NOTES

Polarization at electrodes8,10 and dissociation field effects11, which offer serious limitations for experimental studies at higher voltages may modify the actual form of transport [Eq. (3)]. However, the theoretical approach for predicting instability will remain the same. Further, the concept of local equilibrium has been found to be universally valid, since a thermodynamic theory of stability of steady states in non-linear regions or far from equilibrium situations has not yet been developed9, where the concept of local equilibrium is not valid. Thus the results reported in the present note are fully justified.

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References


A General Isotherm Equation for a Monovalent Ionic Crystal Containing Impurity in $+n$ Valency State

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A general isotherm equation has been derived for an ionic monovalent crystal doped with cation of $+n$ valency state. A general equation is derived for calculation of enthalpy of migration of point defect from the enthalpy of association of [impurity of $+n$ valent state - $(n-1)$ vacancies] complexes.

LIDAIRD1 has derived an isotherm equation to calculate the enthalpies of migration of point defects ($E_m$), association of impurity-vacancy complex ($E_a$) and formation of intrinsic defects ($E_F$) for an ionic crystal containing known amount of a divalent impurity. For similar ionic doped crystals, Dreyfus3 has derived Eq. (1),

$$E_1 = E_m + 0.5E_a$$

where $E_1$ is the observed enthalpy of conduction obtained from the extrinsic region of conductivity plot. Both these derivations need a modification for a monovalent ionic crystal containing dopant of valency greater than two. The present note is an
attempt to derive a general isotherm equation for crystals doped with impurity of $+n$ valent state.

When a monovalent ionic crystal is doped with a divalent impurity, it is assumed that (a) each aliovalent impurity atom induces only one defect and (b) due to electrostatic forces which exist between an aliovalent cation and a cation vacancy, the energy of vacancy is lowest when it occupies one of the nearest neighbour cation sites to the impurity. Such impurity-vacancy pairs are called associated pairs or complexes. At low temperature these complexes do not contribute to the conductance, but at higher temperature some of these complexes get dissociated to contribute towards the conduction. Therefore, it is assumed that each cation with $+n$ valency would produce $(n-1)$ number of vacancies, thus producing $[\text{impurity-} (n-1) \text{ vacancies}]$ complexes. If $\varepsilon$ be the total concentration of a dopant of $+n$ valency and $\phi$ be the degree of association of $[\text{impurity-} (n-1) \text{ vacancies}]$ complexes, and if there exists at any temperature a dynamic equilibrium between the associated vacancies and unassociated vacancies, then from this equilibrium the number of the vacancies can be calculated by applying the law of mass action to the quasi-chemical reaction:

Unassociated $+n$-valent impurity ions + unassociated vacancies $\Rightarrow [\text{impurity-} (n-1) \text{ vacancy}]$ complexes

or

$$c(1-\phi) + (n-1)c(1-\phi) \Rightarrow \phi c$$

According to the law of mass action,

$$K_\phi(T) = \frac{\phi c}{c(1-\phi)(c(1-\phi))^{n-1}} \ldots (2)$$

If $x_\phi$ represents the concentration of impurity complex (i.e., $\phi c$) then Eq. (2) reduces to Eq. (3).

$$K_\phi(T) = \frac{x_\phi}{c(x_\phi)^n} \ldots (3)$$

The mass action constant $K_\phi(T)$ can be expressed as Eq. (4).

$$K_\phi(T) = z_1 \exp(-S_n/k) \exp(E_n/kT) \ldots (4)$$

where $z_1$ is a constant which depends upon the crystal structure, and $S_n$ is the entropy term for the association process. If $x_1$ and $x_2$ are the molar fractions of two complementary intrinsic defects, then one can derive the Eq. (5).

$$x_1 x_2 = x_3 = k_1 \exp(S_n/k) \exp(-E_n/kT) \ldots (5)$$

The presence of unassociated $+n$ valent impurity gives an additional defect $(n-1)(c-x_3)$ which is similar in nature to that of first type (i.e., $x_1$ type) of complementary defects in the intrinsic region ($x_1 = x_3$). Hence the charge neutrality equation can be written as:

$$x_1 = (n-1)(c-x_3) + x_2 \ldots (6)$$

where molar fraction $x_3$ is written for the molar fraction of complementary $x_1$ intrinsic defects (i.e., $x_1 x_2 = x_3$). Substitution of $x_3$ from Eq. (6) in Eq. (3) gives

$$c = \frac{x_1 - x_2}{n-1} \left[ \frac{1}{K_\phi(T)} + \frac{(x_3-x_2)^n}{(n-1)^{n-1}} \right] \ldots (7)$$

Dividing Eq. (7) throughout by $x_3$ and substituting

$$x_0/k_3 = x_2/x_0 = e_1$$

$$c/x_0 = \frac{1}{(n-1)} \left[ e_1 - e_1^1 \right] \left[ 1 + k_1 \frac{(n-1)^{n-1}}{(n-1)^{n-1}} \right] \ldots (8)$$

If $e_1^1$ is very small then,

$$c/x_0 = \frac{1}{(n-1)} e_1 \left[ 1 + k_1 \frac{(n-1)^{n-1}}{(n-1)^{n-1}} e_1^1 \right] \ldots (9)$$

The relative conductivity is shown by Eq. (10),

$$\sigma_c = \frac{\sigma_c - \sigma_0}{\sigma_0} \ldots (10)$$

where $\sigma_c$ and $\sigma_0$ are the mobilities of two complementary defects. $\sigma_c$ and $\sigma_0$ are respectively the specific conductance of doped crystal with concentration $c$ and the specific conductance of ideally pure crystal. Neglecting the value of $e_1^2$ and substituting the $\varepsilon_1$ values from Eq. (10) into Eq. (9) gives Eq. (11).

$$e _{1} ^{1} = \frac{1}{(n-1)} x_0 (1+0) + x_0 k_1 \frac{(n-1)^{n-1}}{(n-1)^{n-1}} \left[ \frac{1}{\sigma_0} \right]$$

$$\times \left( \frac{\sigma_c}{\sigma_0} \right) ^{n-1} \ldots (11)$$

This is a conductivity isotherm equation for a crystal containing $+n$ valent dopant. This is an $n$th order polynomial whose nature can only be predicted if graph is plotted from a large number of $c$ versus $\sigma_c/\sigma_0$ values. When $n = 2$ the Eq. (11) reduces to Lidiard's isotherm equation (Eq. 12).

$$e _{1} ^{1} = \frac{1}{(n-1)} x_0 (1+0) + x_0 k_1 \frac{(n-1)^{n-1}}{(n-1)^{n-1}} \left[ \frac{1}{\sigma_0} \right] \ldots (12)$$

Now a plot of $c/(\sigma_c/\sigma_0)$ versus $(\sigma_c/\sigma_0)^{n-1}$ should be linear with a slope of

$$x_0 k_1 \frac{(n-1)^{n-1}}{(n-1)^{n-1}} \left[ \frac{1}{\sigma_0} \right]$$

and an intercept of $1/(n-1) x_0 (1+0)$.

$K_\phi(T)$ and $x_0$ can be calculated for different temperatures from the slopes and intercepts of the isotherms of different temperatures. The values of enthalpy for the association of $[\text{impurity-} (n-1) \text{ vacancies}]$ complexes ($E_n$) and the enthalpy of the formation of point defects ($E_f$) can then be calculated by using the Eqs. (4) and (5) respectively.

**General equation for the enthalpy for association of complexes**—In order to calculate the enthalpy for the migration of point defects for an ionic crystal containing a cation dopant of $+n$ valency Eq. (1) can be modified as follows:

In Eq. (3), $(n-1)(c-x_3)$ represents the number of unassociated vacancies (the number of defects $N$), which are responsible for the conduction. Hence $(n-1)(c-x_3)$ can be replaced by $N$, provided the number of vacancies created $(n-1)(c-x_3)$ are much greater than the number of intrinsic defects $(x_0)$ present in the association region.
Combining Eqs. (3) and (4) and substituting $N$ for $(n-1)$, we get

$$\frac{z_n}{N(n-1)} = z_1 \exp(-S_\mu/kT) \exp(E_\mu/kT) \quad \ldots (13)$$

Substituting the value of $N$ in the general conductivity equation, i.e., $\sigma = eN\mu$, one gets,

$$\sigma = e\sigma_0(n-1)(x_kn)^{1/n} \exp(S_m/kT) \exp(-E_m/kT) \quad \ldots (14)$$

Hence $T = \left(\frac{a_1^2e^2v_1}{kT}\right)\exp(S_m/kT)$

Ex. (16) shows that the enthalpy value obtained from the slope of linear plot between log $T$ versus $(1/T)$ of the extrinsic region should be given by,

$$E_\mu = E_m + 1/n E_a \quad \ldots (17)$$

When $n = 2$, Ex. (17) takes the form of Ex. (1). The Exs. (11) and (17) are of general form and are applicable to a dopant in any oxidation state. Further work to confirm the validity of these equations shall be published shortly.

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References


Free Energies of Solvation of Silver Halides in Ionic Melts

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The free energies of solution and solvation for silver halides in molten nitrates and perchlorates have been calculated from potentiometric data. The solvation process appears to be influenced by the anion of such ionic solvents.

Most of the thermodynamic properties of the solute are very sensitive to the solvation effects. In aqueous solutions, the ion is considered to be surrounded by three concentric regions. Contrary to this, in ionic melts, the process of solvation is somewhat difficult to visualize, because of the absence of polar solvent molecules and purely ionic nature of the solvent. Flengas and Rideal calculated the enthalpy and free energy of solvation for silver halides in molten NaNO₃-KNO₃. In this communication an effort has been made to correlate the enthalpy and free energy of solvation, with the nature of the solvent.

The solubility product constants ($K_s$) for silver halides at 623 K were determined by measuring the emf of the cell (A) at various concentrations of halide ion. Heat of solution ($\Delta H_{solv}$) was deter-

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Fig. 1 - Modes of dissolution of solid silver halide in excess solvent

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\begin{tabular}{|c|c|}
\hline
Ag & AgNO₃ (M) in molten salt solvent \hline
& in molten salt solvent (sat. with AgX) \hline
\end{tabular}
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(A)

(Reference Half-cell)

(Indicator Half-cell)

The corresponding enthalpy change, $\Delta H_{solv}$, is equal to the heat of solution. Table I gives the calculated values of $\Delta G_{solv}$ and $\Delta H_{solv}$ for the dissolution of silver halides in various ionic melts. For comparison, corresponding values in water are included. It is interesting to note that the thermodynamic data in the two types of media are of the same order, although there exists a fundamental difference in the process of dissolution in ionic melts and in water. The process of dissolution of solid silver halide in excess of solvent may be visualized to take place through either of the two pathways, shown in Fig. 1. Path I, involving the dissolution of solid salt as simple molecular species, gives the heat of solution ($\Delta H_{solv}$). Path II consists of formation of gaseous ions from the solid AgX and their subsequent dissolution; a process which depends largely on the nature of solvent. Hence

$$\Delta G_{solv}^o = -RT \ln K_s$$

The lattice energies at 350° for silver halides were computed through the considerations of Born-Haber thermochemical cycle, which relates lattice energy to the measurable thermal data,

$$\Delta L_{solv} = \Delta L_{solv}^o + \Delta L_{sol} - \Delta L_{latt}$$

where $\Delta L_{solv} = -U_{solv} = -Q_{solv} + S_{solv} + \Delta S_{solv}$,

$Q_{solv}$ = heat of formation of the salt AgX; $S_{solv}$ = heat of sublimation of silver metal; $I_{solv}$ = ionization potential of Ag; $\Delta S_{solv}$ = electron affinity for the halogen; $\Delta H_{solv}$ = heat of dissociation of gaseous halogen into atoms.

Available data at 25° have been corrected for the temperature increase to 350°. The values for the ionization potential of silver and electron affinity for halogens at 25° have not been corrected for the

$$\Delta H_{solv} = \Delta H_{solv}^o + \Delta H_{latt}$$

$$\Delta G_{solv} = \Delta G_{solv}^o + \Delta G_{latt}$$

Fig. 1 - Modes of dissolution of solid silver halide in excess solvent

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