corder. A Picker X-ray diffractometer was used to analyze the buffer assemblage after quench.

EXPERIMENTAL RESULTS

Results of the experiments using the Ni + NiO + H_2O (NB) and Fe_2O_3 + Fe_3O_4 + H_2O (MH) hydrogen buffers are reported in table 2. The measured quench pH was converted to molality of HCl at 25°C by correcting for the hydrogen ion activity coefficient of the diluted sample using data from Garrels and Christ (1965). Next the dilution factor was subtracted, yielding m_{H^+} at 25°C, which we equate with $m_{HCl\,(total)}$ at T and P. These corrected values are also reported in table 2. In figures 4, 5, 6, and 7 the calculated values for m_{HCl° of table 1 are compared with measurements of $m_{HCl\ (total)}$ reported in table 2.

The theoretical curve, shown as a dashed line in all figures, has a break of slope at the melting of AgCl. The melting point of AgCl at pressure was calculated using the 1 atm point (455°C) and the Clausius-Clapeyron slope, assuming $AgCl_{liquid}$ remains in its standard state, that is a pure AgCl liquid.

In figure 4 we also have indicated the estimated error in the theoretical curve, obtained by summation of the uncertainties in the free energy values. Errors of the other theoretical curves (figs. 5, 6, and 7) are of similar magnitude.

Each experiment is reported by a symbol showing direction of approach to equilibrium as well as estimated errors of temperature and $m_{HCl\ (total)}$. Reversal has been achieved in all instances indicating that

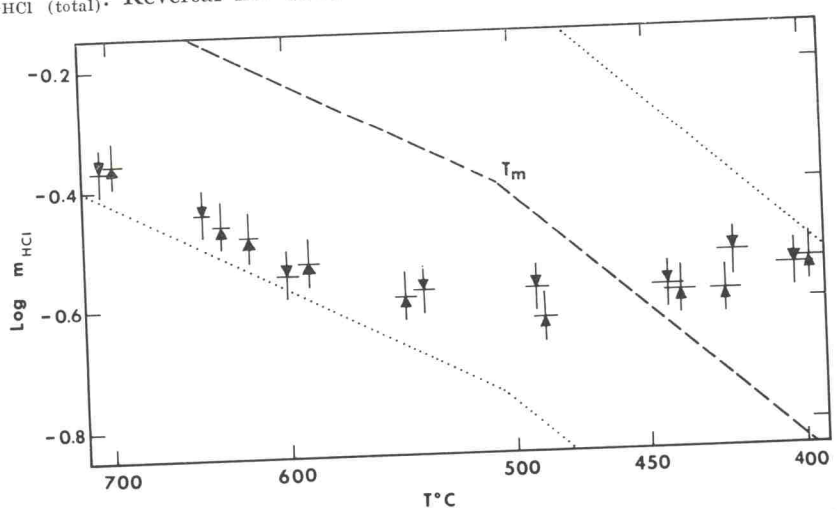

Fig. 4. Experimental data for Ni + NiO at 2000 bars pressure. Each symbol represents log $m_{HCl\ (total)}$ for a single experiment, with the arrow indicating the direction of approach to equilibrium. The horizontal and vertical bars represent errors of measurement. The dashed line is the calculated curve for m_{HCl°, and T_M is the calculated melting point of AgCl. The dotted lines represent the maximum errors associated with the theoretical curve.

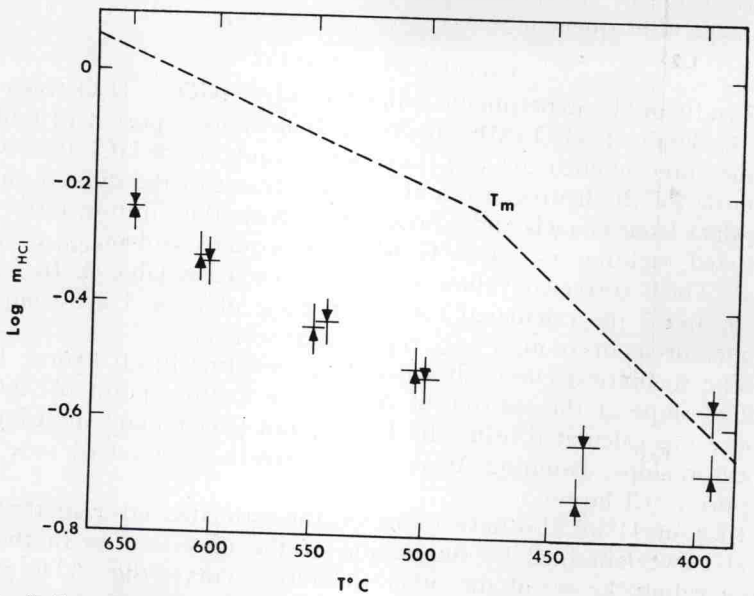

Fig. 5. Experimental data for Ni + NiO at 1000 bars pressure. For explanation of symbols see figure 4.

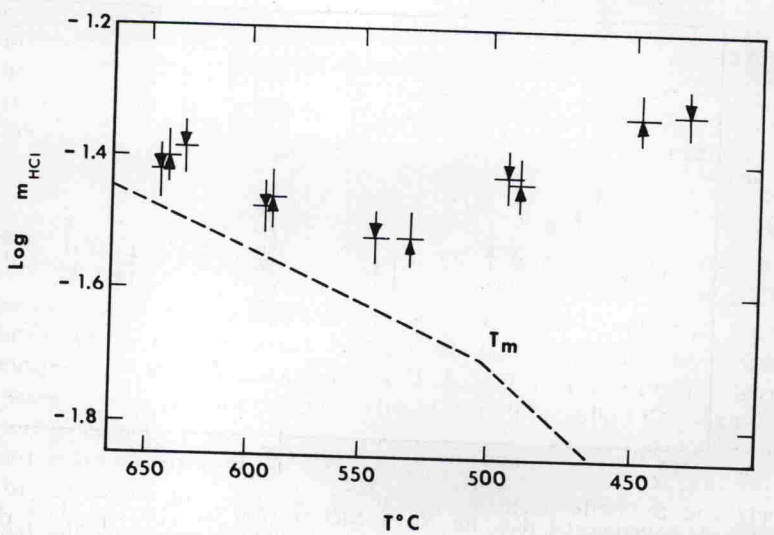

Fig. 6. Experimental data for Fe_2O_3 + Fe_3O_4 at 2000 bars pressure. For explanation of symbols see figure 4.