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Fig. 3. Experimental set-up. For details see text.

We have used successfully platinum and an $Au_{s0}Pd_{20}$ alloy as hydrogen membranes. AgPd alloys were found to be unsuitable, because they are attacked by the HCl solutions. For buffers with low hydrogen fugacities, such as magnetite + hematite, a CO_2 pressure medium was used rather than H_2O , to extend the life of the buffer at higher pressures and temperatures. Rapid quench bombs of the type developed by Wellman (1970) were used throughout the study in order to minimize the effect of quench reactions.

Before the Ag–AgCl buffer can be used to determine equilibrium constants for reactions involving HCl it is necessary to test the buffer and to calibrate it. The most direct approach is to use the buffer by itself, without a solid charge system and to monitor the quench pH of the solution. Next we assume that the molality of the hydrogen ion, m_{H^+} , measured at 25°C and 1 atm is equivalent to the total molality of both associated (HCI°) and "dissociated" HCl at P and T, subsequently referred to as $m_{HCl(total)}$. This assumption is valid, if all HCl associated at P and T dissociates during quenching.

$$m_{H^{+}(25^{\circ}C, 1 \text{ atm})} = m_{H^{+}(T,P)} + m_{HCl^{\circ}(T,P)} = m_{HCl(total)}$$
 (10)

Reversibility can best be checked by using a variety of initial H–O–Cl solutions. Theoretically, the molality of HCl at P and T, and hence the quench pH, should be defined by the buffer and independent of the starting solution. We have used 3N HCl and distilled water as starting solutions, because the quench pH dictated by the Ag–AgCl buffer lies between these two solutions.

80 μ l of initial solution together with the Ag–AgCl buffer were welded into a Pt or AuPd capsule, 2.6 mm ID, 1½ inches long, which was placed with the hydrogen buffer into a sealed Au tube, 4.0 mm ID, 2¼ inches long. Upon completion of the experiment, the inner capsule was pierced on a teflon watch glass with a stainless steel needle. Several 10 μ l aliquots were removed using an Oxford sampler with disposable plastic tips, and each was placed in a one-drop pH electrode (Beckman #40316). 90 μ l of distilled water were then added, using a microsyringe. pH was measured to 0.04 units using an Orion 801 pH meter with a strip chart re-

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Initial Log Temp °K Run no. Time solution Quench pH* m_{HC1} (total)** NB, OH(AgAgClX, HOCl) at 2000 bars pressure 101-C 4 days 3N HCl -0.37977 1.43 101-B 970 1.43 ; 1.41 -0.364 days H_2O 100-Q 917 3N HCl 1.505 -0.455 days 100-P 1.525 907 4 days H_2O -0.47100-R 893 H_2O 1.545 -0.485 days 100-C 871 5 days 3N HCl 1.595; 1.63 -0.55H₂O -0.53100-D 863 1.591; 1.547 5 days 100-F 817 H₂O 1.670; 1.634 -0.595 days 100-E 811 5 days 3N HCl 1.649; 1.630 -0.58100-U 3N HCl 1.64 ; 1.60 -0.58767 5 days 100-V 762 5 days 1.692 -0.63 H_2O days 100-X 718 5 3N HCl 1.65; 1.62 -0.58-0.59100-W 712 1.65 ; H_2O 5 days 1.66 101-I 697 7 days H₀O 1.65 ; 1.66 -0.59101-H 694 4 days 3N HCl 1.59 -0.53100-Y 675 3N HCl 50 days 1.61 -0.557 days 100-Z 673 H₂O 1.60 ; 1.59 -0.54MH, OH(AgAgClX, HOCl) at 2000 bars pressure 100-N 916 3 days 3N HCl 2.45 -1.4232.4 100-M 913 ; 2.45 -1.3983 days H_2O 100-L 903 5 days 3N HCl 2.412 -1.385 $-1.477 \\ -1.463$ 2.504 100-I 868 5 days 3N HCl 100-0 2.49 864 4 days H₂O 100-F 818 5 days 3N HCl 2.545 -1.5182.55 100-J 803 5 days H₂O -1.523100-A 767 3N HCl 2.46 ; 2.45 -1.4235 days 2.47 100-B 762 5 days H_2O 2.46 ; -1.4382.35 ; 2.36 101-G 721 -1.3284 days H_2O 101-F 707 5 days 3N HCI 2.34 ; 2.36 -1.323MH, OH(AgAgClX, HOCl) at 1000 bars pressure -1.28101-V 917 7 days 3N HCl 2.31 101-W 2.30 : 2.298 935 7 days H_2O -1.27101-T 880 7 days 3N HCl 2.355; 2.34 -1.33101-U 868 7 days 2.39 H_2O -1.36NB, OH(AgAgClX, HOCl) at 1000 bars pressure -0.23101-R 919 7 days 3N HCl 1.29 ; 1.27 101-S 919 7 days H₂O 1.307; 1.303 -0.24101-X 879 days -0.3257 H_2O 1.375; 1.40 days -0.33101-Y 876 7 3N HCl 1.390 101-J 101-K 815 7 days 3N HCl 1.50 -0.435-0.445823 7 days 1.51 H_2O 3N HCl 101-L 773 7 days 1.59 -0.53101-M 776 7 days H₂O 1.57 -0.511.78 ; 1.795 101-N 713 14 days H_2O -0.731.690; 1.71 -0.64101-0 711 14 days 3N HCl -0.68101-P 668 7 days H_2O 1.74 ; 1.735 101-Q 668 7 days 3N HCl 1.642; 1.62 -0.57

TABLE 2 Buffer calibration experiments

* Measured after 10:1 dilution. Double numbers represent readings on aliquots of single experiments.

** Corrected for dilution and H^+ activity coefficient (25°, 1 atm) and defined as in equation (10).