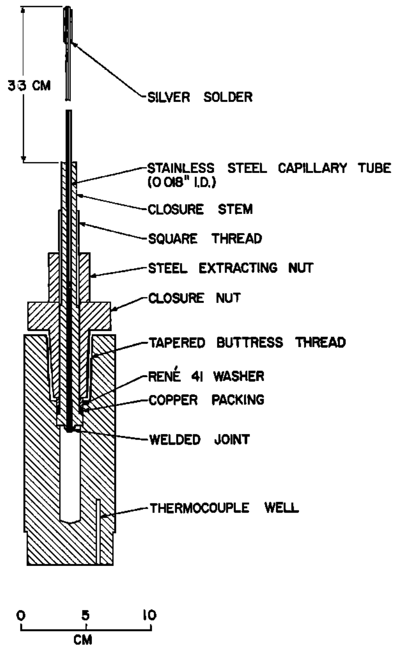

Fig. 2. Detail of pressure vessel, made from René 41 alloy.

with a thermocouple and comparing inside temperatures with the temperature in the thermocouple well (see Figure 2). At 200°C, the temperature gradient inside the bomb chamber was such that all parts of the chamber were within 0.5° of the average value. The temperature gradient increased with bomb temperature to a maximum deviation of 1.3° from the average value at 600°C.

Through the courtesy of H. W. Schamp, Jr., and Ian Spain, the two Heise bourdon-tube pressure gages were calibrated against a Hart pressure balance at the University of Maryland. Pressure measurements below 400 atm, made on the low-pressure gage, were reproducible to ±0.5 atm; all measurements at pressures of 400 atm and above were reproducible to ±1.5 atm.

The experimental procedure was as follows: Before each series of experiments along an isotherm, valve *A* (Figure 1) was opened briefly so as to bring the mercury levels in the two arms of the U tube to the same position. After bringing the bomb up to the desired temperature, the entire apparatus was evacuated. Valve *B* was closed, valve *C* was left just slightly open, and the desired pressure of hydrogen was pumped into the high-pressure part of the apparatus. The gas was then allowed to equilibrate in the bomb for 10–15 minutes. During this time, some hydrogen was lost by diffusion through the walls of the bomb. To maintain the desired pressure, valves *D* and *E* were periodically advanced slightly (but not closed). Then in rapid succession, valve *C* was closed, valve *E* was closed, valve *F* was opened, and valve *D* was closed. This prevented any subsequent leakage of hydrogen past valve *D* from the high-pressure part of the apparatus. Then valve *B* was opened, the tubing between valve *B* and *C* was evacuated, and finally valve *C* was opened to let the hydrogen into the 10-liter bottle. When the hydrogen had fully expanded into the 10-liter bottle, stopcock *G* was closed, and the amount of hydrogen was determined from the pressure on the mercury manometer, the temperature in the 10-liter bottle, and the compressibility data on hydrogen given by *Hilsenrath et al.* [1955]. To this amount of hydrogen was added a correction for the amount of hydrogen remaining in the bomb and in the pressure tubing between the bomb and stopcock *G*. From the time valve *C* was closed to the time it was opened again took about one minute, and an equal amount of time was allowed between the opening of valve *C* and the closing of stopcock *G*. This allowed recovery, through back-diffusion, of the hydrogen that diffused into the bomb walls after closure of valve *C*. It was discovered later that back-diffusion was faster than the diffusion rate into the bomb walls, but, for temperatures up to 600°, the amount of hydrogen diffused back out of the bomb walls in no case exceeded 0.3% of the amount of hydrogen in the bomb. However, diffusion

TABLE 1. Data on René 41 as Supplied by the General Electric Company

Temperature, °C	Mean Linear Coefficient of Thermal Expansion, °C^{-1}	Poisson's Ratio	Young's Modulus, Mb
27	...	0.308	2.182
93	11.95×10^{-6}	0.310	2.141
316	12.60×10^{-6}	0.317	2.007
538	13.46×10^{-6}	0.324	1.862
649	14.04×10^{-6}	0.327	1.793

caused large unknown errors in measurements at 700° and 800°C and these values are therefore not reported.

When the hydrogen was released from the bomb into the 10-liter bottle, the hydrogen in the valve block and capillary stem was released also. Because of a strong temperature gradient along the stem, the amount of hydrogen in the stem and valve block was substracted from the total. The amount of hydrogen to be subtracted was determined by measuring the temperature gradient along the stem and graphically integrating a plot of hydrogen density versus distance along the stem. For this purpose, values for hydrogen density calculated from the equation of *Shaw and Wones* [1964] were used.

'Ultra pure' hydrogen, obtained from the Matheson Company, was used in this investigation. This gas is stated by the Matheson Company to contain no more than 10 parts per million of impurities.

TABLE 2. Experimentally Determined Values for Molar Volume (cm^3/mole) of Hydrogen

Pressure, atm.	200°C	300°C	400°C	500°C	600°C
100	404.5 404.2	486.1	567.4	649	...
150	274.6	329.5 329.3	...	...	...
200	210.4 210.2	251.4 250.7	291.1	331.8	372.6
300	145.4 145.6	172.7 172.7	199.3	226.2	253.3 253.2
400	113.3	133.4 133.5	153.2 153.3	174.0	193.6
500	93.9	109.9	125.6	142.2	158.3
600	80.9 80.8	94.3 94.2	107.5	121.1	134.7
700	71.5	83.1 83.0	94.4	106.0	117.4
800	64.6	74.7	84.7	94.8	104.8
900	59.15	68.1	76.9	85.8	94.7
1000	54.72	62.9	70.7	78.7	86.6
1100	51.15 51.20	58.47 58.55	65.6	72.9	80.1
1200	48.16	54.90	61.4	68.1	74.7
1300	45.63	51.87	57.87	64.0	70.0
1400	43.48	49.22	54.78	60.5	66.1
1500	41.55	46.94	52.08	57.40	62.6
1600	39.86 39.88	44.85 44.92	49.76	54.72	59.57
1700	38.40	43.11	47.65	52.34	56.85
1800	36.99 36.98	41.44	45.73	50.10	54.35

DATA

The experimentally determined values for the molar volume of hydrogen are given in Table 2. Measurements along a given isotherm generally were taken slightly above or below the desired temperature, and the molar volumes subsequently were adjusted all to the same temperature. In making these adjustments, the equations of *Shaw and Wones* [1964] were used to calculate, at each temperature and pressure, the rate of change of molar volume with temperature. From Figure 3, it can be seen that at pressures above about 800 atm the rate of change so calculated is extremely close to the actual rate of change determined here. At lower pressures, the error produced by using the equations of Shaw and Wones increases only slightly and always remains much less than the experimental uncertainty in the measurements.

In Figure 3 are plotted the data obtained in the present study together with those obtained by previous workers. The data obtained by *Amagat* [1893] and *Bartlett et al.* [1928] are believed to lie outside the experimental error of the present method, but no explanation can be given for the systematic deviation of their results.

CALCULATION OF FUGACITY COEFFICIENTS

The equation of state of a real gas may be expressed in virial form as:

$$\bar{V} = \frac{RT}{P} + \sum_{n=0}^{\infty} a_n P^n$$

where $\bar{V}$ = molar volume (cm^3 — mole^{-1}), R = gas constant (82.0567 cm^3 — atm — ° C^{-1}), P = pressure (atm), T = temperature (°K).

If we let $\sigma = (\bar{V}/RT) - (1/P)$, then rearrangement gives

$$RT\sigma = \sum_{n=0}^{\infty} a_n P^n \qquad (1)$$

Each isotherm (Figure 3) was fitted to an equation of this form.

Let e_i = error in the least-squares fit for measurement i. Then, for each isotherm

$$\sum_i e_i^2 = \sum_i \left(RT\sigma_i - \sum_{n=0}^{j} a_n P_i^n\right)^2$$

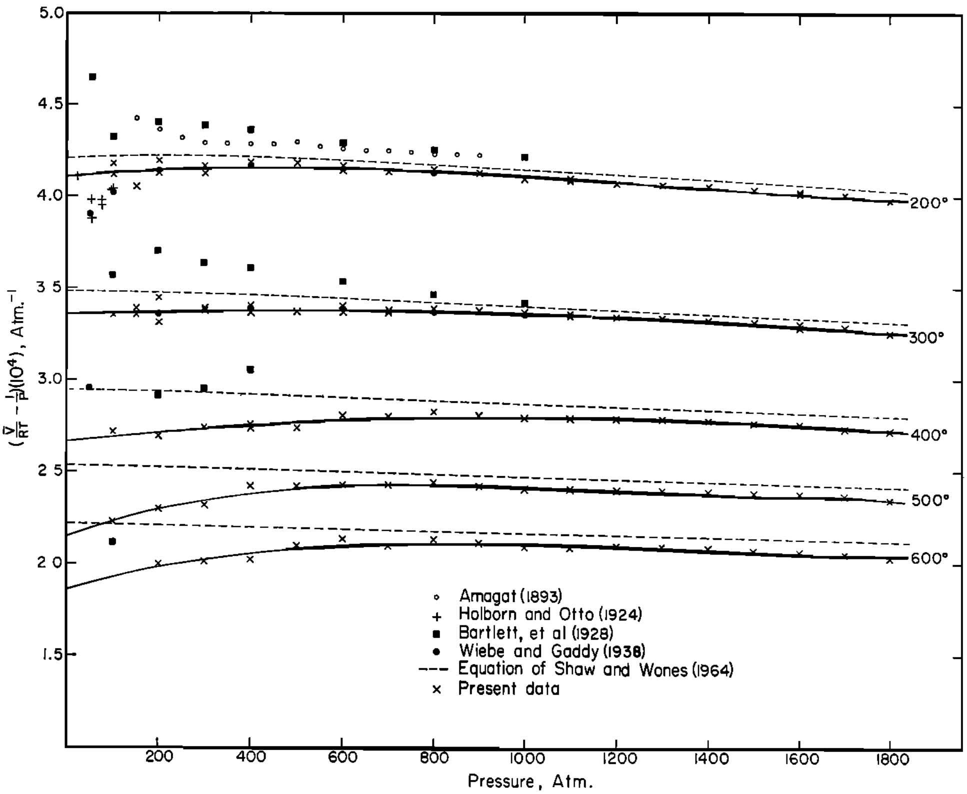

Fig. 3. Isotherms of hydrogen. The data of Amagat are at 200.25°C; those of Holborn and Otto are at 200°C; those of Bartlett et al. are at 198.9°, 299.1°, and 399.3°C (all the scattered squares below a value of $[(\bar{V}/RT) - (1/P)](10^4)$ of 3.2 are at 399.3°C); and those of Wiebe and Gaddy are at 200° and 300°C. Solid lines are least-squares fits to the present data as explained in the text.

For each isotherm, set

$$\frac{\partial \sum_i e_i^2}{\partial a_m} = 0 = \sum_i \left[P_i^m\left(RT\sigma_i - \sum_{n=0}^{j} a_n P_i^{n+m}\right)\right]$$

$$m = 0, 1, 2, \cdots, j$$

This yields $j + 1$ equations for each isotherm, which, when solved simultaneously, give $j + 1$ values of the coefficients a_n. These coefficients are listed in Table 3.

The number of terms to be used in the equation for each isotherm was determined by calculating the quantity $[\Sigma_i e_i^2/(i - j + 1)]^{1/2}$ and finding the number of terms that minimized this quantity. From this criterion, the number

TABLE 3. Coefficients (a_n) for Equations 1

	200°C	300°C	400°C	500°C	600°C
a_0	15.950	15.797	14.747	13.602	13.401
a_1	0.851×10^{-3}	0.369×10^{-3}	1.424×10^{-3}	5.366×10^{-3}	4.758×10^{-3}
a_2	-1.107×10^{-6}	-0.350×10^{-6}	-0.707×10^{-6}	-2.445×10^{-6}	-3.995×10^{-6}
a_3	0.268×10^{-9}	0	0	-5.072×10^{-9}	0.961×10^{-9}
a_4	0	0	0	5.219×10^{-12}	0
a_5	0	0	0	-1.360×10^{-15}	0

of terms in each equation was found to vary from three to six (see Table 3); in Figure 3 it can be seen that the calculated curves fit the data points within the experimental uncertainty.

To calculate fugacity coefficients ($\nu = f/P$, where f is fugacity as defined by *Tunell* [1931]) over the entire range of temperature, each coefficient a_n was fitted by the same method used above to an equation of the form

$$a_n = \sum_{k=0}^{4} b_k T^k \qquad (2)$$

where the coefficients b_k are given in Table 4. Fugacity coefficients, ν, were calculated from the equation

$$\ln \nu = \int_0^P \sigma \, dP$$

where σ is given by equation 1. That is, the fugacity coefficient at any temperature and pressure is given by

$$\nu = \exp\left[\frac{1}{RT}\left(\sum_{n=0}^{5} \frac{a_n P^{n+1}}{n+1}\right)\right] \qquad (3)$$

with each a_n being expressed by (2).

Fugacity coefficients have been calculated from equation 3 at intervals of pressure of 10 atm (and 10 bars) and intervals of temperature of 10°C, and the complete listing has been deposited with the National Auxiliary Publications Service.[2] Representative values are given in Table 5. It will be noted that these values are slightly lower than the values given by *Shaw and Wones* [1964], but the maximum error in the values of Shaw and Wones is only 2%. Crude measurements at 700° and 800°C, not reported here because of excessively large diffusion errors, indicate that the general shape of the curves in Figure 3 is continued at least up to 800°C. This suggests that, for temperatures and pressures beyond the range reported

TABLE 4. Coefficients (b_k) for Equations 2

	a_0	a_1	a_2	a_3	a_4	a_5
b_0	-5.9530	-5.339960×10^{-1}	9.59240×10^{-5}	1.4331645×10^{-6}	$-1.3864592 \times 10^{-9}$	3.612068×10^{-13}
b_1	8.32848×10^{-2}	3.5648890×10^{-3}	-6.918688×10^{-7}	-9.284277×10^{-9}	$8.99667834 \times 10^{-12}$	$-2.3438565 \times 10^{-15}$
b_2	-4.70713×10^{-5}	$-8.7508237 \times 10^{-6}$	1.7788089×10^{-9}	$2.2209980 \times 10^{-11}$	$-2.15438222 \times 10^{-14}$	$5.6126968 \times 10^{-18}$
b_3	-1.12482×10^{-7}	9.3529095×10^{-9}	$-1.9461187 \times 10^{-12}$	$-2.32388561 \times 10^{-14}$	$2.25503501 \times 10^{-17}$	$-5.8749221 \times 10^{-21}$
b_4	9.87500×10^{-11}	$-3.6618958 \times 10^{-12}$	7.630833×10^{-16}	$8.9659248 \times 10^{-18}$	$-8.6978331 \times 10^{-21}$	$2.2660000 \times 10^{-24}$

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[2] This table has been deposited as document NAPS-00554 with the National Auxiliary Publications Service of The American Society for Information Science, 22 West 34th Street, New York, New York 10001. A copy may be obtained by citing the document number and remitting $3.00 for photoprints or $1.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-National Auxiliary Publications Service.

TABLE 5. Fugacity Coefficients for Hydrogen

Pressure	200°C	300°C	400°C	500°C	600°C
200 atm	1.086	1.070	1.055	1.045	1.039
200 bars	1.085	1.069	1.055	1.045	1.039
400 atm	1.180	1.144	1.115	1.096	1.082
400 bars	1.177	1.142	1.113	1.094	1.081
600 atm	1.282	1.224	1.178	1.150	1.128
600 bars	1.278	1.221	1.176	1.148	1.126
800 atm	1.393	1.310	1.246	1.207	1.177
800 bars	1.387	1.305	1.242	1.204	1.174
1000 atm	1.513	1.401	1.317	1.267	1.228
1000 bars	1.505	1.395	1.313	1.263	1.224
1200 atm	1.642	1.498	1.393	1.330	1.280
1200 bars	1.632	1.491	1.387	1.325	1.276
1400 atm	1.781	1.602	1.473	1.395	1.335
1400 bars	1.768	1.592	1.466	1.389	1.330
1600 atm	1.930	1.711	1.557	1.463	1.391
1600 bars	1.914	1.700	1.548	1.455	1.385
1800 atm	2.091	1.827	1.644	1.534	1.449
1800 bars	2.071	1.813	1.634	1.525	1.442
2000 atm	2.264	1.950	1.736	1.605	1.510
2000 bars	2.240	1.933	1.724	1.596	1.502

here, the fugacity coefficients of Shaw and Wones may be used with only a small error.

APPLICATION OF DATA

These data provide a basis for interpreting hydrothermal experiments in which the oxygen fugacity is controlled by a gas mixture. The apparatus described by *Shaw* [1963, 1967] permits the oxygen fugacity of a hydrothermal experiment to be varied continuously and independently of temperature. The calculation of the oxygen fugacity imposed on a sample during an experiment depends on (1) a knowledge of the fugacities of H_2 and H_2O in mixtures of these two gases and (2) the assumption that there are no species other than H_2, H_2O, and O_2 in the gas phase in equilibrium with the sample. With the exception of the very limited data of *Shaw* [1963], there are no data on H_2-H_2O mixtures from which fugacity coefficients of these two gases can be calculated. Alternatively, one can assume ideal mixing of H_2 and H_2O, that is, assume that the fugacity of each species in the mixture is proportional to its mole fraction, and use fugacity coefficients determined from *P-V-T* measurements on the pure gases. Fugacity data for H_2O have been tabulated by *Holser* [1954], *Anderson* [1967], and *Burnham et al.* [1969]. The error in the calculated oxygen fugacity caused by deviations from ideal mixing would increase with increasing pressure, decreasing temperature, and increasing H_2/H_2O ratio. At 700°C and 800 bars, *Shaw* [1963] found that the error increases from a negligible amount at H_2/H_2O ratios less than 0.02, to 1.5% of the logarithm of the oxygen fugacity at an H_2/H_2O ratio of 1.8. Stated differently, the error in the calculated oxygen fugacity is negligible at oxygen fugacities higher than that of the quartz-fayalite-magnetite buffer and increases to 1.4% of log f_{O_2} as the oxgyen fugacity is reduced to that of the wüstite-iron buffer (see also *Shaw* [1967, p. 534]).

The problem of species in the gas other than H_2, H_2O, and O_2 has been considered by *Eugster and Wones* [1962, p. 93]. They found that representative solubilities of silicates and oxides in water vapor would cause a negligible error in the calculated oxygen fugacity.

To summarize, the present data on hydrogen, together with (1) fugacity values for water and (2) the assumption of ideal mixing, provide a basis for calculating oxygen fugacities in H_2-H_2O mixtures with negligible error as long as the oxygen fugacities are higher than those of the quartz-fayalite-magnetite buffer. This same procedure can be used with only a small error for oxygen fugacities as low as those of the wüstite-iron buffer, but a more precise estimate would be obtained by using the procedure described by *Shaw* [1967, pp. 532–534].

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