EXPERIMENT

ELECTRICAL CONDUCTIVITY OF IONIC SOLIDS (NaCl)

AIM: To report resistivity variation of NaCl with temperature and report vacancy migration energy (E_m) and the formation energy of vacancy pairs (Ø)

THEORY:

Electrical conductivity in ionic solids usually arises from the migration of ions under the influence on an electric field. Experiments show that in the alkali halides the positive ions are much more mobile than the negative ones. The mobility of ions in a perfect lattice (a lattice in which all sides are occupied by the ion) is extremely low. This is because of the high energy barrier preventing interchange of atoms. Hence, the presence of some lattice defects (viz. vacancies or interstitials) is essential for the occurrence of ionic conductivity. Such defects are indeed present in ionic crystals (and in metals also) and provide a thermodynamically stable state for the solid. The defect concentration is dependent on temperature. Thus the expression for the concentration of a pair of positive and negative ion vacancies is given by:

$$\boldsymbol{n = C\, exp\left(\frac{-\phi}{2kT}\right)}$$

where:

n is the number of pairs of vacancies
Ø is the formation energy of such a pair
C is a constant
K is the Boltzmann constant
T is the temperature in Kelvin

The positive ions surrounding a positive ion vacancy will have a finite probability of jumping into it. As a result, the vacancy will move through the crystal by virtue of positive ions jumping into it and diffusion.(i.e. ion movement without any external field applied) becomes possible. When an electrical field is applied to the solid, the probabilities of ion jumps in the direction parallel and antiparallel with the field are altered so that there is an effective movement of positive ion vacancies toward the anode. This means that there is a net effective movement of positive charge toward the cathode. The expression of conductivity, o derived on this basis is of the following form:

$$\boldsymbol{\sigma = A\, exp\left[\frac{-(E_m+\phi/2)}{k\,T}\right]}$$

Where A is a constant for a particular crystal

Em is the activation energy for migration

Ø is the formation energy of vacancy pairs

K is the boltzman constant

T is the temperature in Kelvin

Thus, from the plot of **Logl0 σ Vs (l/T)** one can calculate the value of **(Em+Ø/2)**. Plots of this sort for real alkali halides typically have the form of figure shown below:

Fig 3.1

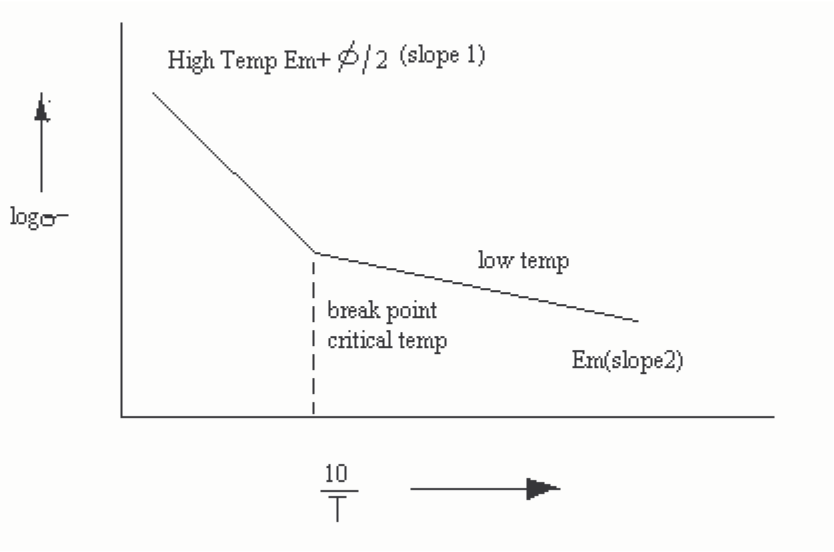


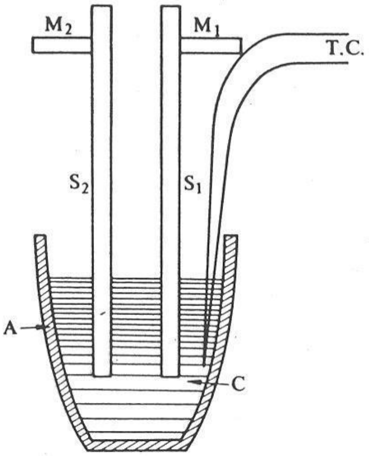
Fig. 3.1 Schematic of Ionic Conductivity behaviour of NaCl

There is a break observed somewhere in the temperature range of 400 to 700^{0}C depending on the purity of the crystal. This is known to arise from divalent positive impurities in the crystal. By the electrical neutrality condition, for each divalent positive ion present, there must be a positive ion vacancy. Thus, at lower temperature such crystals may contain more positive ion vacancies than would be expected on the basis of thermal equilibrium alone. In fact, below a critical temperature essentially all the vacancies arise because of the divalent impurities.

The number thermally generated (Equation.3.l) becomes insignificantly small. Thus the number of vacancies becomes temperature independent and the temperature dependence of the conductivity is controlled only by the mobility energy Em. Above this temperature the number of thermally produced vacancies would predominate over the number due to the impurity atoms and consequently the conductivity will depend on the energy **(Em+ Ø/2)**. This means that the slop of **log10 σ vs 1/T** should be **Em** and **(Em+ Ø/2)** respectively in the two temperature ranges. Hence, by determining these slopes, the values of Em and Ø can be calculated.

EQUIPMENT:

Furnace, Variac, Potentiometer, Temperature controller, Resistance measuring bridge. The arragement is shown in the Figure(2) below:



A is alumina crucible, C is polycrystalline sodium chloride specimen. S1 and S2 are two mild-steel plates for electrical connectivity and act as electrodes. T.C. represents the chromel-alumel thermocouple wires.

PROCEDURE:

1. Fused NaCl salt in a crucible is heated to 700-750^0C (below its melting point 805^0C).

2. It is then allowed to cool in a slow manner from around 700^0C to around 450^0C (by turning off the power to the furnace).

3. Measure the resistance (in kfi) of the fused salt (NaCl) in with the help of LCR meter which is connected across the two electrodes immersed in the salt. Measure the resistance at the interval of 10^0C fall of temperature with a millivoltmeter (mV).

OBSERVATIONS:

1. Report the data in the following table:

S.No.	Thermo EMF (mV)	Temperature (^{0}C)	Temperature (K)	1000/T (K^{-1})	Conductance G (mhos)

2. Plot (Log_{10} G) Vs (l/T). where G is the conductance (G =l/R).
3. Note the critical temperature at which change of slope is observed.
4. Note down the slopes of two different straight lines.
5. By solving two different equations from the two straight lines find out the values of E_m and Ø (in eV).

QUESTIONS:

1. What is the temperature corresponding to the break in the (Log_{10} G) Vs (l/T). plot?

2. From your date determine the values of E_m and Ø (in eV).

3 Why is it important to use a a.c in measuring the conductivity?

4. Equation 3.2 expresses the conductivity(o) as a function of temperature . Whereas you have been asked to use the conductance (G) values for calculating E_m and Ø. What is the assumption involved in this analysis?

5. If some $Cacl_2$ powder were added to the specimen before melting , in which direction would you expect the critical temperature to move?