

Electrical Conductivity of the Molten Co-S, Ni-S, Cu-S, and Ag-S Systems

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The electrical conductivities of Co-S, Ni-S, Cu-S, and Ag-S melts were studied as functions of temperature and composition. The specific conductances of the Co-S and Ni-S systems were high, 3500 to 5500 $\text{ohm}^{-1} \text{cm}^{-1}$ and 4500 to 5500 $\text{ohm}^{-1} \text{cm}^{-1}$, respectively, with minima near the stoichiometric compositions Co_4S_3 and Ni_3S_2 . Temperature dependence was small and negative. The specific conductances of melts with compositions approximating Cu_2S and Ag_2S were lower, 60 $\text{ohm}^{-1} \text{cm}^{-1}$ and 200 $\text{ohm}^{-1} \text{cm}^{-1}$, respectively, with very small, positive temperature coefficients, and, close to stoichiometry on the metal-rich side, negligible composition dependence. Immediately on the sulfur-rich side of Cu_2S the conductivity rose rapidly, but no similar change was observed in the Ag-S system. It was possible to measure the conductivity of the single liquid phase over the whole composition range Ag_2S to pure silver. A rapid increase in conductance, beginning at about 30 at. pct S and continuing to pure silver, was observed. It was accompanied by a change to a negative temperature dependence. A qualitative energy-level model is proposed in which the systems are treated as degenerate semiconductors over most of their composition ranges.

RECENT measurements of the electrical conductivity of the molten Cu-S and Fe-S systems¹⁻⁴ indicated that the conduction was electronic, and this has been interpreted by means of energy-level diagrams of the type used for solids. The present investigation is part of a series in which an attempt is being made to obtain an overall picture of electrical conduction in liquid systems of this kind, and with this end in mind, the specific conductance of molten Co-S, Ni-S, and Ag-S has been measured over as large a range of temperatures and compositions as was found to be practicable, and a few additional measurements were also made in the Cu-S system.

EXPERIMENTAL

Materials. The sulfur compounds were prepared from the elements (reagent grade) by heating together the appropriate proportions in vacuum or in

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an atmosphere of argon. Care is needed in the preparation of the Co-S and Ni-S compounds since, once the reaction starts, at 200° to 400°C, it is violently exothermic.

In the course of a series of measurements, the sulfur content of the melt could be increased at will by passing H_2S through or over the melt; it could be decreased by passing argon, or by dropping pellets of metal into the melt.

Samples were removed from the Co-S, Ni-S, and Cu-S melts by sucking some of the material up into 3 mm quartz tubing. The whole sample was analyzed because of a tendency to segregate. This sampling technique was not entirely satisfactory with Ag-S melts of some compositions (particularly 4 to 11 wt pct) because of separation into two liquids as the material cooled, with loss of some of the dense liquid from the bottom of the sampling tube. This difficulty was overcome by using a silica ladle. The samples were analyzed for the metals, and sometimes for sulfur also, by standard techniques. At high sulfur contents, samples were taken before and after conductivity measurements because of possible loss of sulfur during the readings, but at lower sulfur contents, samples were taken only once, either before or after measurements.

Apparatus. The melt was contained in a straight-side, Δ RR Morganite, recrystallized alumina crucible supported on a small inverted crucible in the bottom of a closed-end mullite tube. Heating was accomplished by means of a Globar furnace, and the temperature was measured by a Pt-Pt/Rh (10 pct) thermocouple which was protected by a McDanel sheath which dipped into the melt at the time of measurement. Auxiliary equipment allowed the passage of pure, dry argon or dry H_2S as required.

Conductivity Cell. The conductivity was measured using a four terminal cell¹⁻⁴ and a dc potentiometer circuit. The cell, with two current carrying electrodes and two null current probes, all of graphite, and enclosed in double-bore clear silica sheathes with a short, single bore capillary at the lower end, was essentially the same as that used in previous work.⁴ However, a slight modification was incorporated so that argon or H_2S could be blown via sidearms through the electrode sheathes between measurements in order to get fresh material from the bulk of the melt into the capillaries for each conductance measurement. The electrode sheathes were held at the upper ends in a rubber stopper together with the thermocouple and a gas outlet tube. This rubber stopper fitted into a glass

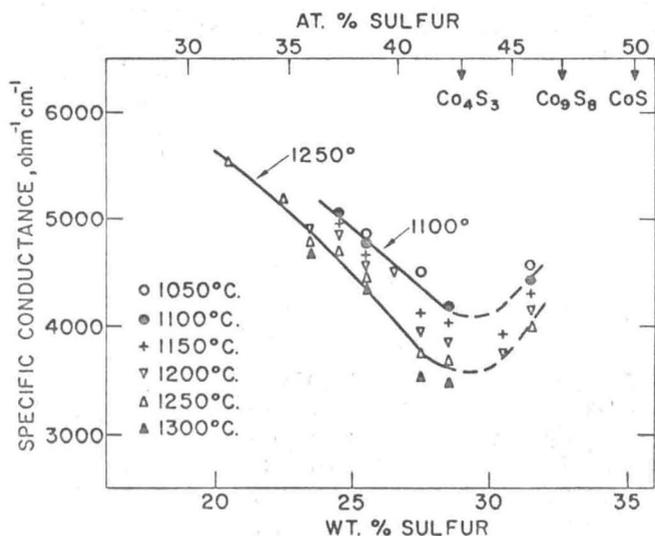


Fig. 1—Specific conductance vs sulfur content for Co-S.

tube, about 9 in. long and with a gas inlet sidearm, and which passed through a large rubber stopper fitted into the top of the McDanel reaction jacket, which was cooled by a fan. When the glass tube was lubricated with silicone grease, it slid readily through the large stopper, enabling the cell to be lowered into or raised from the melt at will.

Measurements. Before use, the conductance cells, which usually had a cell constant of about 15 cm^{-1} , were calibrated using mercury at room temperature. In this calibration, and in the measurements on the melts, direct current of about 5 amp from a lead storage battery was used, and the potential drop across the cell was compared with the potential drop across a standard 0.001 ohm resistor, using a Leeds and Northrup K2 potentiometer.

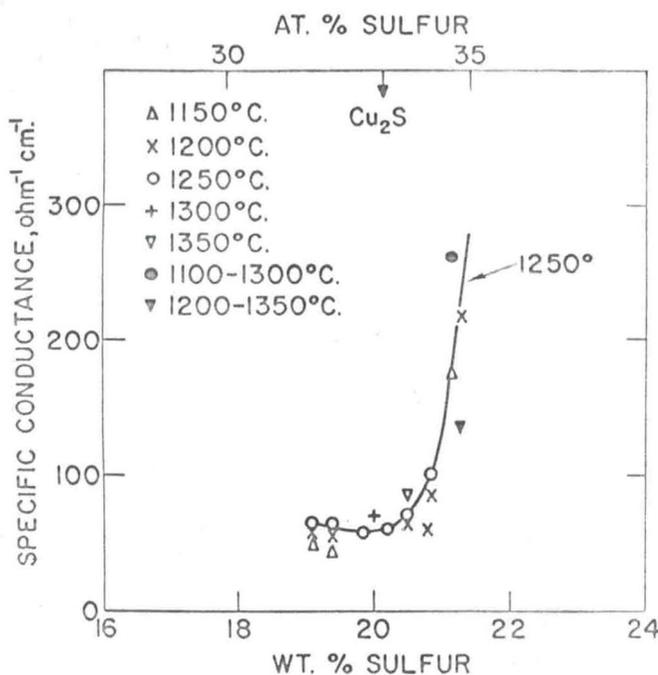


Fig. 3—Specific conductance vs sulfur content for Cu-S.

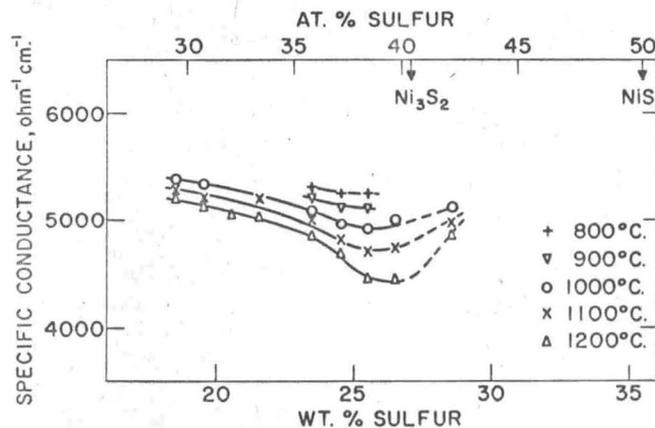


Fig. 2—Specific conductance vs sulfur content for Ni-S.

When taking measurements on the melts, the potential drop was measured, the polarity was reversed, the measurements were repeated, and an average value of the two readings was used to calculate the conductivity. This technique eliminated errors caused by thermal electromotive forces produced at the junctions of the graphite electrodes and the molybdenum leads. Although these junctions were constructed identically, and were in the same temperature zone, it was found, in practice, that considerable error could be introduced if readings were taken with the current passing in one direction only.

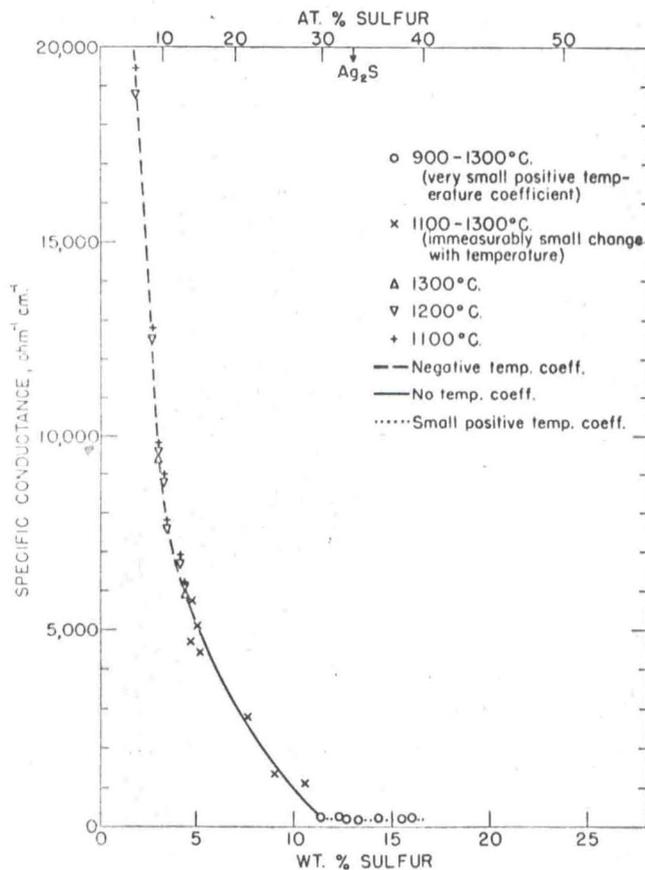


Fig. 4—Specific conductance vs sulfur content for Ag-S.

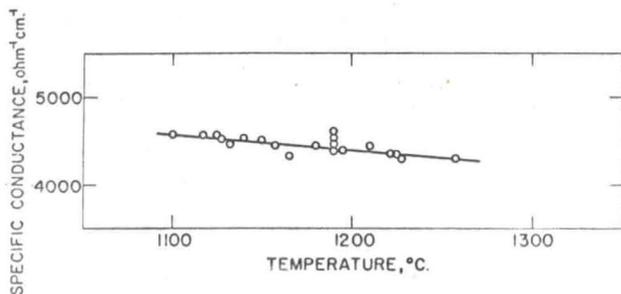


Fig. 5—Specific conductance vs temperature for Co-S at 26.5-27.5 wt pct S.

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 Ag_2S 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, Co_4S_3 or Ni_3S_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,

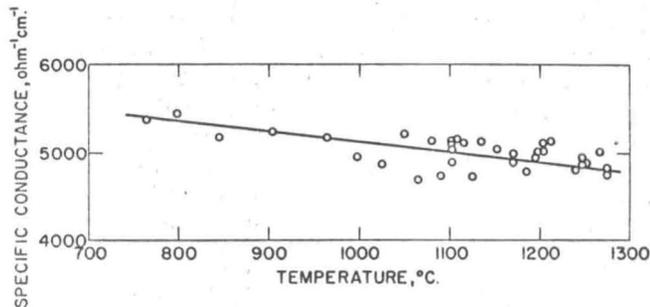


Fig. 6—Specific conductance vs temperature for Ni-S at 23-24 wt pct S.

even under an atmosphere of pure H_2S .

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.⁵ 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,⁶ 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,³ 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 Cu_2S . 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

much wider composition range than in any of the other systems. Measurements were made from sulfur-rich Ag_2S to almost pure silver, and Fig. 4 shows that around stoichiometry the conductivity was fairly low, $200 \text{ ohm}^{-1} \text{ cm}^{-1}$, and was almost independent of composition. However, as the immiscibility region was approached, the conduction of the single liquid phase developed a marked composition dependence, which continued all the way to almost pure silver. Fig. 7 shows details of the region around the composition Ag_2S . On the sulfur-rich side of stoichiometry, readings were very difficult to obtain because of the high sulfur pressure, but there might be a slight upward slope. On the silver-rich side, as in the copper system, there also seemed to be a very slight composition dependence until very close to the boundary of the immiscibility region at about 30 at. pct S at 1000°C . At compositions slightly on the sulfur-rich side of this boundary, the conductivity increased rapidly with increases in the silver content of the melt. Across the almost horizontal portion of the plot, the temperature coefficient was small and positive, but when the region of sudden increase in conductivity was reached, the temperature coefficient became immeasurably small and remained thus until, at about 15 at. pct S, it became definitely negative. This negative dependence on temperature became progressively larger as the silver content increased.

The conductivity of the solid Ag-S system, around the composition Ag-S, has been investigated by a number of workers, and the available data are summarized by Hebb.⁷ Essentially, the high temperature, α , form exhibits predominantly electronic conductivity of between 30 and $70 \text{ ohm}^{-1} \text{ cm}^{-1}$, with the conductance of the sulfur-rich material showing a positive temperature coefficient and that of the metal-rich material a negative temperature coefficient at temperatures between 177° and 500°C . The conductivity of molten Ag_2S has been investigated by Velikanov⁸ and was found to fit the equation $\log \sigma = 1.6245 + 553.72/T$. This equation gives values in rough agreement with the data obtained in the present investigation, but, of course, the temperature coefficient carries the opposite sign. No explanation can be offered for this.

It should be mentioned that it is unlikely that any of the measurements reported above for any of the systems studied were inadvertently taken at temperatures below the melting points or other phase boundaries. Accidental passage through a phase boundary, if it did not cause the silica sheaths to break, was always detectable because of a very definite and sudden change in the conductivity, and such readings have not been included in the results quoted in this paper.

DISCUSSION

The copper and silver systems will be discussed first, and in each case it will be assumed that the molten material would behave as an intrinsic semi-

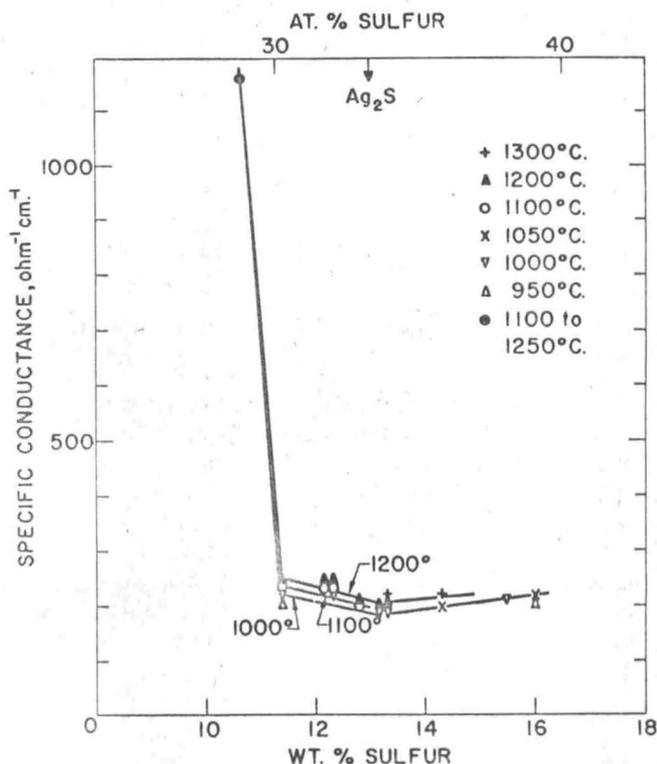


Fig. 7—Details of specific conductance vs sulfur content in the region of the stoichiometric composition Ag_2S .

conductor at the stoichiometric composition M_2S . Practical and statistical considerations at these elevated temperatures make it extremely unlikely that any measurements were made with the melt precisely at the stoichiometric composition. No attempt will be made to speculate whether electron or hole conduction is predominant, since only the relative mobilities of electrons and holes are involved, and these are immaterial to the present discussion.

As metal is added to the stoichiometric material, assuming that excess metal atoms act as donor impurities, some of the electrons from the ionized donors go into the conduction band and the others progressively reduce the number of holes in the valence band. Meanwhile, as more donor atoms are added, the Fermi level rises, and at a composition only slightly on the metal-rich side of stoichiometry, the concentration of free electrons becomes sufficiently large, at 1100°C , $3 \times 10^{10} \text{ cm}^{-3}$, for degeneracy to begin to appear.⁹ From this composition onwards, the addition of more metal causes the Fermi level to rise in the conduction band. The number of conducting electrons increases and the number of holes decreases. The very nearly constant conductivity over a considerable composition range, in both the Ag-S and Cu-S systems, bears out this postulation, *i.e.*, electron conduction is increasing while hole conduction is decreasing. The approximately constant value of the positive temperature coefficient across the same range is also consistent, since it implies that the energy of the gap is large compared with the distance the Fermi level moves in the conduction band.

Eventually, a metal-rich composition is reached at which the Fermi level is sufficiently high in the conduction band for there to be no further excitation of electrons from the valence band, and hence no further production of holes. Thenceforth, the conductivity is metallic in nature. It would be expected that the conductivity would begin to rise rapidly, and would continue to do so all the way to the pure metal, and that the positive temperature coefficient would disappear and be replaced by a negative one. These changes were observed in the Ag-S system. Phase diagram difficulties precluded similar observations on the Cu-S system, but there is no reason to doubt that it would behave similarly.

A similar explanation can probably be offered for the sulfur-rich side, with sulfur acting as an acceptor impurity close to stoichiometry, and the Fermi level moving down until it is in the valence band, when the system becomes degenerate. At some more sulfur-rich composition a rapid increase in conductivity would be expected; this was observed in the Cu-S system but not in the Ag-S system, even at the most sulfur-rich composition that could be studied. Of course, the distance from stoichiometry at which the discontinuous rise in conductivity occurs depends on the shape of the bands and will be specific to each case. It is hoped that current measurements on Cu-Te and Ag-Te melts will clarify the behavior on the metalloid-rich side of stoichiometry.

The suggestions made in the above paragraphs will be discussed rigorously by W. R. Bitler¹⁰ in a forthcoming paper.

Considering next the Co-S and Ni-S systems, it will be assumed, as with Fe-S,⁴ that the stoichiometric compounds, Co₄S₃ and Ni₃S₂, are intrinsic semiconductors where the forbidden gap between valence band and conduction band is small. This assumption is supported by the high conductivities and small negative temperature dependence; the latter would indicate that thermal promotion of electrons is more than offset by loss of mobility of the conducting species through thermal scattering. The minima in specific conductance in the region of stoichiometry can be explained qualitatively using the model proposed for the Cu-S and Ag-S systems. However, a rigorous examination of the cobalt and nickel systems would probably be difficult because of the complicated band structure of the transition metals.

One fact emerges clearly from the above considerations. In none of the systems studied would it be legitimate to attempt to describe the behavior of the donor or acceptor impurities in the manner of

Baumbach and Wagner.¹¹ These workers were considering only very small deviations from stoichiometry, and hence only low concentrations of carriers, where classical statistics are applicable and

$$n = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\epsilon/kT}$$

In the present investigation and in the work of Argyriades, Derge, and Pound⁴ on the molten Fe-S system, vastly larger composition ranges were covered, and the classical approximation would be inapplicable to all but a minute portion of the range since, for example, at 1100°C this approximation breaks down when the total number of free electrons is greater than $3 \times 10^{19} \text{ cm}^{-3}$. This number would be exceeded when the composition deviated from stoichiometry by less than 0.001 wt pct Ag in the case of Ag₂S, and the system would then begin to become degenerate. Thus the Baumbach and Wagner treatment can be applied only in a very small composition range on either side of the stoichiometric compound, and measurements within such small limits would be virtually impossible with these molten materials.

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