

$$P_T = P_{\text{gas}} = P_{\text{H}_2\text{O}} + P_{\text{H}_2} + P_{\text{HCl}} + P_{\text{O}_2} + P_{\text{Cl}_2} =$$

$$\frac{f_{\text{H}_2\text{O}}}{\gamma_{\text{H}_2\text{O}}} + \frac{f_{\text{H}_2}}{\gamma_{\text{H}_2}} + \frac{f_{\text{HCl}}}{\gamma_{\text{HCl}}} + \frac{f_{\text{O}_2}}{\gamma_{\text{O}_2}} + \frac{f_{\text{Cl}_2}}{\gamma_{\text{Cl}_2}} \quad (1)$$

$$\text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O} \quad (K_w)_T = \frac{f_{\text{H}_2\text{O}}}{f_{\text{H}_2} \cdot f_{\text{O}_2}^{1/2}} \quad (2)$$

$$1/2 \text{H}_2 + 1/2 \text{Cl}_2 \rightleftharpoons \text{HCl} \quad (K_{\text{HCl}})_T = \frac{f_{\text{HCl}}}{f_{\text{H}_2}^{1/2} \cdot f_{\text{Cl}_2}^{1/2}} \quad (3)$$

$$\text{Ag} + 1/2 \text{Cl}_2 \rightleftharpoons \text{AgCl} \quad (K_{\text{AgCl}})_{P,T} = f_{\text{Cl}_2}^{-1/2} \quad (4)$$

$$f_{\text{H}_2} \text{ external} = f_{\text{H}_2} \text{ internal} \quad (5)$$

where f_{H_2} external is defined by the particular hydrogen buffer employed. Solving equations (1) to (5), we obtain

$$f_{\text{HCl}} = K_{\text{HCl}} f_{\text{H}_2}^{1/2} f_{\text{Cl}_2}^{1/2} \quad (6)$$

$$f_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}} \left(P_T - \frac{f_{\text{HCl}}}{\gamma_{\text{HCl}}} - \frac{f_{\text{H}_2}}{\gamma_{\text{H}_2}} \right) \quad (7)$$

$$f_{\text{O}_2}^{1/2} = \frac{\left(P_T - \frac{f_{\text{HCl}}}{\gamma_{\text{HCl}}} - \frac{f_{\text{H}_2}}{\gamma_{\text{H}_2}} \right) \gamma_{\text{H}_2\text{O}}}{f_{\text{H}_2} \cdot K_w} \quad (8)$$

Calculations for four hydrogen buffers, 600° to 900°K, 500 to 3000 bars are reported in table 1. In general, procedures and data are as reported in Eugster and Skippen (1967). For the buffer assemblage fayalite + magnetite + quartz, f_{O_2} values reported by Wones and Gilbert (1969) were used. Equilibrium constants for (2), (3), and (4) were calculated using Gibbs free energy data from Robie and Waldbaum (1968) and molar volume data at 25°C from Robie, Bethke, and Beardsley (1967), except for liquid AgCl, which was obtained from Smithells (1967) as a function of temperature. To obtain pressure corrections (see Eugster and Wones, 1962), all solids and the melt were considered incompressible. Fugacity coefficients used were as follows: H₂O from Burnham, Holloway, and Davis (1969), H₂ from Presnall (1969), HCl from reduced variables chart of Hougen and Watson (1946). Ideal mixing of real gases was assumed in the calculations.

The calculated HCl fugacity may be evaluated independently of the buffering process by measuring pH of the solution after quenching. In order to make this comparison possible, we need to calculate the molality of HCl° at P and T.

Assuming ideal mixing of real gases, we can express Raoult's law in terms of fugacities:

TABLE I
Theoretical calculations

Buffer	Pressure bars	Temp °K	f_{H_2} bars	Log f_{Cl_2} bars	Log f_{O_2} bars	f_{HCl} bars	f_{H_2O} bars	Log m_{HCl}°	
MH, OH(AgAgClX, HOCl)*	500	600	0.0007	-16.197	-33.175	0.074	111.0	-2.083	
		700	0.0020	-13.172	-26.402	0.274	241.0	-1.512	
		800	0.0037	-11.082	-21.501	0.548	345.6	-1.216	
	1000	900	0.0050	-9.561	-17.784	0.763	403.9	-1.072	
		600	0.0008	-16.060	-32.968	0.091	141.0	-2.287	
		700	0.0026	-13.056	-26.170	0.352	314.9	-1.751	
	2000	800	0.0052	-10.952	-21.163	0.757	509.7	-1.438	
		900	0.0079	-9.442	-17.342	1.10	671.4	-1.293	
		600	0.0013	-15.792	-32.589	0.153	218.0	-2.553	
	3000	700	0.0039	-12.825	-25.793	0.564	485.9	-2.000	
		800	0.0083	-10.694	-20.761	1.28	809.7	-1.653	
		900	0.0132	-9.204	-16.889	1.87	1131.4	-1.504	
	NB, OH(AgAgClX, HOCl)	500	600	0.0019	-15.522	-32.240	0.257	327.0	-2.721
			700	0.0056	-12.594	-25.460	0.885	713.9	-2.184
			800	0.0118	-10.435	-20.429	2.050	1188.0	-1.818
1000		900	0.0199	-8.965	-16.555	3.020	1661.3	-1.650	
		600	0.240	-16.197	-33.178	1.326	110.7	-0.828	
		700	0.724	-13.172	-26.412	5.164	238.2	-0.237	
2000		800	1.380	-11.082	-21.520	10.568	337.8	0.069	
		900	1.995	-9.561	-17.812	15.223	390.7	0.228	
		600	0.295	-16.062	-32.969	1.718	140.7	-1.012	
3000		700	0.955	-13.056	-26.175	6.776	312.8	-0.466	
		800	1.995	-10.952	-21.175	14.757	502.6	-0.147	
		900	3.162	-9.442	-17.360	21.979	658.0	0.007	
500		600	0.4169	-15.792	-32.590	2.786	217.8	-1.295	
		700	1.4125	-12.825	-25.796	10.752	484.1	-0.721	
		800	3.1623	-10.694	-20.769	25.004	802.9	-0.363	
	900	5.2481	-9.204	-16.900	37.239	1117.3	-0.203		
	600	0.5623	-15.522	-32.237	4.416	326.8	-1.486		
	700	1.9055	-17.594	-25.461	16.293	712.2	-0.919		
800	4.2658	-10.435	-20.433	39.129	1181.0	-0.538			
	900	7.4131	-8.965	-16.563	58.277	1646.9	-0.365		

$$f_{HCl}^{\text{mixture}} = f_{HCl}^{\circ} \cdot x_{HCl}^{\circ}$$

where f_{HCl}^{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.

$$x_{HCl}^{\circ} = \frac{f_{HCl}^{\text{mixture}}}{P_{HCl}^{\circ} \cdot \gamma_{HCl}^{\circ}}$$

x_{HCl}° is the number of moles of HCl divided by the total number of moles in the mixture. If we neglect the presence of hydrogen, we can calculate the molality of HCl, m_{HCl}° from

$$m_{HCl}^{\circ} = x_{HCl}^{\circ} \cdot 55.5 = \frac{f_{HCl}^{\text{mixture}} \cdot 55.5}{P_{HCl}^{\circ} \cdot \gamma_{HCl}^{\circ}} \quad (9)$$

where P_{HCl}° and γ_{HCl}° refer to the partial pressure and fugacity coefficient of pure HCl at P and T. To check the approximations in-