Fig. 1 — Test of instability for quartz/methanol system
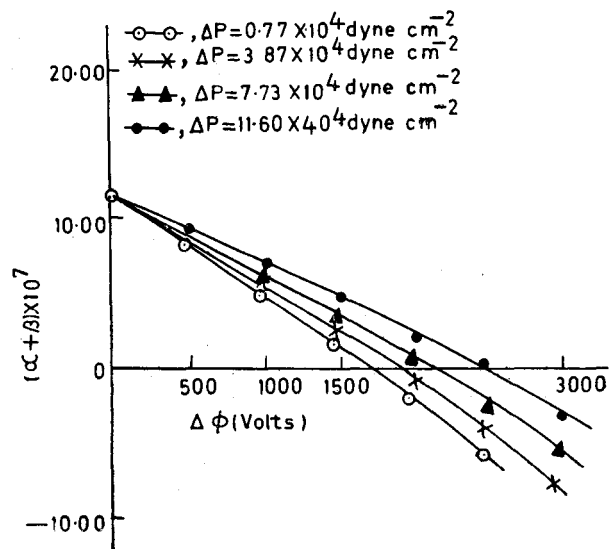

Fig. 2 — Test of instability for quartz/methyl ethyl ketone system
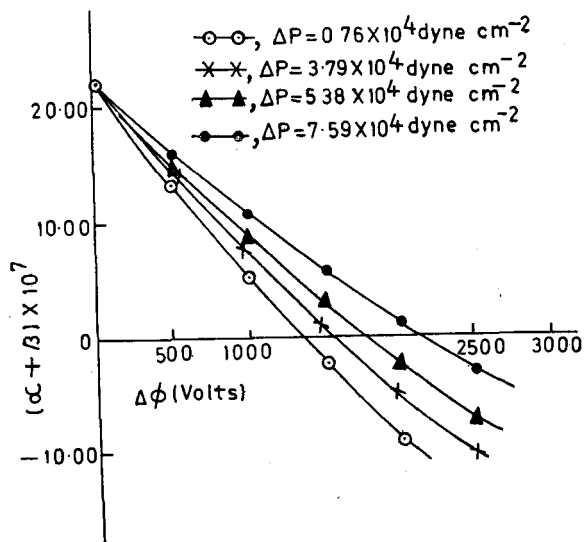

Fig. 3 — Test of instability for quartz/acetone system

Polarization at electrodes[9,10] and dissociation field effects[11], 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 developed[1], where the concept of local equilibrium is not valid. Thus the results reported in the present note are fully justified.

The authors are highly thankful to Prof. R. P. Rastogi for suggesting the problem and to Dr K. D. S. Yadava for valuable suggestions.

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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.

L IDIARD[1] 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, Dreyfus[2] has derived Eq. (1),

$$E_1 = E_m + 0.5E_a \qquad \qquad ...(1)$$

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 introduces 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 [impurity-$(n-1)$ vacancies] complexes. If c be the total concentration of a dopant of $+n$ valency and p be the degree of association of [impurity-$(n-1)$ 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 $\rightleftharpoons$ [impurity-$(n-1)$ vacancy] complexes
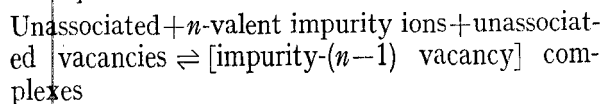
or

$$c(1-p)+(n-1)c(1-p) \rightleftharpoons pc$$

According to the law of mass action,

$$K_n(T) = \frac{pc}{c(1-p)\{c(1-p)\}^{n-1}} \qquad ...(2)$$

If x_k represents the concentration of impurity complex (i.e. pc) then Eq. (2) reduces to Eq. (3).

$$K_n(T) = \frac{x_k}{(c-x_k)^n} \qquad ...(3)$$

The mass action constant $K_n(T)$ can be expressed[1] as Eq. (4).

$$K_n(T) = z_1 \exp(-S_a/k) \exp(E_a/kT) \qquad ...(4)$$

z_1 is a constant which depends upon the crystal structure, and S_a 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[1] the Eq. (5).

$$x_1 x_2 = x_0^2 = k_1^{-1} = \exp(S_s/k) \exp(-E_s/kT) \qquad ...(5)$$

The presence of unassociated nth valent impurity gives an additional defect $(n-1)(c-x_k)$ which is similar in nature to that of first type (i.e., x_1 type) of complementary defects in the intrinsic region $(x_1 = x_2)$. Hence the charge neutrality equation can be written as:

$$x_1 = (n-1)(c-x_k)+x_2 \qquad ...(6)$$

where molar fraction x_2 is written for the molar fraction of complementary x_1 intrinsic defects (i.e., $x_1 x_2 = x_0^2$). Substitution of x_k from Eq. (6) in Eq. (3) gives

$$c = K_n(T) \frac{x_1-x_2}{n-1}\left[\frac{1}{K_n(T)} + \frac{(x_1-x_2)^{n-1}}{(n-1)^{n-1}}\right] \qquad ...(7)$$

Dividing Eq. (7) throughout by x_0 and substituting $x_0/x_1 = x_2/x_0 = \epsilon_1$

$$c/x_0 = \left[\frac{1}{(n-1)}\right](\epsilon_1-\epsilon_1^{-1})\left[1 + \frac{k_1^{-(n-1)/2}K_n(T)}{(n-1)^{n-1}}\right.$$
$$\left.(\epsilon_1-\epsilon_1^{-1})^{n-1}\right] \qquad ...(8)$$

If ϵ_1^{-1} is very small then,

$$c/x_0 = \frac{1}{(n-1)}\epsilon_1\left[1 + \frac{k_1^{-(n-1)/2}K_n(T)}{(n-1)^{n-1}} \epsilon_1^{n-1}\right] \qquad ...(9)$$

The relative conductivity[1] is shown by Eq. (10),

$$\frac{\sigma_c}{\sigma_0} = \frac{\epsilon_1+\theta\epsilon_1^{-1}}{1+\theta} \qquad ...(10)$$

where $\theta = \mu_2/\mu_1$.

μ_1 and μ_2 are the mobilities of two complementary defects. σ_c and σ_0 are respectively the specific conductance of doped crystal with concentration c and the specific conductance of ideally pure crystal. Neglecting the value of ϵ_1^{-1} and substituting the ϵ_1 values from Eq. (10) into Eq. (9) gives Eq. (11).

$$c\Big/\left(\frac{\sigma_c}{\sigma_0}\right) = \frac{1}{n-1} x_0(1+\theta)+x_0\frac{k_1^{-(n-1)/2}K_n(T)}{(n-1)^n}(1+\theta)^n$$
$$\times\left(\frac{\sigma_c}{\sigma_0}\right)^{n-1} \qquad ...(11)$$

This is a conductivity isotherm equation for a crystal containing $+n$ valent dopant. This is an nth order polynomial whose nature can only be predicted if graph is plotted from a large number of c versus σ_c/σ_0 values. When $n = 2$ the Eq. (11) reduces to Lidiard[1] isotherm equation (Eq. 12).

$$c/(\sigma_c/\sigma_0) = x_0(1+\theta)+x_0 k_1^{-0.5}K_2(T)(1+\theta)^2\left(\frac{\sigma_c}{\sigma_0}\right) \qquad ...(12)$$

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

$$\frac{x_0 k_1^{-[n-1/2]}K_n(T)}{(n-1)^n}(1+\theta)^n$$

and an intercept of $\frac{1}{(n-1)}x_0(1+\theta)$.

$K_n(T)$ 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 [impurity-$(n-1)$ vacancies] complexes (E_a) 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), $(n-1)(c-x_k)$ represents the number of unassociated vacancies (the number of defects N), which are responsible for the conduction. Hence $(n-1)(c-x_k)$ can be replaced by N, provided the number of vacancies created $\{(n-1)(c-x_k)\}$ 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 $(n-1)(c-x_k)$,

$$\frac{x_k}{\{N/(n-1)\}^n} = z_1 \exp(-S_a/k) \exp(E_a/kT) \qquad \ldots(13)$$

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

$$\sigma = e\mu(n-1)(x_k z_1^{-1})^{1/n} \exp(S_a/nk) \exp(-E_a/nkT)$$

where $\mu = (a^2 e v_0^2)/kT \exp(S_m/k) \exp(-E_m/kT)$.

Hence $\sigma T = [(a^2 e^2 v_0^2)/k](n-1)(x_k z^{-1})^{1/n}$
$\times \exp(S_m + 1/n\, S_a) \exp[-(E_m + 1/n\, E_a)/Tk]$ $\ldots(16)$

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

$$E_1 = E_m + 1/n\, E_a \qquad \ldots(17)$$

When $n = 2$, Eq. (17) takes the form of Eq. (1). The Eqs. (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.

One of us (A.A.K.) wishes to thank the UGC, New Delhi, for financial assistance.

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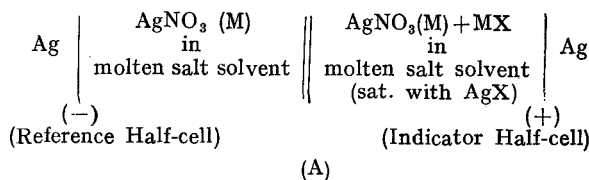## Free Energies of Solvation of Silver Halides in Ionic Melts

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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[1]. 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[2] calculated the enthalpy and free energy of solvation for silver halides in molten $NaNO_3$-KNO_3. 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 (ΔH_{soln}) was deter-

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$$\begin{array}{c|c|c}
\text{Ag} & \begin{array}{c} AgNO_3 \text{ (M)} \\ \text{in} \\ \text{molten salt solvent} \end{array} & \begin{array}{c} AgNO_3(\text{M})+MX \\ \text{in} \\ \text{molten salt solvent} \\ \text{(sat. with AgX)} \end{array} & \text{Ag}
\end{array}$$

(−)
(Reference Half-cell)
(+)
(Indicator Half-cell)

(A)

mined from the temperature-dependence of the cell emf, in the presence of excess of AgX in the melt. The details have been reported earlier[3,4].

In a saturated solution of a salt, the free energy change (ΔG°_{soln}) for the transfer of one mole of salt from solid to the solution in standard state is given by

$$\Delta G^\circ_{soln} = -RT \log_e K_s$$

The corresponding enthalpy change, ΔH°_{soln} is equal to the heat of solution. Table 1 gives the calculated values of ΔG°_{soln} and ΔH°_{soln} for the dissolution of silver halides in various ionic melts. For comparison, corresponding values in water[5] (at 25°) 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 (ΔH_{soln}). 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

$$-U_{AgX} = (\Delta H_{soln})_{AgX} - (\Delta H_{solv})_{AgX} \qquad \ldots(1)$$

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,

$$-U_{AgX} = Q_{AgX} + S_{Ag} + I_{Ag} + \tfrac{1}{2}D_X - E_X$$

where U_{AgX} = lattice energy of the salt AgX; Q_{AgX} = heat of formation of the salt from its elements in their standard states; S_{Ag} = heat of sublimation of silver metal; I_{Ag} = ionization potential of Ag; E_X = electron affinity for the halogen; $\tfrac{1}{2}D_X$ = heat of dissociation of gaseous halogen into atoms.

Available data[6] 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
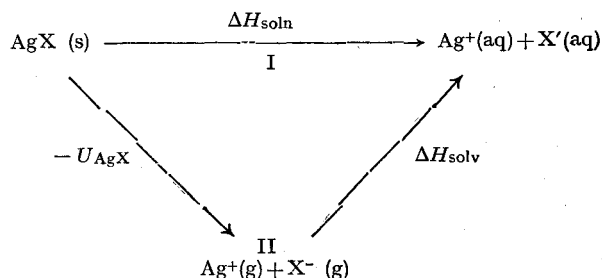

Fig. 1 — Modes of dissolution of solid silver halide in excess solvent