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RECALIBRATION OF Ag + AgCl ACID BUFFER AT ELEVATED PRESSURES AND TEMPERATURES

I-MING CHOU* and J. D. FRANTZ**

ABSTRACT. The Ag + AgCl acid buffer developed by Frantz and Eugster (1973) for the experimental investigation of mineral solution equilibria at elevated temperatures and pressures has been recalibrated. The original calibration was done using 20 cm bombs and either water or carbon dioxide as the pressure medium. Because of the possibility of significant temperature gradients in these experiments (Rudert, Chou, and Eugster, in preparation), the buffer has been recalibrated using 30 cm pressure vessels and argon as the pressure medium. The dissociation constant of HCl was redefined and found to be approximately a half order of magnitude larger than that obtained from electrical conductive measurements.

The Ag + AgCl acid buffer developed by Frantz and Eugster (1973) has proved to be very versatile in hydrothermal experiments at elevated P and T. Frantz (ms) has applied the method to obtain free energy data for aqueous $MgCl_2$ through solubility measurements for forsterite, talc, and serpentine. Using the same experimental arrangement, Gunter (ms) has studied the mineral-solution equilibria, expressed as functions of concentrations of aqueous species including KCl, $MgCl_2$, $CaCl_2$, and HCl, in the system K_2O–CaO–MgO–Al_2O_3–SiO_2–H_2O–HCl at temperatures and pressures of metamorphic range. Chou and Eugster (in preparation), using the same approach, determined the solubility of magnetite and obtained free energy data for aqueous $FeCl_2$ at 2 kb and temperatures. Recently, the Ag + AgCl acid buffer technique has been modified to act as a sensor for hydrogen fugacity in hydrothermal experiments (Chou and Eugster, 1976b).

The accuracy of all these studies depends on the calibration of Ag + AgCl acid buffer. The original calibration (Frantz and Eugster, 1973) was carried out using short, rapid-quench pressure vessels (20 cm bombs and 21 cm water-cooling extensions) and water or CO_2 as a pressure medium. Because of the possibility of significant temperature gradients in such pressure vessels (Rudert, Chou, and Eugster, in preparation), it was decided to recalibrate this buffer, using long (30 cm), rapid-quench pressure vessels and an argon pressure medium. The temperature gradient over the length of the sample in this experiment has been shown to be less than 5°C (Rudert, Chou, and Eugster, in preparation).

The experimental set-up and procedures are similar to those of Frantz and Eugster (1973) and Chou and Eugster (1976a). Depending upon the temperature and pressure of the run, 15 ~ 50 μl of initial solution together with ~30 mg Ag and ~30 mg AgCl powder were placed into a welded Pt capsule, 2.6 mm ID, 2.5 cm long, which was placed with the hydrogen buffer into a sealed Au tube, 4.0 mm ID, 3.8 cm long. After quench, pH and chloride concentration were measured by using a MI-41° micro-combination pH probe (Microelectrodes, Inc.) in conjunc-

* Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland 21218

** Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton St., N.W., Washington, D.C. 20008

TABLE 1

Calibration experiments for the Ag + AgCl buffer

Temp. (°C)	Time (days)	Initial Solution	Quench* pH	Log** $m_{HCl(tot,H)}$	Log*** $m_{Cl^-(1\ atm\ 25°C)}$
		(A) MH, OH (AgAgClX, HOCl) at 2 kb pressure			
800	1	3N HCl	n.d.†	n.d.	−1.056
798	1	H_2O	n.d.	n.d.	−1.039
747	2	H_2O	1.185	−1.111	−1.086
697	2	3N HCl	n.d.	n.d.	−1.137
696	2	H_2O	n.d.	n.d.	−1.192
648	5	H_2O	2.391;2.411	−1.335	−1.265
647	2	3N HCl	n.d.	n.d.	−1.230
602	5	3N HCl	2.421;2.420	−1.354	−1.299
596	5	H_2O	2.461;2.458	−1.393	−1.319
548	5	3N HCl	2.457	−1.390	−1.349
544	5	H_2O	2.482;2.468	−1.410	−1.346
498	5	H_2O	2.429;2.396	−1.342	−1.332
497	5	3N HCl	2.421;2.419	−1.354	−1.325
448	5	3N HCl	2.309;2.310	−1.236	−1.208
447	5	H_2O	2.316;2.320	−1.245	−1.224
		(B) NB, OH (AgAgClX, HOCl) at 2 kb pressure			
803	1	H_2O	1.154	−0.038	−0.040
797	1	3N HCl	1.109	−0.007	−0.010
748	2	H_2O	1.188	−0.072	−0.102
747	2	3N HCl	n.d.	n.d.	−0.101
711	3	H_2O	1.273;1.247	−0.146	−0.131
711	2	3N HCl	1.293	−0.180	−0.161
700	4	H_2O	n.d.	n.d.	−0.155
700	4	3N HCl	n.d.	n.d.	−0.160
669	3	H_2O	1.374	−0.267	−0.261
667	3	3N HCl	1.415;1.406	−0.298	−0.241
647	3	3N HCl	1.399;1.398	−0.294	−0.266
599	3	H_2O	1.511	−0.406	−0.434
598	3	3N HCl	1.558	−0.459	−0.416
549	3	H_2O	1.613	−0.513	−0.519
548	3	3N HCl	1.603	−0.508	−0.469
498	4	H_2O	1.682	−0.582	−0.558
497	4	3N HCl	1.612	−0.513	−0.488
447	4	H_2O	1.686	−0.561	−0.560
447	4	3N HCl	1.580	−0.479	−0.474
		(C) MH, OH (AgAgClX, HOCl) at 1 kb pressure			
764	3	3N HCl	1.989	−0.906	−0.888
763	3	H_2O	2.024;2.326*	−0.953	−0.919
747	4	H_2O	1.983	−0.902	−0.859
735	3	3N HCl	2.037;2.312*	−0.932	−0.923
733	3	H_2O	2.048;2.053	−0.970	−0.941
706	4	3N HCl	2.042;2.064	−0.971	−0.982
695	4	H_2O	2.071;2.066	−0.987	−0.972
645	4	3N HCl	2.173;2.169	−1.093	−1.055
644	4	H_2O	2.206;2.204	−1.128	−1.102

* Measured after 11:1 dilution, except those indicated by stars, which were measured after 21.6:1 dilution. Duplicates where indicated.

** Derived from pH measurements after making corrections for the H^+ activity coefficient at 1 atm and 25°C.

*** Measured with chloridometer; average of several measurements.
$m_{Cl^-(1\ atm,\ 25°C)} = m_{HCl(tot,\ Cl)}$

† n.d. indicates measurement was not determined.

tion with an Orion 801 pH meter and a Buchler chloridometer respectively.

Data for hematite–magnetite and nickel–bunsenite at 2 kb and for hematite–magnetite at 1 kb are given in table 1 and plotted in figures 1, 2, and 3. Where both chloride and pH data are available, the agreement is excellent. Least squares refinement to the high temperature data gives the following results:

for hematite–magnetite, 2 kb, using the chloride data

$$\log m_{HCl(ex)} = -\frac{1267.3}{T, °K} + 0.14 \quad (1)$$

for NB, 2 kb, using Cl-data

$$\log m_{HCl(ex)} = -\frac{1841.2}{T, °K} + 1.71 \quad (2)$$

for MH, 1 kb, using pH and Cl-data

$$\log m_{HCl(ex)} = -\frac{1524.9}{T, °K} + 0.58 \quad (3)$$

where $m_{HCl(ex)}$ represents molality of associated HCl at P and T derived from quench pH and chloride measurements. In figures 1 and 2 the solid lines show breaks at 466°C. This break is the temperature of the eutectic melting of Ag + AgCl + H_2O at 2 kb as determined from heating and cooling curves (for the method, see Chou and Eugster, 1976a). The melt-

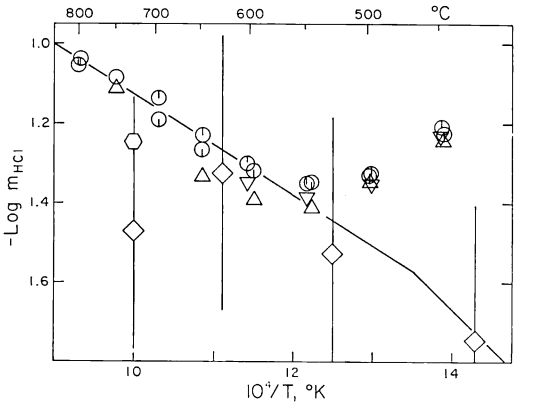

Fig. 1. Experimental data for the Ag + AgCl buffer, using MH + H_2O as external hydrogen buffer at 2 kb pressure. Triangles represent values obtained by pH measurements with the apeces pointing in the direction of approach to equilibrium. Circles refer to chloride measurements. Plotted are the values for log $m_{HCl(tot,H)}$ (triangles) and log $m_{Cl-(1\ atm\ 25°C)}$ (circles) of table 1. Uncertainties in measurement of log m_{HCl} are ±0.04 units. Diamonds are from Robie and Waldbaum (1968) with their associated uncertainties and the hexagon represents thermochemical data obtained by Metz and Seifert (1970). The solid line is a least squares fit to the high temperature chloride data and represents log $m_{HCl(ex)}$. The break occurs at 466°C, the eutectic of Ag + AgCl + H_2O of 2 kb pressure. Below 466°C the line has the slope of the thermochemical curve.

ing at 1 kb takes place at 456°C (see fig. 3), compared with the melting of pure AgCl at 1 atm of 455°C.

Combining data for $m_{HCl(ex)}$ with the measured chloride concentration, m_{Cl^-}, of table 1, one can calculate the dissociation constant for HCl

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$k_4 = \frac{a_{H^+} \cdot a_{Cl^-}}{a_{HCl}} \approx \frac{[m_{HCl(tot)} - m_{HCl(ex)}]^2}{m_{HCl(ex)}} \quad (4)$$

where a_i represents activity of i at P and T, and

$$m_{HCl(tot)} = [m_{HCl} + m_{H^+}]_{P,T} = [m_{H^+}]_{1\ atm,\ 25°C} = [m_{Cl^-}]_{1\ atm,\ 25°C} \quad (5)$$

Results are listed in table 2 and plotted in figure 4. They agree well with those of Frantz and Eugster (1973) and of Franck (1956). The temperature range is too narrow to obtain a reliable slope. The values obtained with

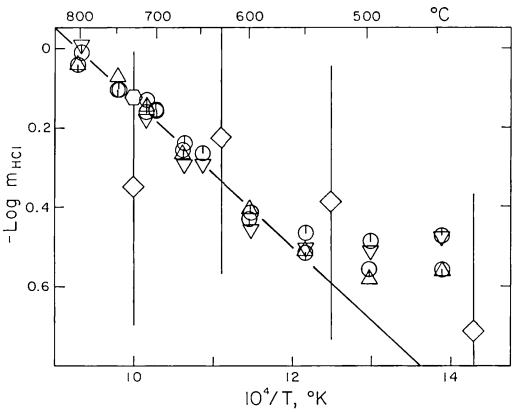

Fig. 2. Experimental data for the Ag + AgCl buffer using NB + H_2O as external hydrogen buffer at 2 kb pressure. Symbols as in figure 1.

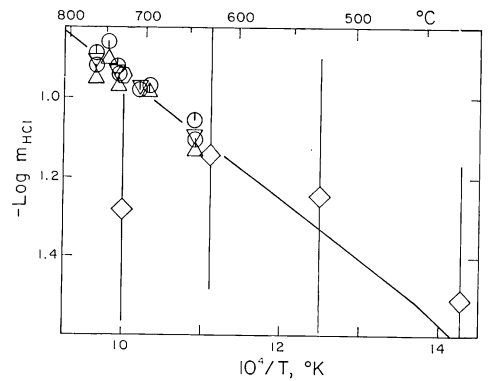

Fig. 3. Experimental data for the Ag + AgCl buffer, using MH + H_2O as external hydrogen buffer at 1 kb pressure. Symbols as in figure 1.

TABLE 2

Equilibrium constant K_4 for the reaction
$HCl \rightleftharpoons H^+ + Cl^-$ at 2 kb pressure

Temp. (°C)	Log* $m_{HCl(ex)}$	Log** $m_{Cl^-(1\ atm\ 25°C)}$	Log K_4
	(A) MH, OH (AgAgClX, HOCl)		
548	−1.404	−1.349	−3.144
544	−1.411	−1.346	−2.987
498	−1.504	−1.332	−2.131
497	−1.506	−1.325	−2.080
448	−1.643	−1.208	−1.169
447	−1.647	−1.224	−1.214
	(B) NB, OH (AgAgClX, HOCl)		
549	−0.530	−0.519	−3.642
548	−0.533	−0.469	−2.137
498	−0.678	−0.558	−1.671
497	−0.681	−0.488	−1.182
447	−0.861	−0.560	−0.857
447	−0.861	−0.474	−0.543

* From eqs (1) and (2).
** From table 1.

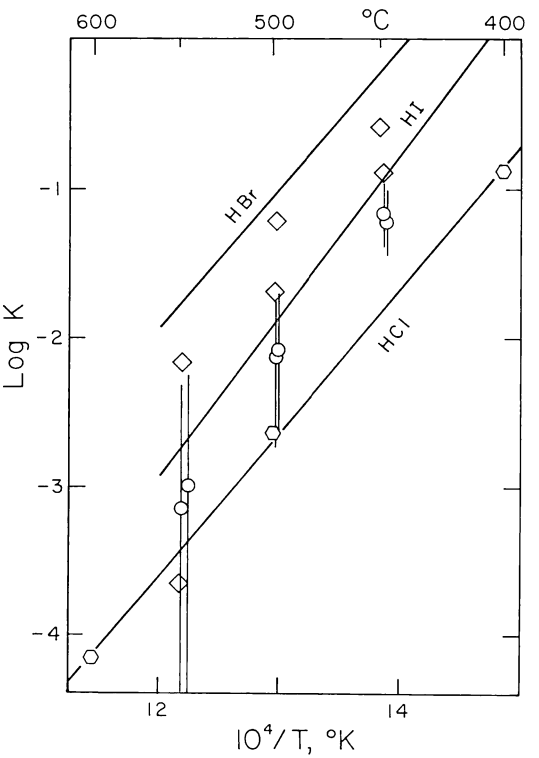

Fig. 4. Dissociation constant of HCl at 2 kb pressure. Circles with vertical uncertainty bars are data using MH buffer from table 2. Data using NB buffer are indicated by diamonds, which bear the same magnitude of uncertainties as circles at the same temperature. Hexagons are from Franck (1956). For comparison, the dissociation constants of HBr and HI obtained by Chou and Eugster (1976a) are shown as two solid lines.

the hematite–magnetite and nickel–bunsenite buffers are consistent with each other even though the former are slightly larger. The dissociation constants of HBr and HI at 2 kb and T were recently determined by Chou and Eugster (1976a) using the same technique. It is interesting to note that the dissociation constant of acid derived from this method is consistently about a half order of magnitude larger than that obtained from electrical conductance measurements.

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