A simple gas analytical technique for the Dickson-type hydrothermal apparatus and its application to the calibration of MH, NNO and FMQ oxygen buffers

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A simple gas chromatographic technique was developed for the determination of dissolved gases in the aqueous samples taken out from Dickson-type hydrothermal apparatus, and H_2 concentration was measured at temperatures below $500^\circ C$ and pressures below 1,000 bars in aqueous systems containing magnetite-hematite, Ni-NiO and fayalite-magnetite-quartz oxygen buffers. Oxygen-fugacity ratios between buffers A and B can be obtained by using a relation: $f_{O_2}(A)/f_{O_2}(B) = [C_{H_2}(B)/C_{H_2}(A)]^2$, where $C_{H_2}(A)$ and $C_{H_2}(B)$ are equilibrium H_2 concentrations in the systems A-water and B-water under the same P-T condition. Using a few f_{O_2} ratios thus obtained, corrections were evaluated for the f_{O_2} -T relationships of the buffers given by a thermochemical compilation of ROBIE *et al.* (1979).

INTRODUCTION

The Dickson-type gold-cell apparatus (RYTUBA and DICKSON, 1974; SEYFRIED *et al.*, 1979) is an excellent device that enables us to conduct long-term hydrothermal experiments in chemically clean, large-volume reaction vessels and to take out solution samples easily from reacting systems without disturbing experimental conditions. This paper describes a simple technique of determining dissolved gases in these samples and its application to the calibration of oxygen fugacity *vs.* temperature relationships of magnetite-hematite (MH), nickel-nickel oxide (NNO) and fayalite-magnetite-quartz (FMQ) oxygen buffers:

The method of the calibration is as follows. Each of these buffers is put in water, equilibrated under appropriate P-T conditions and the hydrogen (H_2) concentration in water is measured. The oxygen buffer defines the oxygen fugacity (f_{O_2}), the hydrogen fugacity (f_{H_2}) and the H_2 concentration in water (C_{H_2}) in the system according to the relation:

$$\begin{aligned} f_{O_2} &= (f_{H_2O}/K_W f_{H_2})^2 \\ &= (f_{H_2O}/K_W Y)^2 (1/C_{H_2})^2 \end{aligned} \quad (4)$$

where f_{H_2O} is the water fugacity in the system, K_W is the equilibrium constant for the reaction $H_2 + 1/2 O_2 = H_2O$ and Y denotes the f_{H_2}/C_{H_2} ratio. In all systems dealt with in this study, the aqueous phase can be regarded as pure water with respect to f_{H_2O} , and f_{H_2} is low enough to be proportional to C_{H_2} , so that the first term of the right side of eq. (4) becomes a quantity dependent only on temperature and pressure of water. The values of Y will be presented in another paper (KISHIMA and SAKAI, 1984), but without knowing them at present, we can get f_{O_2} ratios for a pair of oxygen

buffers A and B by measuring equilibrium CH_2 's in the aqueous systems containing each of these buffers under the same P-T conditions and by using a relation:

$$f_{\text{O}_2}(\text{A})/f_{\text{O}_2}(\text{B}) = [\text{C}_{\text{H}_2}(\text{B})/\text{C}_{\text{H}_2}(\text{A})]^2 \quad (5)$$

which can be derived easily from eq. (4) for the two buffers. The f_{O_2} ratio under 1 bar standard pressure is obtained by subtracting the effect of pressure P on the $\log f_{\text{O}_2}$ of each of the buffers which is evaluated by $-\Delta V_{\text{S}} \cdot (P - 1)/(RT \ln 10)$, where ΔV_{S} is the volume change of solids in the reactions (1), (2) and (3); the numerical values of ΔV are -3.548 , -8.764 and $-17.942 \text{ cm}^3/\text{mol}$ (ROBIE *et al.*, 1979), respectively. Thus, the present calibration of f_{O_2} -T relationships of oxygen buffers is essentially a relative one.

EXPERIMENTAL METHODS

Hydrothermal equipment and materials The Dickson-type apparatus used in this study is schematically illustrated in Fig. 1. The reaction vessel is a deformable, cylindrical gold bag of 2.7 cm diam., 26 cm long and 0.2 mm wall thickness. A gold capillary tube (0.5 mm I.D., 2.0 mm O.D. and 42 cm long) leads the solution in the vessel to the sampling valve, which is an ordinary 3-way high pressure valve.

Temperature was monitored with three thermocouples placed at the both ends and the center of the pressure vessel and controlled to $\pm 0.5^\circ\text{C}$ by a temperature recorder/controller according to the output from the central thermocouple. The accuracy of the thermocouple-controller system was calibrated to about $\pm 0.7^\circ\text{C}$ by using the melting-point method and a guaranteed thermocouple. The furnace winding is divided into three units and the power supplies to each of them were adjusted so as to bring the three temperature readings within $\pm 0.5^\circ\text{C}$. The temperature difference between the wall and the interior of the pressure vessel has been confirmed to be negligible. Taking all possible errors into account, the

Fig. 1. Dickson-type gold-cell hydrothermal apparatus and the set-up for solution sampling and gas extraction.

uncertainty of individual temperature is estimated to be within $\pm 1.0^\circ\text{C}$ and the reproducibility of temperature between separated runs is estimated to be within $\pm 0.6^\circ\text{C}$. Pressure is adjusted to a desired level usually by controlling the amount of water outside the reaction vessel. Helium was added to the outside water so that any accidental leakage of the gold bag could be detected easily by the appearance of a helium peak on the gas chromatogram of the dissolved gases in the sample solution. The pressure was monitored by a monitoring gauge and its precise value was read on the occasion of sampling using a standard Boudon gauge calibrated to a certified dead-weight pressure gauge. The uncertainty of pressure is estimated to be less than 1 bar. The experimental condition was limited below 500°C and 1 kbars by the durability of the pressure vessel.

MH buffer was made by mixing 10 g each of chemical reagents Fe_3O_4 and Fe_2O_3 . These materials were fine powder with grain diameters less than 0.2 and 6 μm , respectively, and gave X-ray powder patterns identical with those of typical magnetite and hematite. Their purities (for Fe + O) were better than 99.9 wt. % and O/Fe atomic ratios were 1.36 and 1.49, respectively. The slight analytical non-stoichiometry was ignored, because the above mixture obviously could stabilize only into a mixture of magnetite and hematite under the experimental conditions. NNO buffer was prepared from 20 g of fine powder of NiO (grain size < 8 μm , purity > 99.98 %) by reducing about a half of it with H_2 in water in the reaction vessel. FMQ buffer was composed of 10 g of fayalite (grain size < 150 μm), 5 g of Fe_3O_4 (the same reagent as above) and 2 g of SiO_2 (precipitated silica identified with quartz by its X-ray powder pattern, purity > 99.98 %). The fayalite used here was synthesized by heating a stoichiometric mixture of Fe_2O_3 (the same reagent as above), Fe (reduced iron, metallic impurity < 0.04 wt. %) and SiO_2 (the same reagent as above) at 1,000°C in an evacuated, sealed silica tube. The synthetic product (well-crystallized fayalite) contained small amounts of wüstite and quartz but it was used without further treatment since wüstite is unstable under the experimental conditions. The water used was basically deaired, de-ionized water but oxygen or hydrogen was added occasionally in order to condition the oxygen buffers.

Determination of H_2 in the aqueous sample

The sampling of the hydrothermal solution and the extraction of dissolved gases in the sample were conducted by using a set-up illustrated in Fig. 1. Two plastic syringes (12 ml in capacity; silicone oil was used as lubricant for the piston), three plastic 3-way stopcocks, a hypodermic needle (15 cm long; it can be fastened to the sampling valve by the aid of a small piece of metal pipe cemented at the end of the needle) and other parts shown in Fig. 1 are all inexpensive materials.

The sampling procedure is as follows. The upper syringe containing a known amount (*ca.* 9 cm^3) of nitrogen (N_2), and other parts except the lower syringe and stopcock, are attached to the sampling valve as illustrated in Fig. 1. A small fraction (*ca.* 0.5 ml) of solution is discarded. Nitrogen is let flow through the sampling valve and the needle, the moisture in the flow path is expelled, the lower syringe is attached and, after its inner space is flushed with N_2 , the piston of the lower syringe is pushed up, the pressure of N_2 flow is released and the flow path is cut off enclosing a small, known amount of N_2 . An appropriate amount (*ca.* 2 ml) of solution is taken to the lower syringe (note here that the solution sample is cooled efficiently on the way to the syringe), the N_2 in the upper syringe is also transferred there, the lower syringe (kept attached to the acceptor of the needle) is shaken for about 3 minutes, and then the resulting gas mixture is transferred back to the upper syringe and submitted to the following gas chromatographic analysis. The solution remaining in the lower syringe is weighed and submitted to chemical analyses, if necessary. Our sampling set-up was tested and found satisfactory with regard to leak-out of H_2 , leak-in of air and H_2 evolution from the materials used, as long as all the above procedures are carried out in succession.

The gas analysis was performed by using a Shimadzu GC-6AM gas chromatograph equipped with a thermal conductivity detector (TCD), a dual separating column (3 mm I.D. $\times$ 5 m) packed with Porapak-Q (Waters Associate Ltd.; 80-100 mesh), and a constant-volume (2 cm^3) gas sampler. The carrier gas was N_2 and the column temperature was set at 60°C. To obtain a higher sensitivity for H_2 analysis, argon might have been better than N_2 for the carrier gas (and hence the stripping gas as well). The output of the chromatograph was fed to a strip chart recorder and a data processor (Shimadzu C-R1A 'Chromatopac') in order to measure peak areas. The sensitivity of the gas chromatographic system was calibrated under a standardized set of conditions with accuracies

ranging from 0.7 to 5 % for H_2 concentrations ranging from 100 % to 14 ppm using mixtures of N_2 and H_2 of known compositions. In calculating the C_{H_2} in the solution sample, corrections were made for the water vapor present in the gas mixture sample and for the drift of sensitivity of the gas chromatographic system. The reliability of the analytical scheme was confirmed by measuring solubility of H_2 in water at a room temperature. Throughout this report, C_{H_2} is given in cm^3 of H_2 at STP dissolved in 1 g of water.

EXPERIMENTAL OBSERVATIONS and RESULTS

C_{H_2} in the MHW system An example of variation with time in H_2 concentration in the MHW system is shown in Fig. 2.* The system was first brought up to 420°C and 982 bars in 5 hours and kept at the condition afterward (stage (a)). The C_{H_2} passed a peak after 9 hours, returned quickly to a basic, slowly rising curve and finally reached a constant level after about 170 hr. These features can be explained respectively by quick decomposition of organic

Fig. 2 Variation with time of H_2 concentration in a virgin MHW system.

* Here and hereafter, W denotes water.

Table 1. Equilibrium H_2 concentrations in the MHW system

T(°C)	P (bar)	$C_{H_2} \times 10^4$	T(°C)	P (bar)	$C_{H_2} \times 10^4$
296	986	2.09	387	296	25.5
—	720	2.23	416	999	13.0
—	478	2.33	—	853	14.3
—	286	2.39	—	707	16.8
—	98	2.89	—	558	21.0
326	972	3.65	—	430	29.8
—	575	4.13	—	365	48.3
—	286	5.05	455	980	22.5
—	145	5.76	—	478	63.7
356	974	5.82	456	723	31.4
—	575	7.05	486	974	32.4
—	332	9.01	—	773	42.8
—	238	10.9	—	624	60.4
—	198	12.6	—	548	79.5
386	286	25.6	—	503	99.1
387	757	10.3	—	485	112
—	731	10.4	—	440	133
—	623	11.6	—	380	176
—	336	19.4	487	974	33.2

impurities included in the starting material, reactive nature of hematite or of an oxidation layer formed over magnetite by the action of water and the oxygen dissolved in the water (this time the water was saturated with air), and slow change of the solid phase to the stable magnetite-hematite assemblage. Then, the temperature was lowered to 300°C maintaining the previous pressure (stage (b)). The C_{H_2} value reached a new equilibrium level in 3 days, more quickly than before in spite of the lower temperature. In the next stage (c), after the system was stabilized at 300°C and 120 bars and a sample was taken (marked by 'S'), an aliquot of water saturated with oxygen was injected into the reaction vessel. The H_2 in the vessel was killed immediately but recovered the initial concentration at 'S' within 3 days.

The measured equilibrium C_{H_2} values of MHW systems are listed in Table 1 and shown in Fig. 3. Most of these data are mean values from replicate measurements that agreed within ± 1.5 % (± 4 % in the worst case). We allotted times longer than 7, 4 and 2 days at 300, 400 and 500°C, respectively, for the re-equilibration of the system after a change of pressure or temperature. The lower limit of experimental

Fig. 3 Equilibrium CH_2 values in the MHW system. Isotherms for 455, 416 and 387°C are extrapolated by using Y values given by KISHIMA and SAKAI (1984). SVP: the saturation vapor pressure curve of water.

temperature ($\sim 295^\circ$) was imposed by the decrease in the accuracy of hydrogen determination with decreasing CH_2 .

CH_2 in the NNOW system Equilibration curves of CH_2 in the NNOW system initiated under out-of-equilibrium conditions can be featured by a superposition of a fast and a slow processes, and these are supposed to be the redox reactions on the surface of Ni or NiO grains and the diffusion of hydrogen into or out of Ni grains, respectively. It should be noted that, owing to the slow process, the NNOW system requires considerably long time to attain the true equilibrium. Even in the present NNOW system which comprised fine powder of Ni, the time necessary for equilibration was about 5 to 6 times as long as that for the MHW system under the similar conditions.

The measured equilibrium CH_2 values of the NNOW system and the differences of $\log f_{\text{O}_2}$ between MH and NNO buffers calculated therefrom are given in Table 2. The activity of Ni was assumed to be unity in the calculation of the $\log f_{\text{O}_2}$ difference on the basis of the facts

Table 2. Equilibrium H_2 concentrations in the NNOW system, corresponding values in the MHW system and $\log f_{\text{O}_2}$ differences ($\Delta \log f_{\text{O}_2}$) between MH and NNO buffers

$T(^{\circ}\text{C})$	$P(\text{bar})$	$\text{CH}_2 \times 100$ in NNOW	$\text{CH}_2 \times 10^4$ in MHW	$\Delta \log f_{\text{O}_2}$ at T, P	$\Delta \log f_{\text{O}_2}$ at $T, 1 \text{ bar}$
486	980	28.3	32.6	3.88	3.91 ± 0.04^a
466	978	20.8	26.2	3.80	3.84 ± 0.04
396	337	20.1	26.2	3.77	3.81 ± 0.05
355	980	3.59	5.70	3.60	3.64 ± 0.05
327	195	3.66	5.50	3.65	3.66 ± 0.06

^a Errors are for the possible temperature discrepancy of $\pm 0.6^\circ\text{C}$ between MHW and NNOW systems and for the possible analytical error of $\pm 2\%$ in the CH_2 ratios.

that (1) the H/Ni atomic ratio in the Ni grains, which can be calculated from the CH_2 data, the Y values given by KISHIMA and SAKAI (1983) and the reported solubility data for hydrogen in Ni (STAFFORD and McLELLAN, 1974), remained at about 1.6×10^{-4} even in the case of 486°C and 980 bars, and that (2) gold did not deposit on the Ni grains under the experimental conditions, as confirmed by SEM observation of the solid phase after the run.

CH_2 in the FMQW system The CH_2 values in the FMQW system were measured only at 487°C and 970 bars; the temperature is just above the low-temperature boundary (which falls within 478–484°C (FLASCHEN and OSBORN, 1957)) of the stability field of fayalite in the presence of water and quartz. All the measured CH_2 data are given in Table 3. Somewhat higher values of the earlier measurements may be attributed to the wüstite contained in the starting material. A mean value of $\text{CH}_2 = 0.530 \pm 0.007$ is obtained from the later seven measurements but the actual error range is estimated to be about ± 0.015 taking possible temperature and analytical errors into account.

The water in this system is saturated with quartz under the given P-T condition (in fact, 2290–2335 ppm of silica was observed in agreement with the data of KENNEDY, 1950, and FOURNIER and POTTER, 1982). If the solution

Table 3. Measured H_2 concentrations in the FMQW system at 487°C and 970 bars

Lapse of time (Days)	CH_2
5	0.575 ^a
16	0.630
22	0.630
75	0.543, 0.518 ^a
87	0.530
93	0.525 ^a
102	0.538, 0.525, 0.531

^a H_2 was injected after these samplings.

stays long in the capillary tube, quartz will precipitate and eventually clog the tube. In order to avoid this trouble, water was injected into the reaction vessel after every sampling except for three samplings that were immediately followed by the next sampling. Sometimes 10–15 cm^3 at STP of H_2 and sometimes no H_2 was put into the vessel together with the water. The observed constancy of CH_2 , therefore, can be regarded as a manifestation of the buffering function of FMQ assemblage.

Though the concentrations of dissolved silica and H_2 are fairly high, the solute/solvent molar ratio remains at about 8×10^{-4} and therefore the f_{H_2O} can still be taken to be equal to that of pure water. Then, from the above mean CH_2 value and the corresponding value of the MHW system, $3.28 \pm 0.10 \times 10^{-3}$, the $\log f_{O_2}$ difference between MH and FMQ buffers is calculated to be 4.417 ± 0.05 at 487°C and 970 bars or 4.513 ± 0.05 at the same temperature and 1 bar.

DISCUSSION

We will now discuss the f_{O_2} - T relationships of individual oxygen buffers on the basis of the data obtained above and related data in the literature. The thermochemical compilation of ROBIE *et al.* (1979) (abbreviated to RHF in the following) will be chosen as a main

reference and corrections will be evaluated for the $\log f_{O_2}$ - $1/T$ relationships of MH, NNO and FMQ buffers given by RHF.

Fig. 4 Comparison of reported $\log f_{O_2}$ - $1/T$ scales of NNO buffer determined by the high-temperature emf method. $\Delta \log f_{O_2}$ denotes the difference from a temporary scale: $\log f_{O_2} (\text{atm}) = 8.9 - 24500/T$. Data sources: 1, KIUKKOLA and WAGNER (1957); 2, MARKIN and BONES (1962); 3, BARBI (1964); 4, ALCOCK and BELFORD (1964); 5, TAYLOR and SCHMALZRIED (1964); 6, TRETYKOV and SCHMALZRIED (1965); 7, STEELE and ALCOCK (1965); 8, SELLARS and MAAK (1966); 9, PIZZINI and MORLOTTI (1967); 10, ANTILL and WARBURTON (1967); 11, CHARETTE and FLENGAS (1968); 12, MORIYAMA *et al.* (1969); 13, HUEBNER and SATO (1970); 14, FISCHER and PATEISKY (1970); 15, OISHI *et al.* (1972); 16, KLINEDINST and STEVENSON (1972); 17, VASIL'eva *et al.* (1975); 18, IWASE *et al.* (1975); 19, MOSER *et al.* (1975); 20, BERGLUND (1976); 21, MYERS and GUNTER (1979); 22, KEMORI *et al.* (1979); 23, SCHWAB and KÜSTNER (1981); 24, JACOBSSON and ROSÉN (1981). Two marks with arrows indicate the positions where these data converge; dashed line M, the mean of these data; dashed line RHF, the $\log f_{O_2}$ (atm)- $1/T$ relation given by ROBIE *et al.* (1979).

The NNO buffer is the most convenient one to be discussed first, since (1) its buffering reaction involves the smallest mole number of compounds, (2) comparatively good thermochemical data are available for its components, and (3) its f_{O_2} -T relation at higher temperatures has been measured repeatedly by the solid-electrolyte emf method.

Arbitrarily collected twenty-four electrochemical data for the NNO system are plotted in Fig. 4 using their differences ($\Delta \log f_{O_2}$) from a temporary scale. These data, mostly given in the form of $\log f_{O_2} = a-b/T$, can be averaged to a scale of $\log f_{O_2}$ (atm) = $9.08-24650/T$ (dashed line M in Fig. 4) by taking average for coefficients a and b , while they appear to converge around the two points marked by circles with arrows that indicate $\pm 10\%$ span of f_{O_2} (including some scales extended out of their original temperature ranges, 13 and 15 scales cross the arrows at the left and the right marks, respectively). The $\log f_{O_2}$ - $1/T$ relation of NNO given by the tabulated values of RHF (which we call "reference scale" for short) is also plotted as the curve RHF.

The following comments can be made with regard to Fig. 4: (1) Although the high-temperature emf method is generally accepted as an accurate one, the plotted data show a fairly large scatter. One of the possible causes giving rise to such a scatter is erratic influence of high f_{O_2} reference gases or of ambient air on the low f_{O_2} , NNO system in the cell assembly and this implies the possibility that some of the plotted scales have been biased toward higher f_{O_2} . In any case, it is apparent that assertions dependent on only one or two of these data must be considered with reserve (see, for example, KELLOGG, 1969); (2) The two marks mentioned above are in good accord with the reference scale but this is not a sufficient proof for the validity of the scale; (3) If the reference scale is conformable with the plotted experimental data, a tangent (not shown) touching the curve RHF at about 1,150°K (i.e., an approximate median temperature for the plotted scales) should have the same slope as that of the line

M. The difference of slope now existing, then, can be interpreted as suggesting a reduction (by about 1.6 KJ/mol) of the ΔH_f° of NiO given by RHF.

Independently from these and thermochemical data, a $\log f_{O_2}$ value of NNO at 300°C can be obtained as follows: The solubility of H_2 in water at 300°C has been given by GILPATRICK and STONE (1962) as $C_{H_2} = 0.10996$ for 1 bar H_2 partial pressure. The f_{H_2} corresponding to this H_2 pressure is estimated to be 1.06 (see the discussion in KISHIMA and SAKAI, 1984) and therefore we obtain $Y = 9.6$ for hydrogen in water at 300°C and under the saturation vapor pressure (SVP = 85.81 bars). The error ranges of the solubility data and the estimated f_{H_2} are unknown, so we tentatively assume that the uncertainty of the Y value is $\pm 5\%$. If the MH buffer is put in this water, the C_{H_2} would be found at 3.25×10^{-4} (within 4 % error) as is estimated from the data given in Table 1, and hence the $\log f_{H_2}$ is calculated to be -2.499 ± 0.030 using the above Y value. Under the same P-T condition, $\log K_w = 19.627 \pm 0.015$ and $\log f_{H_2O} = 1.828 \pm 0.001$ have been given by RHF and HAAS (1970), respectively. Therefore, by using eq. (4), the $\log f_{O_2}$ of the MH buffer is calculated to be -30.586 ± 0.108 under the SVP, or -30.588 ± 0.108 under 1 bar standard pressure. As the difference of $\log f_{O_2}$ between MH and NNO buffers at 300°C and 1 bar is estimated to be 3.55 ± 0.063 (Table 2 with extrapolation), the $\log f_{O_2}$ of NNO is calculated to be -34.14 ± 0.17 , which is compared with -33.970 given by the reference scale.

This result, the two marks in Fig. 4 and the uncertainty interval of the $\log f_{O_2}$ value of NNO at 25°C as given in RHF are plotted in the lower part of Fig. 5 (bars 3, 1, 2 and 4, respectively) relative to the reference scale using the ordinate marked by δ_1 . In interpreting this plot, we have to inquire also into the credibility of the data at 25°C.

The $\Delta H_{f,298}^\circ$ of NiO adopted in RHF is -239743 ± 418 J/mol (-57.3 ± 0.1 kcal/mol) which was obtained by BOYLE *et al.* (1954). Compared to this, however, the majority of the

Fig. 5 (Top) Comparison of $\log f_{O_2}$ differences between MH and NNO buffer. Data sources: CF, CHARETTE and FLENGAS (1968); Ch, CHOU (1978); BKK, BARIN *et al.* (1973, 1977); RHF, ROBIE *et al.* (1979); HDNB, HELGESON *et al.* (1978); five data points are from the present study. (Bottom) δ_1 : $\log f_{O_2}$ of NNO relative to that given by RHF. Using this ordinate plotted are four data points with vertical bars: 1 and 2 are from Fig. 4, 3 is an estimated value at 300°C based on the present study (see text), and 4 is the uncertainty of RHF at 25°C . δ_2 : $\log f_{O_2}$ difference between MH and NNO relative to that from RHF. CF and the present five data are plotted using this ordinate. For lines A and B, see text.

data presented so far for the same quantity are more negative. For example, the N.B.S. compilation (ROSSINI *et al.*, 1952) has adopted -58.4 kcal/mol on the basis of eleven determinations, a more recent databook of BARIN and KNACKE (1973) adopts a data of -57.5 ± 0.5 kcal/mol, and RUTNER and HAURY (1974) have quoted a mass spectrometric result of -58.0 ± 0.3 kcal/mol. Though KELLOGG (1969) has obtained -57.24 ± 0.13 kcal/mol from two

sets of high-temperature emf data and a set of gas equilibrium data, a large number of emf data plotted in Fig. 4 as a whole suggest a value near -57.7 kcal/mol as mentioned above. Thus, in order to reject these more negative data and to adopt -57.3 ± 0.1 kcal/mol as the best value, an additional precise calorimetric measurement of $\Delta H_{f,298}^\circ$ of NiO would have to be made.

In order to compromise the above discussions on the four data points 1 to 4 in Fig. 5, we first adopt -57.5 kcal/mol for the $\Delta H_{f,298}^\circ$ of NiO, secondly assume that our data of $\log f_{O_2}$ difference between MH and NNO buffers are true at the negative ends of the indicated error ranges and finally draw simply a straight line through the four points as indicated by line A in Fig. 5. In this way, the correction to be added to the reference scale is estimated to be $\delta \log f_{O_2} = 0.08-106/T$.

The present data for the $\log f_{O_2}$ difference between MH and NNO buffers are compared with some experimental and calculated results in Fig. 5 (top). Electrochemical data of CHARETTE and FLENGAS (1968) obtained with a cell composed of a pair of MH and NNO buffers are supposed to be highly accurate. Our results are in good accord with the extension of these data, but not so good with CHOU's (1978) data which were obtained by the 'Ag-AgCl hydrogen sensor' method, and are closest to RHF among the thermodynamic calculations, less close to HELGESON *et al.* (1978) and far from BARIN *et al.* (1973, 1977). HELGESON *et al.* (1978) have used the CHOU's data to retrieve the $\Delta G_{f,298}^\circ$ of hematite and therefore the coincidence between their results is quite natural.

The above $\log f_{O_2}$ difference data of us and of CHARETTE and FLENGAS (1968) are replotted at the bottom of Fig. 5 (using the ordinate marked by δ_2) relative to the same difference given by RHF. Recalling the above interpretation of our data, we can draw a straight B through the plotted data. The difference between the lines A and B gives the correction, $\delta \log f_{O_2} = -0.05-160.5/T$, to be

applied to the $\log f_{O_2}$ - $1/T$ relationship of MH buffer given by RHF. Provided that the heat capacity equations of magnetite and hematite given in RHF are free from errors, this correction indicates increase of 3,070 J/mol in the ΔH° and decrease of -1.0 J/mol K in the ΔS° for reaction (1). These corrections are small compared to the corresponding uncertainties given by RHF, $\pm 15,898$ J/mol and ± 2.94 J/mol K, respectively. The corrected $\log f_{O_2}$ - $1/T$ scale of MH buffer is compared in Fig. 6 with some reported ones. The validity of our

Fig. 6 Comparison of $\log f_{O_2}$ - $1/T$ relations of MH buffer. $\Delta \log f_{O_2}$ denotes the difference from a temporary scale: $\log f_{O_2}(\text{atm}) = 15.26000/T$. Data sources: 1, SCHMAHL (1941); 2, NORTON (1955) quoted by EUGSTER and WONES (1962); 3, CHARETTE and FLENGAS (1968); 4, MORIYAMA *et al.* (1969); 5, CHOU (1978); 6, SCHWAB and KÜSTNER (1982); 7, MYERS and EUGSTER (1983); 8, this work; JANAF, STULL and PROPHET (1971); BK, BARIN and KNACKE (1973); RHF, ROBIE *et al.* (1979); HDNB, HELGESON *et al.* (1978).

scale is demonstrated in a related paper (KISHIMA and SAKAI, 1983), which shows consistency between the Y values (for temperatures between 296 to 487°C) derived from the C_{H_2} data in Table 1 and the new scale, and the Y values for lower and higher temperature ranges which are derived from other sorts of data.

The $\log f_{O_2}$ value of FMQ buffer at 487°C is calculated to be $-24.01 (\pm 0.09)$. This is obtained by combining the $\log f_{O_2}$ value of MH at 487°C given by RHF (-19.230), the correction for the MH buffer determined above and the $\log f_{O_2}$ difference between FMQ and MH buffer measured in the present study. The result is compared in Fig. 7 with some reported experimental data (CHOU, 1978; WONES and GILBERT, 1969; HEWITT, 1978; SCHWAB and KÜSTNER, 1981; MYERS and EUGSTER 1983) and calculated $\log f_{O_2}$ - $1/T$ relationships of FMQ (ROBIE *et al.*, 1979, 1982; HELGESON *et al.*, 1978). Our data point is concordant

Fig. 7 Comparison of $\log f_{O_2}$ - $1/T$ relations of FMQ buffer. $\Delta \log f_{O_2}$ denotes the difference from a temporary scale: $\log f_{O_2}(\text{bar}) = 9.526300/T$. Data sources: 1, WONES and GILBERT (1969); 2, HEWITT (1978); 3, CHOU (1978); 4, SCHWAB and KÜSTNER (1981); 5, MYERS and EUGSTER (1983); 6, this work; HDNB, HELGESON *et al.* (1978); RHF + RFH, ROBIE *et al.* (1979, 1982).

with the recent data of MYERS and EUGSTER (1983) and less but fairly concordant with the scales of CHOU (1978), HEWITT (1978) and SCHWAB and KÜSTNER (1981) (the high-temperature branch of their scale). From these five data, the correction to be applied to the $\log f_{\text{O}_2}$ - $1/T$ relationship of FMQ given by ROBIE *et al.* (1979, 1982) is roughly evaluated as $\delta \log f_{\text{O}_2} = -0.3 + 460/T \pm 0.2$.

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