

Fig. 7. Experimental data for $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$ at 1000 bars pressure. For explanation of symbols see figure 4.

the Ag–AgCl buffer functions effectively. At 2000 bars, time necessary for equilibration is 2 to 3 days or less above 500°C . At 400°C reactions are more sluggish and runs up to 30 days were employed. The rate determining step may be the diffusion of hydrogen into the inner capsule. At 1000 bars equilibration is slower still. Much of the silver was found to plate out on the inside of the platinum capsule. Agreement between experimental data points and calculated curves is quite good, considering the errors associated with the thermochemical data and the assumption of ideal mixing. A curve drawn through the experimental points would have a slope similar to the theoretical curve at higher temperatures, but there is a pronounced divergence in slopes toward lower temperatures. The most reasonable explanation for this divergence is that the dissociation of HCl° increases in magnitude toward lower temperatures.



$$(K_1)_{P,T} = \frac{a_{\text{H}^+} \cdot a_{\text{Cl}^-}}{a_{\text{HCl}^\circ}} = \frac{m_{\text{H}^+} \cdot m_{\text{Cl}^-}}{m_{\text{HCl}^\circ}} \frac{\lambda_{\text{H}^+} \cdot \lambda_{\text{Cl}^-}}{\lambda_{\text{HCl}^\circ}} \quad (11)$$

where K_1 is the dissociation constant of HCl° and λ_i is the activity coefficient of component i in the solution based upon a hypothetical one-molal solution of i at P and T as the standard state. Remember that the Ag–AgCl buffer at P and T only controls $m_{\text{HCl}^\circ}(T,P)$ and hence a_{HCl° . Thus, if HCl dissociation increases toward lower temperatures, then according to (11) a_{H^+} is present in increasing amounts at lower temperatures and thus affects the measurement of $m_{\text{HCl}(total)}$ according to equation (10). The procedure used for adjusting the experimental data is demonstrated in figure 8, drawn for the MH buffer at 2000 bars pressure. The dashed calculated lines as well as the experimental points are those of figure 6. Next we determined experimentally the melting tempera-

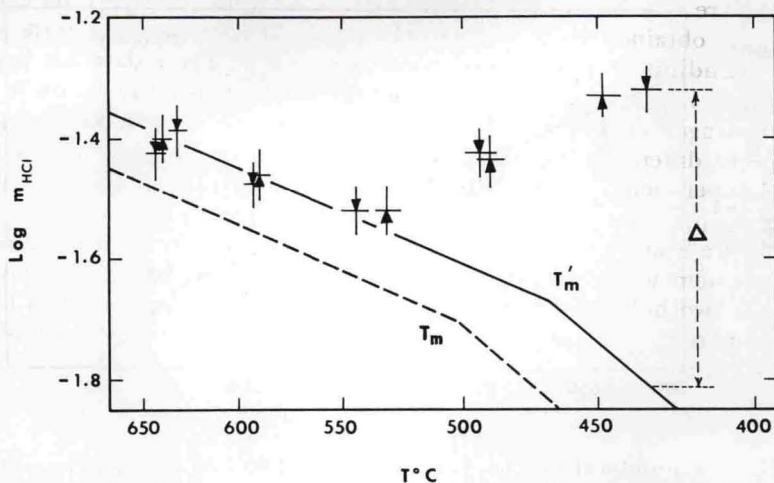


Fig. 8. Adjustment of experimental data for $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$ at 2000 bars pressure. The symbols and the dashed curve are those of figure 6. The solid curve represents the adjusted experimental data. T_m and T_m^1 are the calculated and observed melting temperatures of AgCl respectively. For the meaning of Δ see text.

ture, T_m^1 , of AgCl in H-O-Cl solutions at 2000 and 1000 bars pressure, and we obtained $465 \pm 5^\circ\text{C}$ and $460 \pm 5^\circ\text{C}$ respectively. The difference between the calculated (T_m) and observed (T_m^1) melting temperature is presumably due to solution of H_2O in the AgCl melt.

Next we drew a line fitted through the high-temperature experimental points with the slope of the theoretical curve. This line was extended to T_m^1 . Below T_m^1 , another line was drawn, with the slope of the theoretical curve below T_m . These lines (solid lines in fig. 8) are considered to represent the adjusted experimental values of m_{HCl° which are defined as $m_{\text{HCl}^\circ(\text{ex})}$, to distinguish them from the calculated values of m_{HCl° of table 1. The deviation at lower temperatures between the adjusted curve and the experimental points is then assigned to the dissociation of HCl° according to equation (11). Assuming

$$m_{\text{H}^+} = m_{\text{Cl}^-} = X$$

and that the activity coefficient quotient in (11) is unity, we have

$$\log (K_1)_{P,T} = 2 \log X - \log m_{\text{HCl}^\circ(\text{ex})} \quad (12)$$

For each temperature, the magnitude of X is defined by the difference Δ between the experimentally determined values for $m_{\text{HCl}(\text{total})}$ and the adjusted experimental curve (see fig. 8).

$$X = (10^{\log m_{\text{HCl}(\text{total})}} - 10^{\log m_{\text{HCl}^\circ(\text{ex})}}) \quad (13)$$

$$\log (K_1)_{P,T} = 2 \log (10^{\log m_{\text{HCl}(\text{total})}} - 10^{\log m_{\text{HCl}^\circ(\text{ex})}}) - \log m_{\text{HCl}^\circ(\text{ex})} \quad (14)$$