

Calibration of oxygen buffers at elevated *P* and *T* using the hydrogen fugacity sensor

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Abstract

An internally-consistent set of data for the oxygen-fugacity buffers magnetite-hematite (MH), manganosite-hausmannite ($\text{MnO}-\text{Mn}_3\text{O}_4$), nickel-nickel oxide (NNO), fayalite-magnetite-quartz (FMQ), and cobalt-cobalt oxide (Co-CoO) at 1 atm has been obtained by using the hydrogen-fugacity sensor technique of Chou and Eugster (1976a) at 2 and 4 kbar total pressures between 600° and 800°C.

Using the $f\text{O}_2$ values given by Huebner and Sato (1970) for NNO buffer as a reference, the data can be represented by the following equations (at 1 atm) with *T* in K:

For MH buffer:

$$\log f\text{O}_2 (\pm 0.12) = 0.0260 + 0.4381 (10^4/T) - 0.1572 (10^4/T)^2 \text{ for } 1073 \geq T \geq 873,$$

$$\text{and } \log f\text{O}_2 (\pm 0.12) = (-26629/T) + 15.288 \text{ for extrapolation to } T \geq 1073;$$

for $\text{MnO}-\text{Mn}_3\text{O}_4$ buffer:

$$\log f\text{O}_2 (\pm 0.12) = (-25793/T) + 13.714;$$

for FMQ buffer:

$$\log f\text{O}_2 (\pm 0.08) = (-23973/T) + 7.985 \text{ for } T \geq 873;$$

and for Co-CoO buffer:

$$\log f\text{O}_2 (\pm 0.08) = (-24391/T) + 7.382.$$

The present $f\text{O}_2$ values for $\text{MnO}-\text{Mn}_3\text{O}_4$ and Co-CoO buffers are in good agreement with those of Huebner and Sato (1970) and Robie and Waldbaum (1968) respectively. However, for MH and FMQ buffers, the present $f\text{O}_2$ values are consistently lower and higher respectively than those reported previously. The difference can be minimized if the values of Gibbs free energy of formation for magnetite are 0.68, 0.35, and 0.17 kcal/mole less negative than those reported by Haas and Robie (1973) at 900, 1100, and 1300 K respectively.

Introduction

The oxygen-buffer technique developed by Eugster (1957) has been applied extensively to study mineral-gas equilibria of igneous and metamorphic reactions (Eugster and Wones, 1962; Huebner, 1971). Recently the acid-base buffer technique (Frantz and Eugster, 1973; Chou and Eugster, 1976b) makes it possible to measure quantitatively the equilibrium constants for reactions between minerals and the coexisting supercritical aqueous solutions (Frantz, 1973; Gunter,

1974; Chou and Eugster, 1976b; Chou and Eugster, 1977; Gunter and Eugster, in press).

To obtain a set of reliable thermodynamic data for minerals as well as aqueous species using the buffer techniques, we first have to have a set of internally consistent data for the oxygen buffers. The importance of the latter is demonstrated by Eugster and Wones (1962), Wones and Eugster (1965) and Wones (1972), and emphasized by Zen (1977). The internal consistency of the data for the oxygen buffers is tested

Appendix A: Thermodynamic derivations for equation (4).

The fluid phase in the sensor capsules can be described by three components, H-O-Cl. To define the system (according to the phase rule), we need to specify at least four intensive parameters. This is achieved by fixing P and T, buffering chlorine fugacity, f_{Cl_2} , internally by the Ag + AgCl assemblage, and buffering hydrogen fugacity, f_{H_2} , externally. Since in the P-T region of this study HCl is mostly associated (Frank, 1956; Frantz and Eugster, 1973; Helgeson and Kirkham, 1976), the amount of ionic species present is negligible, and the dominant species present in the H-O-Cl gas are H_2O , H_2 , O_2 , Cl_2 , and HCl. The system is defined, and the fugacities of the species can be calculated from five independent equations. Four of these are:

$$P_{(total)} = P_{gas} = P_{H_2O} + P_{H_2} + P_{O_2} + P_{Cl_2} + P_{HCl}$$

$$= \frac{f_{H_2O}}{\gamma_{H_2O}} + \frac{f_{H_2}}{\gamma_{H_2}} + \frac{f_{O_2}}{\gamma_{O_2}} + \frac{f_{Cl_2}}{\gamma_{Cl_2}} + \frac{f_{HCl}}{\gamma_{HCl}} \approx \frac{f_{H_2O}}{\gamma_{H_2O}} \quad (A-1)$$



where γ_i is the fugacity coefficient of i at P and T. The approximation relation in equation (A-1) holds only for systems with low f_{H_2} and f_{Cl_2} ;

all buffer systems in this study fulfill these requirements. The fifth equation can be derived from pH or chloride measurements of the quench solution by assuming that HCl and H₂O mix ideally at P and T (Frantz and Eugster, 1973). If Lewis and Randall's rule is obeyed,

$$f_{\text{HCl}}^{\text{mixture}} = f_{\text{HCl}}^* \cdot X_{\text{HCl}} \quad (\text{A-5})$$

where $f_{\text{HCl}}^{\text{mixture}}$ is the fugacity of HCl in the gas mixture, f_{HCl}^* is the fugacity of pure HCl at the same P and T, and X_{HCl} is the mole fraction of HCl in the mixture.

$$X_{\text{HCl}} = \frac{m_{\text{HCl}}}{m_{\text{H}_2\text{O}} + m_{\text{HCl}} + m_{\text{H}_2} + m_{\text{Cl}_2} + m_{\text{O}_2}} \approx \frac{m_{\text{HCl}}}{m_{\text{H}_2\text{O}}} = \frac{m_{\text{HCl}}}{55.5} \quad (\text{A-6})$$

Since HCl dissociates completely upon quenching and from equations (A-5) and (A-6), we have

$$\begin{aligned} f_{\text{HCl}}^{\text{mixture}} &= \frac{f_{\text{HCl}}^* \cdot (m_{\text{HCl}})_{\text{P,T}}}{55.5} = \frac{P_{\text{HCl}}^* \cdot \gamma_{\text{HCl}}^*}{55.5} \cdot (m_{\text{H}^+})_{1,25^\circ\text{C}} \\ &= \frac{P_{\text{HCl}}^* \cdot \gamma_{\text{HCl}}^*}{55.5} \cdot (m_{\text{Cl}^-})_{1,25^\circ\text{C}} \end{aligned} \quad (\text{A-7})$$

where P_{HCl}^* and γ_{HCl}^* are the partial pressure (= total pressure) and fugacity coefficient of pure HCl at P and T respectively.

The $(f_{\text{H}_2})_{\text{P,T}}$ in the sensor can be obtained by combining equations (A-3), (A-4), and (A-7).

$$(f_{\text{H}_2})_{\text{P,T}} = [(k_4)_{\text{P,T}} \cdot (m_{\text{H}^+})_{1,25^\circ\text{C}}]^2 = [(K_4)_{\text{P,T}} \cdot (m_{\text{Cl}^-})_{1,25^\circ\text{C}}]^2 \quad (4)$$

$$\text{where } (k_4)_{\text{P,T}} = \frac{P_{\text{HCl}}^* \cdot \gamma_{\text{HCl}}^* \cdot (K_{\text{AgCl}})_{\text{P,T}}}{55.5 \cdot (K_{\text{HCl}})_T} = (K_1)_{\text{P,T}} \cdot P_{\text{HCl}}^* \cdot \gamma_{\text{HCl}}^* / 55.5$$

At equilibrium,

$$f_{\text{H}_2, \text{ sensor A}} = f_{\text{H}_2, \text{ sensor B}} = f_{\text{H}_2, \text{ outer system}} \quad (\text{A-8})$$

hence

$$\begin{aligned} (m_{\text{H}^+})_{1,25^\circ\text{C}, \text{ sensor A}} &= (m_{\text{Cl}^-})_{1,25^\circ\text{C}, \text{ sensor A}} = (m_{\text{H}^+})_{1,25^\circ\text{C}, \text{ sensor B}} \\ &= (m_{\text{Cl}^-})_{1,25^\circ\text{C}, \text{ sensor B}}. \end{aligned} \quad (\text{A-9})$$

Table B-1. Experimental results at 2 kb total pressure.

Run No.	Oxygen Buffer	$\log_{10} (m_{\text{Cl}^-})_{1,25^\circ\text{C}}$	$\log_{10} f_{\text{H}_2}^{(2)}$	$\log_{10} (f_{\text{O}_2})_{\text{P,T}}^{(3)}$	$\log_{10} (f_{\text{O}_2})_{1,T}^{(4)}$
(a) T = 600°C, duration = 4 days					
BC-17	MH	-1.314	-1.232	-15.460	-15.504
		-1.310	-1.223	-15.478	-15.522
BC-85	MH	-1.259	-1.121	-15.682	-15.726
		-1.287	-1.178	-15.563	-15.612
BC-18	MnO-Mn ₃ O ₄	-1.223	-1.048	-15.827	-16.013
		-1.305	-1.214	-15.497	-15.632
BC-84	MnO-Mn ₃ O ₄	-1.304	-1.211	-15.503	-15.638
		-1.266	-1.135	-15.654	-15.839
BC-70	NNO	-0.409	0.584	-19.091	-19.197
		-0.411	"	"	"
BC-82	NNO	-0.401	"	"	"
		-0.406	"	"	"
BC-15	FMQ	-0.372	0.654	-19.232	-19.442
		-0.362	0.672	-19.268	-19.479
BC-34	Co-CoO	-0.107; -0.093; -0.096	1.213	-20.350	-20.469
		-0.083; -0.084	1.230	-20.384	-20.503
(b) T = 650°C, duration = 4 days					
BC-93	MH	-1.299	-1.308	-13.562	-13.603
		-1.289	-1.287	-13.603	-13.644
BC-92	MnO-Mn ₃ O ₄	-1.245	-1.199	-13.779	-13.955
		-1.257	-1.224	-13.730	-13.905
BC-90	NNO	-0.301	0.687	-17.550	
		-0.303	"	"	
BC-91	FMQ	-0.248	0.794	-17.766	-17.965
		-0.249	0.794	-17.765	-17.964
(c) T = 700°C, duration = 2 days					
BC-6	MH	-1.282	-1.352	-11.940	-11.979
		-1.264	-1.318	-12.008	-12.047
BC-9	MnO-Mn ₃ O ₄	-1.116; -1.105	-1.009	-12.625	-12.791
		-1.134	-1.058	-12.529	-12.695
BC-115	MnO-Mn ₃ O ₄	-1.130	-1.048	-12.547	-12.714
		-1.140	-1.069	-12.507	-12.673
BC-5	NNO	-0.231	0.762	-16.167	
		-0.218	"	"	
BC-11	FMQ	-0.145	0.921	-16.485	-16.674
		-0.163	0.884	-16.412	-16.601
BC-33	Co-CoO	0.148; 0.151	1.510	-17.664	-17.771
		0.150; 0.156; 0.150	1.515	-17.674	-17.781

Table B-1 (continued)

Run No.	Oxygen Buffer	\log_1 (m_{Cl^-}) _{1,25°C}	\log_2 f_{H_2}	\log_3 (f_{O_2}) _{P,T}	\log_4 (f_{O_2}) _{1,T}
(d) T = 750°C, duration = 2 days					
BC-116	III	-1.190 -1.200	-1.273 -1.293	-10.703 -10.662	-10.740 -10.700
BC-112	InO-In ₃ O ₄	-1.038 -1.034	-0.968 -0.962	-11.312 -11.325	-11.470 -11.484
BC-113	InO-In ₃ O ₄	-1.039 -1.037	-0.971 -0.967	-11.306 -11.314	-11.464 -11.472
BC-103	NNO	-0.133 -0.134	0.836 "	-14.920 "	
BC-114	FIQ	-0.035 -0.026	1.038 1.055	-15.324 -15.358	-15.504 -15.538
BC-100	Co-CoO	0.232;0.227 0.229;0.230	1.566 1.566	-16.380 -16.380	-16.462 -16.482
(e) T = 800°C, duration = 1 day					
BC-24	III	-1.106 -1.110	-1.235 -1.243	-9.537 -9.521	-9.572 -9.556
BC-21	InO-In ₃ O ₄	-0.952;-0.957 -0.940;-0.949	-0.933 -0.913	-10.141 -10.181	-10.292 -10.332
BC-23	NNO	-0.042 -0.043	0.890 "	-13.788 "	
BC-20	FIQ	0.073 0.056	1.123 1.088	-14.253 -14.183	-14.424 -14.355
BC-38	Co-CoO	0.296;0.298 0.273;0.287	1.570 1.537	-15.148 -15.081	-15.245 -15.178

- 1) Each number represents one measurement. Two sets of data are given for each run, the first of which is from sensor A and the other is from sensor B.
- 2) Calculated from eq. (4), using $(K_4)_{P,T}$ of table 2. Values for NNO buffer are from table 2.
- 3) Calculated from eq. (A-2), using $f_{\text{H}_2\text{O}}$ of table 2 and $(K_{ij})_T$ of Robie and Waldbaum (1968). Values for NNO buffer are from table 2.
- 4) For pressure correction, see Eugster and Wones (1962). The coefficients of the pressure correction term for the buffers are given in table 6.

Table B-2. Experimental results at ~4 kb total pressure.

Run ¹⁾ No.	Oxygen Buffer	\log_2 (m_{O_2}) _{25°C}	\log_2 (f_{H_2})	\log_2 (f_{O_2}) _{P,T}	\log_2 (f_{O_2}) _{1,T}
(a) T = 600°C, P = 4020 bars, duration = 4 days					
BC-28* ³⁾	MH	-1.323; -1.315	-0.919	-15.450	-15.537
		-1.240; -1.234	-0.755	-15.778	-15.865
BC-66	MH	-1.349	-0.979	-15.331	-15.418
		-1.337	-0.956	-15.377	-15.464
BC-67	MnO-Mn ₃ O ₄	-1.287	-0.954	-15.530	-15.953
		-1.303	-0.887	-15.514	-15.887
BC-68	NNO	-0.439; -0.433	0.848	-18.985	
		-0.443; -0.426	"	"	
BC-35*	FMQ	-0.419	0.820	-19.048	-19.472
		-0.415	0.890	-19.068	-19.491
BC-69	FMQ	-0.411; -0.410	0.898	-19.085	-19.503
		-0.404	0.911	-19.110	-19.534
BC-70	Co-CoO	-0.121; -0.106	1.491	-20.271	-20.510
		-0.120	1.480	-20.248	-20.487
INT-1	--	-1.029; -1.036	-0.347	---	---
		-1.014	-0.309	---	---
INT-2*	--	-0.654; -0.686	0.379	---	---
		-0.667; -0.680	0.378	---	---
INT-3*	--	-0.689	0.341	---	---
		-0.672	0.375	---	---
(b) T = 650°C, P = 4006 bars, duration = 4 days					
BC-110	MnO-Mn ₃ O ₄	-1.283	-0.780	-13.987	-14.334
		-1.259	-0.732	-14.081	-14.432
BC-111	MnO-Mn ₃ O ₄	-1.258	-0.730	-14.084	-14.435
		-1.260	-0.733	-14.078	-14.429
BC-109	NNO	-0.415	0.953	-17.451	
		-0.417	"	"	
(c) T = 650°C, P = 4006 bars, duration = 4 days					
BC-39	MH	-1.316	-0.901	-13.731	-13.814
		-1.333	-0.934	-13.665	-13.748
BC-88	MnO-Mn ₃ O ₄	-1.261	-0.792	-13.951	-14.305
		-1.287	-0.842	-13.850	-14.204
BC-87	NNO	-0.384	0.957	-17.449	
		-0.390	"	"	
BC-86	FMQ	-0.349	1.033	-17.600	-18.002
		-0.353	1.025	-17.585	-17.986

Table B-2 (continued)

Run No.	Oxygen Buffer	$\log_2(m_{Cl^-})_{1,25^\circ C}$	$\log_2(\bar{r}_{H_2})$	$\log_2(f_{O_2})_{P,T}$	$\log_2(f_{O_2})_{P,T}$
(d) T = 700°C, P = 4055 bars, duration = 2 days					
BC-72	MH	-1.339	-0.966	-12.059	-12.138
		-1.314	-0.916	-12.158	-12.238
BC-81	MH	-1.343	-0.973	-12.044	-12.123
		-1.305	-0.898	-12.194	-12.273
BC-73	MnO-Mn ₃ O ₄	-1.227	-0.741	-12.508	-12.845
		-1.236	-0.759	-12.472	-12.810
BC-75	NNO	-0.302	1.040	-16.070	
		-0.341	"	"	
BC-79	NNO	-0.339	"	"	
		-0.334	"	"	
BC-74	FMQ	-0.322	1.069	-16.128	-16.511
		-0.321	1.070	-16.131	-16.514
BC-80	FMQ	-0.277	1.158	-16.306	-16.689
		-0.269	1.174	-16.338	-16.721
BC-71	Co-CoO	0.046	1.805	-17.601	-17.817
		0.049	1.810	-17.611	-17.828
INT-4	--	-0.826; -0.802	0.085	---	---
		-0.833; -0.813	0.067	---	---
INT-5*	--	-0.577	0.559	---	---
		-0.596	0.521	---	---
(e) T = 750°C, P = 4080 bars, duration = 1 day					
BC-94	MH	-1.360	-1.064	-10.452	-10.527
		-1.317	-0.979	-10.622	-10.697
BC-98	MnO-Mn ₃ O ₄	-1.205	-0.755	-11.070	-11.393
		-1.203	-0.752	-11.076	-11.399
BC-97	NNO	-0.266	1.123	-14.826	-15.010
		-0.265	"	"	"
BC-96	FMQ	-0.187	1.280	-15.140	-15.507
		-0.197	1.258	-15.095	-15.462
BC-95	Co-CoO	0.113; 0.124	1.892	-16.364	-16.571
		0.118; 0.112	1.885	-16.350	-16.558
(f) T = 750°C, P = 4110 bars, duration = 1 day					
BC-108	MH	-1.323	-1.042	-10.488	-10.564
		-1.327	-1.049	-10.473	-10.550
BC-107	NNO	-0.236	1.126	-14.825	-15.010
		-0.243	"	"	"

Table B-2 (continued)

Run No.	Oxygen Buffer	$\log (m_{Cl^-})_{1,25^\circ C}^{(2)}$	$\log (f_{H_2})^{(2)}$	$\log (f_{O_2})_{P,T}^{(2)}$	$\log (f_{O_2})_{1,T}^{(2)}$
(g) T = 800°C, P = 4070 bars, duration = 1/3 day					
BC-56	MH	-1.237 -1.219	-0.928 -0.892	-9.477 -9.549	-9.549 -9.621
BC-61	MH	-1.219 -1.222	-0.892 -0.898	-9.549 -9.537	-9.621 -9.609
BC-50	MnO-Mn ₃ O ₄	-1.053 -1.071	-0.560 -0.596	-10.213 -10.141	-10.520 -10.448
BC-55	MnO-Mn ₃ O ₄	-1.105 -1.087	-0.664 -0.628	-10.005 -10.077	-10.312 -10.384
BC-53	NNO	-0.187 -0.207	1.184 "	-13.699 "	
BC-61	NNO	-0.191;-0.182 -0.183;-0.175	" "	" "	
BC-63	NNO	-0.166 -0.162	" "	" "	
BC-64	FMQ	-0.124 -0.110	1.298 1.326	-13.929 -13.985	-14.275 -14.331
BC-65	Co-CoO	0.155;0.166 0.157;0.160	1.868 1.864	-15.069 -15.061	-15.266 -15.258
INT-6	--	0.798 -0.786	-0.049 -0.026	--- ---	--- ---
INT-7	--	-0.856;-0.849 -0.825	-0.159 -0.103	--- ---	--- ---

1) All runs were performed in internal heated pressure vessel A ("Big Boy"), except those runs indicated by stars, which were performed in vessel B ("Little Sister").

2) See footnotes of table B-1.

3) Not equilibrated.

Appendix C: Calculations of $\Delta G_{f, Fe_3O_4}^{\circ}$ from the data of FMQ and IQF buffers.

For the reaction, assuming pure solids



Williams (1971) gives the equilibrium constant, K_{fa} , at 1 atm.

$$K_{fa} = \frac{13,262}{T} - 2.77 \quad (C-2)$$

Hence

$$\begin{aligned} \Delta G_{r,C-1}^{\circ} &= -2.303 RT \log K_{fa} \\ &= -60682 + 12.675 T \text{ (cal)} \end{aligned} \quad (C-3)$$

From $3 \times (C-1) - \frac{(22)}{2}$, we have



$$\begin{aligned} \Delta G_{r,C-4}^{\circ} &= \Delta G_{f, Fe_3O_4}^{\circ} = 3(\Delta G_{r,C-1}^{\circ}) - 1/2 (\Delta G_{r,22}^{\circ}) \\ &= 56,292 T - 236,893 \text{ (cal)} \end{aligned} \quad (C-5)$$

Appendix D: The derivation of equation (30)

For the outer system at P and T, from eq. (A-2),

$$(K_w)_T = \frac{f_{H_2O}^R}{f_{H_2}^R \cdot (f_{O_2}^R)^{1/2}} = \frac{f_{H_2O}^S}{f_{H_2}^S \cdot (f_{O_2}^S)^{1/2}} \quad (D-1)$$

where the superscripts R and S indicate reference and sample run, respectively. Since in the present investigated buffer systems,

$$f_{H_2O}^R \approx f_{H_2O}^S \quad (D-2)$$

hence

$$f_{H_2}^R \cdot (f_{O_2}^R)^{1/2} \approx f_{H_2}^S \cdot (f_{O_2}^S)^{1/2} \quad (D-3)$$

From eq. 4,

$$\left[\frac{f_{H_2}^S}{f_{H_2}^R} \right]_{P,T} = \left[\frac{(m_{Cl^-})_{1,25^\circ C}^S}{(m_{Cl^-})_{1,25^\circ C}^R} \right]^2 \quad (D-4)$$

Combining eqs. (D-3) and (D-4), we have

$$\left[\frac{f_{O_2}^S}{f_{O_2}^R} \right]_{P,T} \approx \left[\frac{f_{H_2}^R}{f_{H_2}^S} \right]_{P,T}^2 = \left[\frac{(m_{Cl^-})_{1,25^\circ C}^R}{(m_{Cl^-})_{1,25^\circ C}^S} \right]^4 \quad (D-5)$$

therefore

$$\log \left(\frac{f_{O_2}^S}{f_{O_2}^R} \right)_{P,T} \approx \log \left(\frac{f_{H_2}^R}{f_{H_2}^S} \right)_{P,T}^2 + 4 \log (m_{Cl^-})_{1,25^\circ C}^R - 4 \log (m_{Cl^-})_{1,25^\circ C}^S \quad (30)$$