

Ag + AgCl in the experimental control of solution equilibria 283
 break occurring at the melting of AgCl. Constants for these straight lines are given in table 4.

TABLE 4
 $\text{Log } m_{\text{HCl}}^{\circ}(\text{ex}) = A/T^{\circ}\text{K} + B$

Buffer	Pressure (bars)	Temp Range °K	A*	B
Ni + NiO	2000	673-738	-2330	2.396
		738-1000	-1160	0.816
	1000	673-733	-2302	2.58
		733-1000	-1136	0.99
Fe ₂ O ₃ + Fe ₃ O ₄	2000	673-738	-2300	1.435
		738-1000	-1083	-0.208
	1000	673-733	-2245	1.482
		733-1000	-1037	-0.166

* Slopes are those of calculated curves

To facilitate thermodynamic calculations, it is convenient to convert the adjusted molalities of HCl(ex) of table 4 to fugacities of HCl by solving equation (9) for f_{HCl} :

$$f_{\text{HCl}}^{\text{mixture}} = f_{\text{HCl}}^{\circ}(\text{ex}) = \frac{m^{\circ}_{\text{HCl}}(\text{ex}) \cdot P_{\text{HCl}}^{\circ*} \cdot \gamma_{\text{HCl}}^{\circ*}}{55.5}$$

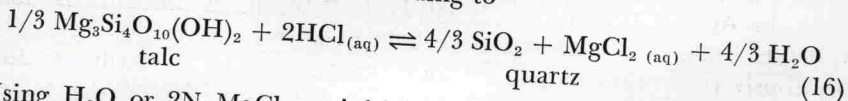
using γ_{HCl} values from reduced variables charts (Hougen and Watson, 1946) and $m^{\circ}_{\text{HCl}}(\text{ex})$ values from table 4. The results are given in table 5. $f_{\text{HCl}}(\text{ex})$ can be considered a direct calibration of f_{HCl} in the solution at P and T, regardless of other species present, if the assumption of ideal mixing holds and if the fugacity coefficients used are reliable. The $f_{\text{HCl}}(\text{ex})$ values shown in table 5 are independent of the theoretical f_{HCl} values of table 1, calculated from thermochemical data.

TABLE 5
 Experimentally derived values of $f_{\text{HCl}}(\text{ex})$

Buffer	Pressure (bars)	Temp (°K)	$f_{\text{HCl}}(\text{ex})$ (bars)
NB, OH(AgAgClX, HOCl)	2000	600	1.82
		700	6.62
		800	13.39
		900	20.01
		1000	27.26
	1000	600	0.98
		700	3.87
		800	7.70
		900	11.56
		1000	16.09
MH, OH(AgAgClX, HOCl)	2000	600	0.22
		700	0.80
		800	1.58
		900	2.31
		1000	3.11
	1000	600	0.10
		700	0.37
		800	0.72
		900	1.04
		1000	1.41

APPLICATIONS AND CONCLUSIONS

To test the usefulness of the HCl buffer for the study of mineral-solution equilibria, we have investigated the stability of talc and quartz in MgCl₂-HCl-H₂O solutions, according to



Using H₂O or 2N MgCl₂ as initial solutions, together with a mixture of synthetic talc and natural quartz, experiments were run at 2000 bars between 477° and 727°C. Total magnesium concentration was measured upon quenching. Values for $m_{\text{Mg}(\text{total})}/(m_{\text{HCl}^\circ(\text{ex})})^2$, using the values of table 4, are shown in figure 11. Reversibility was achieved within narrow limits for one-week runs, demonstrating that the HCl buffer can be used to study mineral equilibria. Details of the experiments on talc-quartz, as well as applications to other equilibria can be found in Frantz (ms) and Gunter (ms).

The f_{HCl} range imposed by the HCl buffer described in this paper is probably much higher than that of most igneous and metamorphic solutions. For the experimental determination of mineral equilibria, and hence the measurement of thermodynamic constants, this is irrelevant. Some minerals, however, are not stable in acid solutions, and for their study less acid buffers must be developed. Such buffers may involve acids other than HCl, such as HF, H₂SO₄. For studying mineral equi-

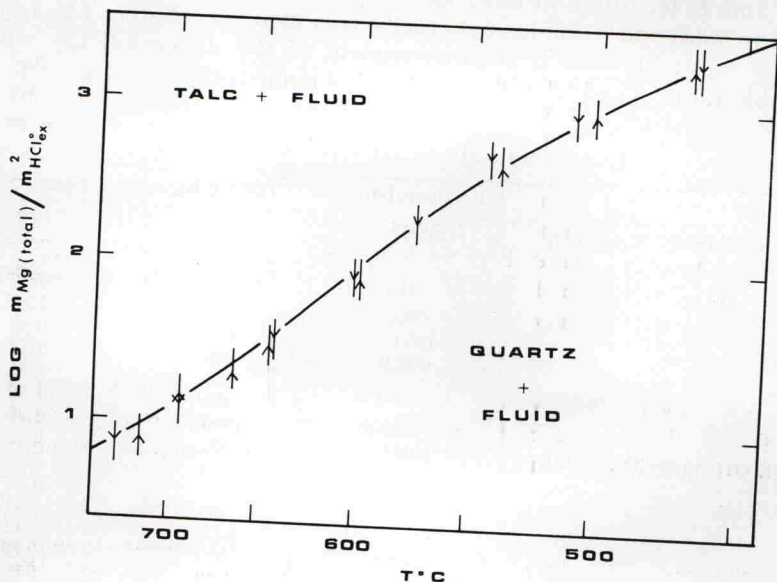


Fig. 11. Experimental data for the talc-quartz equilibrium taken from Frantz (ms). Each symbol is an individual experiment; the bar length represents the combined error of Mg measurement and buffer calibration, and the arrow indicates the direction from which equilibrium was approached.