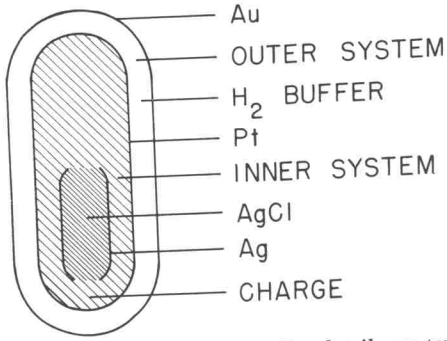

Fig. 3. Experimental set-up. For details see text.

We have used successfully platinum and an $Au_{80}Pd_{20}$ 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 (HCl°) 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.

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

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 μl 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 μl aliquots were removed using an Oxford sampler with disposable plastic tips, and each was placed in a one-drop pH electrode (Beckman #40316). 90 μl 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-

TABLE 2

Buffer calibration experiments

Run no.	Temp °K	Time	Initial solution	Quench pH*	Log $m_{HCl\ (total)}$**
NB, OH(AgAgClX, HOCl) at 2000 bars pressure					
101-C	977	4 days	3N HCl	1.43	−0.37
101-B	970	4 days	H_2O	1.43 ; 1.41	−0.36
100-Q	917	5 days	3N HCl	1.505	−0.45
100-P	907	4 days	H_2O	1.525	−0.47
100-R	893	5 days	H_2O	1.545	−0.48
100-C	871	5 days	3N HCl	1.595; 1.63	−0.55
100-D	863	5 days	H_2O	1.591; 1.547	−0.53
100-F	817	5 days	H_2O	1.670; 1.634	−0.59
100-E	811	5 days	3N HCl	1.649; 1.630	−0.58
100-U	767	5 days	3N HCl	1.64 ; 1.60	−0.58
100-V	762	5 days	H_2O	1.692	−0.63
100-X	718	5 days	3N HCl	1.65 ; 1.62	−0.58
100-W	712	5 days	H_2O	1.65 ; 1.66	−0.59
101-I	697	7 days	H_2O	1.65 ; 1.66	−0.59
101-H	694	4 days	3N HCl	1.59	−0.53
100-Y	675	50 days	3N HCl	1.61	−0.55
100-Z	673	7 days	H_2O	1.60 ; 1.59	−0.54
MH, OH(AgAgClX, HOCl) at 2000 bars pressure					
100-N	916	3 days	3N HCl	2.45	−1.423
100-M	913	3 days	H_2O	2.4 ; 2.45	−1.398
100-L	903	5 days	3N HCl	2.412	−1.385
100-I	868	5 days	3N HCl	2.504	−1.477
100-O	864	4 days	H_2O	2.49	−1.463
100-F	818	5 days	3N HCl	2.545	−1.518
100-J	803	5 days	H_2O	2.55	−1.523
100-A	767	5 days	3N HCl	2.46 ; 2.45	−1.423
100-B	762	5 days	H_2O	2.46 ; 2.47	−1.438
101-G	721	4 days	H_2O	2.35 ; 2.36	−1.328
101-F	707	5 days	3N HCl	2.34 ; 2.36	−1.323
MH, OH(AgAgClX, HOCl) at 1000 bars pressure					
101-V	917	7 days	3N HCl	2.31	−1.28
101-W	935	7 days	H_2O	2.30 ; 2.298	−1.27
101-T	880	7 days	3N HCl	2.355; 2.34	−1.33
101-U	868	7 days	H_2O	2.39	−1.36
NB, OH(AgAgClX, HOCl) at 1000 bars pressure					
101-R	919	7 days	3N HCl	1.29 ; 1.27	−0.23
101-S	919	7 days	H_2O	1.307; 1.303	−0.24
101-X	879	7 days	H_2O	1.375; 1.40	−0.325
101-Y	876	7 days	3N HCl	1.390	−0.33
101-J	815	7 days	3N HCl	1.50	−0.435
101-K	823	7 days	H_2O	1.51	−0.445
101-L	773	7 days	3N HCl	1.59	−0.53
101-M	776	7 days	H_2O	1.57	−0.51
101-N	713	14 days	H_2O	1.78 ; 1.795	−0.73
101-O	711	14 days	3N HCl	1.690; 1.71	−0.64
101-P	668	7 days	H_2O	1.74 ; 1.735	−0.68
101-Q	668	7 days	3N HCl	1.642; 1.62	−0.57

* 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).