

Fig. 5—Specific conductance vs temperature for Co-S at 26.5-27.5 wt pct S.

Conductance measurements were performed over as wide a range of temperature and composition as phase diagrams, upper operating temperature limit of the apparatus (1350°C) and partial pressure of sulfur over the melt at the sulfur-rich end would allow. With the Ag-S system, it was possible to extend measurements from sulfur-rich  $\text{Ag}_2\text{S}$  to almost pure silver, but investigations in the Co-S, Ni-S, and Cu-S systems were more limited by the above considerations.

Temperature coefficients were determined over at least a 100°C interval for the whole composition range. At the sulfur-rich end of all four systems it was necessary to allow the temperature to drop very rapidly so that the sulfur content of the melt would not change significantly during the measurements.

## RESULTS

The experimental results are shown graphically in Figs. 1 through 4. The Co-S and Ni-S results, Figs. 1 and 2, have been idealized because of the very large number of points obtained and because of the rather wide scatter. In each case, all the results in a 1 pct composition range were plotted as specific conductance vs temperature. This was repeated over the whole composition range, and typical examples are given in Figs. 5 and 6. From these plots, conductances at various temperatures could be read off and replotted as conductance against composition. The Cu-S and Ag-S results, Figs. 3 and 4, were plotted as they were obtained with interpolation only where necessary to give results at suitable temperatures.

The Co-S and Ni-S results can be described together. In each case, specific conductance was high, 3500 to 5500  $\text{ohm}^{-1} \text{cm}^{-1}$  for Co-S, and 4500 to 5500 for Ni-S, and showed a minimum at or near the stoichiometric composition,  $\text{Co}_4\text{S}_3$  or  $\text{Ni}_3\text{S}_2$ . The temperature coefficients, which were negative over the whole range, were slightly larger near the stoichiometric compositions on the metal-rich side. Precise behavior of temperature coefficients on the sulfur-rich side was uncertain because of difficulties encountered while making the measurements. At these high sulfur contents, and at the experimental temperatures, the partial pressure of sulfur over the melts was almost atmospheric and a great deal of bubbling occurred at the graphite electrodes,

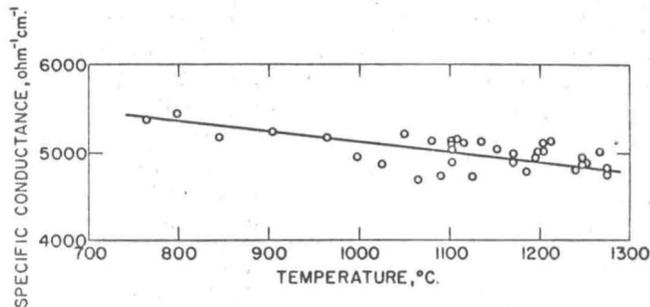


Fig. 6—Specific conductance vs temperature for Ni-S at 23-24 wt pct S.

even under an atmosphere of pure  $\text{H}_2\text{S}$ .

The only specific conductance value quoted in the literature for either of these molten systems is 4540  $\text{ohm}^{-1} \text{cm}^{-1}$  and a small negative coefficient for Ni-S at 900°C.<sup>5</sup> The order of magnitude is in agreement with the present results, but it is difficult to believe that the composition was Ni-S, since the partial pressure of sulfur over Ni-S at 900°C would be considerably above atmospheric,<sup>6</sup> and measurements would be impossible unless a high-pressure system was used.

The Cu-S system, which has been studied extensively by Bourgon, Derge, and Pound,<sup>3</sup> was only briefly studied in the present investigation. While showing good agreement with the previous workers' results, the present work indicated that there might be a very slight composition dependence of conductivity on the metal-rich side of  $\text{Cu}_2\text{S}$ . In addition, the rapid rise in conductivity on the sulfur-rich side appeared to begin more gently than was previously reported. The present work also showed that the temperature coefficient of specific conductance becomes immeasurably small on the sulfur-rich side of the rapid rise in conductivity. Two sets of measurements were made over temperature intervals of more than 150°C, and in neither of them could an appreciable change in conductivity be detected. These results, at 1200° to 1350°C and 1100° to 1300°C, do not lie on the curve as drawn in Fig. 3, but it should be realized that at these sulfur-rich compositions, loss of sulfur from the melt is rapid, and therefore the experimental error on values quoted for the composition is potentially high, in spite of the precaution of taking samples for analysis before and after the conductivity readings and averaging the analyses. Thus, although these two points may be slightly wrongly placed along the composition axis, it is felt that each of them undeniably demonstrates the temperature independent nature of the conductivity in this composition range. Finally, a single set of measurements, not shown on the graph, was made on the copper-rich side of the two-liquid region at 3 at. pct S. Conduction was metallic, increasing from 14,090  $\text{ohm}^{-1} \text{cm}^{-1}$  at 1307°C to 18,150  $\text{ohm}^{-1} \text{cm}^{-1}$  at 1112°C.

With the Ag-S system, because of lower melting points and a lower critical temperature of the immiscibility region, it was possible to examine a