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Relative behaviour of electrical conductance for solid and molten mercuric halides

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Résumé. — On étudie les conductance et capacité électrostatique des halides de mercure solide. La comparaison des valeurs avec halides de mercure en fusion montre que l'influence de la température et pression sur la conductance électrique est la même pour les deux systèmes, qui sont très différents.

Abstract. — The paper reports the conductance and capacitance measurements on solid mercuric halides with a view to compare the results reported for molten mercuric halides. The study reveals that the temperature and pressure dependence of their electrical conductance remains unaltered for the two systems which are so widely different.

1. **Introduction.** — Considerable amount of work has been reported [1-9] on molten mercuric halides relating to their electrical conductivity. Darnell and McCollum [10] have lately reported their interesting measurements of conductivity for molten HgCl_2 and HgI_2 at elevated pressures upto 22 kbar. A summary of their important findings is worth a mention. For molten HgCl_2 they observed that (i) the material has a low conductivity and therefore remains slightly dissociated, (ii) an increase in pressure brings about a large increase in conductivity which will go back to its original value after the pressure is released, (iii) the temperature dependence of the isobaric conductance at an elevated pressure can, to a first approximation, be represented by the Arrhenius equation

$$K = A \exp\left(-\frac{E_k}{RT}\right),$$

and (iv) their measurements tend to support the suggestion made by Grantham and Yosim [8], i.e., the system becomes more molecular with decreased density when heated at ordinary pressures. For molten HgI_2 , however, their only important observation was that an increase in pressure causes a decrease in conductivity.

While reporting measurements upon solid HgCl_2 and HgI_2 at very low pressure (atmospheric, and few hundred bars), the present authors provide an interesting evidence which indicates a great similarity in the behaviour of molten and solid mercuric halides even

when the later is subjected to a very low pressure as compared to the former. In addition to conductance, we have also made capacitance measurements and our results indicate that almost all the characteristics, mentioned above for molten HgCl_2 and HgI_2 , remain the same for the solid material as well. In case of HgI_2 , however, our results indicate that the solid material predominantly exists as a molecular species.

2. **Experimental.** — Powders of HgCl_2 (A. R., Allied Chemicals, Canada) and HgI_2 (A. R., Mallinckrodt Chemical Works, New York) were finely ground and compressed to a known pressure to form very thin strong pellets (thickness ≈ 0.075 cm ; dia ≈ 0.67 cm). The measurements of capacitance were made on an instrument described earlier [11], having an accuracy of 0.000 5 pF. The instrument remains stable within ± 0.001 pF during a period of two hours. The conductance was measured on a B.P.L. megohmmeter, type RM 160/3. Both for conductance and capacitance measurements, the pellet is locked tight between the electrodes, having the same dimension as of pellet, of a sample holder with a thermostatic jacket through which a temperature-controlled liquid was circulated during the course of measurements.

The time dependent measurements of capacitance and conductance were made in the following manner. After compressing the material to a known pressure, the pellet was immediately taken out of the die and transferred to the sample holder for measurements at atmospheric pressure. Care was taken to consume

minimum time (one minute) in the process of transfer. By using a device [12], it was made sure that the pellet did not change its dimensions during the course of measurements.

3. Results. — **3.1 MERCURIC CHLORIDE.** — Darnell and McCollum [10] observed that an increase in pressure brings about a large increase in conductance of molten HgCl_2 . Figure 1 shows the results of our

Fig. 1. — Variation of conductance as a function of time, immediately after the release of pressure (500 bar).

Fig. 2. — $\log K$ vs $1000/T$ for solid HgCl_2 .

measurements made at room temperature for solid HgCl_2 . Immediately after the application of pressure (only 500 bar), the conductance of the material increased. But this increase was temporary, because after the release of pressure ($t = 0$, Fig. 1), the conductance started decreasing rapidly in the beginning and thereafter reached a steady state to its value at atmospheric pressure. Such a reversible character of conductivity was also observed by Darnell and McCollum for molten HgCl_2 . Figure 3 shows the results of temperature dependence of conductance at atmospheric pressure for solid HgCl_2 . We observed that the conductance passes through a minimum around 90 °C.

Darnell and McCollum pointed out that their data on molten mercuric halides [10] and molten bismuth trihalides [13] at elevated pressures tend to support the suggestion made by Grantham and Yosim [8]. Incidentally, our results (shown in Figs. 1 and 3) are also consistent with the suggestion of Grantham and Yosim, i.e., the system becomes more molecular (less conducting) with decreased density.

Figure 1 directly confirms the above statement. The compression of the material causes an increase in density and, according to Grantham and Yosim, the system should become less molecular (or more ionic) which results into a temporary increase in conductance as observed by us. After the release of

Fig. 3. — Temperature dependence of conductance for solid HgCl_2 and HgI_2 at atmospheric pressure.

pressure, the enhanced ionicity, produced due to compression, will slowly disappear and eventually the conductance of the system will decrease gradually till a steady state is reached (see Fig. 1). Similar arguments can be given for the results shown in figure 3. The initial fall in conductance can also be explained on the basis of suggestion made by Grantham and Yosim, because heating causes a reduction in density. As the temperature is increased above 90 °C, the dissociation seems to play a dominant role and therefore conduction keeps increasing with temperature.

Darnell and McCollum pointed out the validity of Arrhenius equation for the molten system of HgCl_2 . We have also observed that beyond 90 °C, the conductance (K) of the solid system can, to a first approximation, be represented by Arrhenius equation

$$K = A \exp\left(-\frac{E_k}{RT}\right).$$

This is evidenced by the plot of $\log K$ vs. $1000/T$ shown in figure 2. The value of activation energy for conduction (E_k), calculated from the data of figure 2, is 17.5 kcal/mole as against 8.46 kcal/mole obtained by Darnell and McCollum for molten HgCl_2 at a pressure of 5.4 kbar. It is not surprising to see that the activation energy for conduction increases if one goes from a molten to a solid-state system.

The striking feature of the above study is that the conductance behaviour of solid HgCl_2 remains the same as that of molten HgCl_2 . The object of the present work is indeed to emphasize upon the similarity of behavior characteristics without attaching any importance to the absolute values of K and E_k for the two situations.

3.2 MERCURIC IODIDE. — Figures 3 and 4 show the results of our measurements for the temperature dependence of conductance and capacitance of solid HgI_2 at atmospheric pressure. In both the cases, a

transition peak is obtained at 127 °C. It is well known that HgI_2 undergoes a polymorphic transition from red to yellow at a temperature 127 °C. A hysteresis was observed during the cooling cycle for capacitance measurements, as shown in figure 4.

Fig. 4. — Temperature dependence of capacitance for solid HgCl_2 and HgI_2 at atmospheric pressure.

The effect of pressure on the capacitance of solid HgI_2 is rather more interesting. Figure 5 gives the results of these measurements made immediately after the application of pressure which was only 500 bar at room temperature. One can easily see that the pressure causes a temporary reduction in the electrical capacitance which gradually increases to a steady-state value corresponding to the capacitance at atmospheric pressure. The phenomenon is reversible in the sense that if the same pellet is again compressed then its capacitance will again go down and thereafter would increase to reach the same steady state value. In our earlier communication [14], we have discussed at length that solid HgI_2 predominantly exists as molecular species and application of pressure causes a slight change in the I-Hg-I angle which results into a change in the value of dipole moment in a manner that causes a reduction in the value of dielectric constant or capacitance. What we wish to emphasize here is that solid HgI_2 exists mainly as molecular species at room temperature, as otherwise the measured capacitance of the system would not be so sensitive to temperature and pressure. This is obviously not true with solid HgCl_2 whose capacitance remains insensitive to temperature and pressure (see Figs. 4 and 5). This further confirms our earlier statement that ionic species play a dominant role in the observed behaviour of solid HgCl_2 .

Figure 1 gives the effect of pressure on the conductance of solid HgI_2 . Unlike HgCl_2 , the conductance of HgI_2 decreases when the material is compressed only to a pressure of 500 bar. After the release of pressure, the conductance gradually increases to reach a steady-state corresponding to its value at atmospheric-

Fig. 5. — Pressure dependence of capacitance for solid HgCl_2 and HgI_2 at room temperature.

ric pressure. The reversible character of conductance has also been reported by Darnell and McCollum [10] for molten HgI_2 . Their other finding too is in agreement with what we have observed, i.e., reduction in conductance with increasing pressure. Darnell and McCollum reported two sets of different measurements, e.g., (i) temperature dependence of conductance at a fixed pressure of 5.4 kbar (ii) the pressure dependence of conductance at a fixed temperature of 555 ± 5 °C. The straight-forward measurement in case (ii) showed that the conductance of molten HgI_2

Fig. 6. — Temperature dependence of conductance for molten HgI_2 at pressures < 0.1 kbar and 5.4 kbar [8], [10].

decreased when the pressure was increased from 3 kbar to 20 kbar. Whereas their isobaric measurements (case i) don't seem to be so apparent and therefore need an explanation. In figure 6 we have shown the conductance behaviour as observed by Darnell and McCollum [10] and Grantham and Yosin [8] (full lines). The two curves clearly indicate that at any given temperature, the conductance of the material increases if the pressure is increased from about 0.1 kbar to 5.4 kbar. It may however be noted that the magnitude of increase in conductance goes on decreasing at relatively lower temperatures. If we extrapolate the curves to still lower temperatures (dotted lines) then, by way of argument, one can say that the reverse

might happen. In other words, the conductance at 5.4 kbar will be lesser than the conductance at 0.1 kbar for temperatures below 250 °C which is in agreement with what we have observed for solid HgI_2 at room temperature.

One can therefore conclude that the temperature and pressure dependence of conductance of mercuric halides seems to remain unaltered for the two systems which are so widely different, i.e., *Molten* and *solid state*.

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