We are now in a position to evaluate $K_1$ as a function of T by using $m_{HCl(total)}$ obtained from quench pH (table 2) and $m_{HCl°(ex)}$ obtained from the adjusted experimental curve of figure 8. These data are listed in table 3. Log $K_1$ is plotted as a function of temperature in figure 9 for both hydrogen buffers used. Errors indicated are based on maximum and minimum differences between the values of log $m_{HCl(total)}$ and the adjusted experimental values, log $m_{HCl°(ex)}$ (see fig. 8). The error assigned to log $m_{HCl°(ex)}$ is $\pm\ 0.04$.

Figure 9 shows that $K_1$ values obtained with the NB and MH buffers are consistent with each other even though the gas compositions imposed by these two buffers are very different. The solid line was obtained by a least-squares fit through the values of $K_1$ listed in table 3. Its analytical expression is

$$\log K_1 = \frac{9376}{T} - 14.24 \tag{15}$$

An independent set of values for $K_1$, derived from conductivity measurements at P and T, has been reported by Franck (1956, 1961). His two values falling into our experimental range are also shown in figure 9. The agreement between the two sets of data is surprisingly good, considering the errors and assumptions involved in the two entirely independent techniques. This reinforces the interpretation of our experimental data (eq (11) to (14) and fig. 8) and provides an independent check on Franck's values for $K_1$. Experiments at 1000 bars (see fig. 5) show a similar trend.

In figure 10 we have summarized the adjusted experimental data. Each set of data for a particular hydrogen buffer and pressure can be expressed as two straight lines in $m_{HCl°(ex)}$ versus $1/T$ space, with the

TABLE 3

Equilibrium constant $K_1$ for the reaction:

$$HCl° \rightleftharpoons H^+ + Cl^- \text{ (eq 11)}$$

| Run no. | Temp °K | Log $m_{HCl\,(total)}$ | Log $m_{HCl°(ex)}$ | Log $K_1$ |
|---|---|---|---|---|
| NB, OH(AgAgClX, HOCl) at 2000 bars pressure | | | | |
| 100-F | 817 | −0.59 | −0.60 | −3.8436 |
| 100-E | 811 | −0.58 | −0.615 | −2.7614 |
| 100-U | 767 | −0.58 | −0.70 | −1.514 |
| 100-V | 762 | −0.63 | −0.71 | −2.130 |
| 100-X | 718 | −0.58 | −0.85 | −0.9772 |
| 100-W | 712 | −0.59 | −0.87 | −0.9572 |
| 101-I | 697 | −0.59 | −0.93 | −0.780 |
| 101-H | 694 | −0.53 | −0.94 | −0.5494 |
| 100-Y | 675 | −0.55 | −1.03 | −0.4170 |
| 100-Z | 673 | −0.54 | −1.05 | −0.3522 |
| MH, OH(AgAgClX, HOCl) at 2000 bars pressure | | | | |
| 100-A | 767 | −1.423 | −1.62 | −2.1182 |
| 100-B | 762 | −1.438 | −1.63 | −2.1354 |
| 101-G | 721 | −1.328 | −1.75 | −1.319 |
| 101-F | 707 | −1.323 | −1.81 | −1.180 |
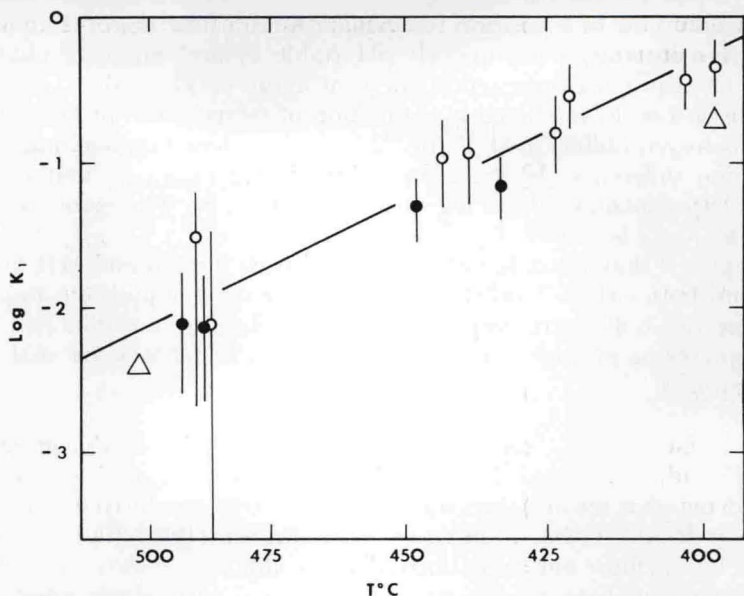
Fig. 9. Dissociation constant of HCl°, $K_1$, at 2000 bars pressure. Plotted are the values of table 3, with open circles representing Ni + NiO and closed circles, $Fe_2O_3$ + $Fe_3O_4$. The length of each bar represents the maximum possible error for an individual data point. The solid line is the least squares fit through these points (see eq 15). The two triangles are values for $K_1$ derived by Franck (1956, 1961).
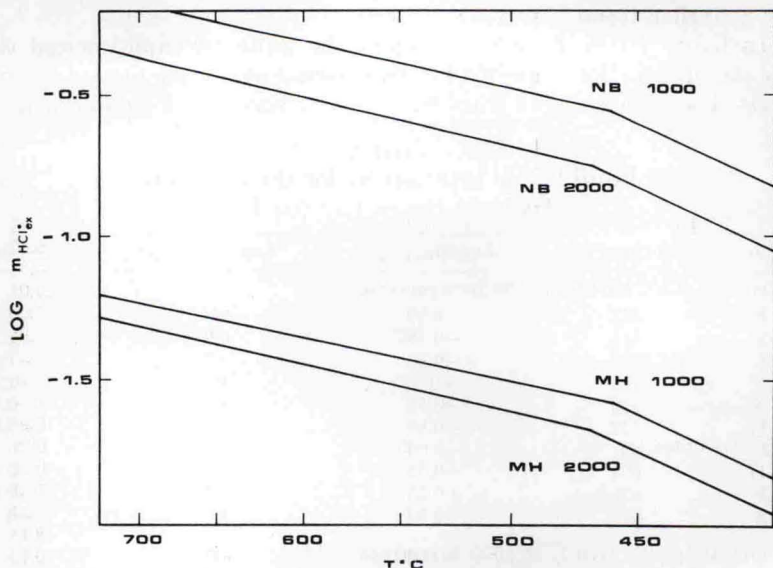


Fig. 10. Summary of adjusted experimental data. The data of figures 4, 5, 6, and 7 have been adjusted by the procedure illustrated in figure 8. The breaks in slope are the observed melting points of AgCl at 1000 and 2000 bars pressure. Buffer notation as in figure 1.