

Combining Eqs. (3) and (4) and substituting  $N$  for  $(n-1)(c-x_k)$ ,

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

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  $\sigma T = [(a^2 e^2 v_0^2) / k] (n-1) (x_k z_1^{-1})^{1/n} \times \exp(S_m + 1/n S_a) \exp[-(E_m + 1/n E_a) / kT] \quad \dots(16)$

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,

$$E_1 = E_m + 1/n E_a \quad \dots(17)$$

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.

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

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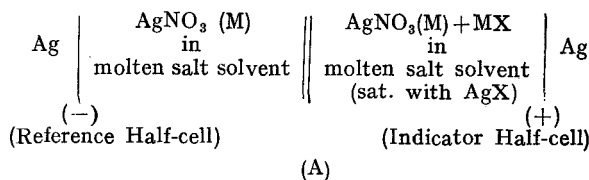
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The free energies of solution and solvation for silver halides in molten nitrates and perchlorates have been calculated from potentiometric data. The solvation process appears to be influenced by the anion of such ionic solvents.

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<sup>1</sup>. 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<sup>2</sup> calculated the enthalpy and free energy of solvation for silver halides in molten  $\text{NaNO}_3\text{-KNO}_3$ . 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 ( $\Delta H_{\text{soln}}$ ) was deter-



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<sup>3,4</sup>.

In a saturated solution of a salt, the free energy change ( $\Delta G_{\text{soln}}^\circ$ ) for the transfer of one mole of salt from solid to the solution in standard state is given by

$$\Delta G_{\text{soln}}^\circ = -RT \log_e K_s$$

The corresponding enthalpy change,  $\Delta H_{\text{soln}}^\circ$  is equal to the heat of solution. Table 1 gives the calculated values of  $\Delta G_{\text{soln}}^\circ$  and  $\Delta H_{\text{soln}}^\circ$  for the dissolution of silver halides in various ionic melts. For comparison, corresponding values in water<sup>5</sup> (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 ( $\Delta H_{\text{soln}}$ ). 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

$$-U_{\text{AgX}} = (\Delta H_{\text{soln}})_{\text{AgX}} - (\Delta H_{\text{soln}})_{\text{AgX}} \quad \dots(1)$$

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,

$$-U_{\text{AgX}} = Q_{\text{AgX}} + S_{\text{Ag}} + I_{\text{Ag}} + \frac{1}{2}D_{\text{X}} - E_{\text{X}}$$

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

Available data<sup>6</sup> 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

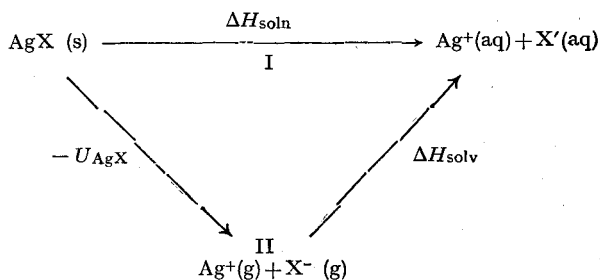


Fig. 1 — Modes of dissolution of solid silver halide in excess solvent

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TABLE 1 — FREE ENERGY AND ENTHALPY CHANGES FOR THE DISSOLUTION OF SILVER HALIDES

Solvent	$\Delta G_{\text{soln}}^{\circ}$ (kcal/mole)			$\Delta H_{\text{soln}}^{\circ}$ (kcal/mole)		
	AgCl	AgBr	AgI	AgCl	AgBr	AgI
Water	18.05	21.50	26.67	16.05	20.33	26.50
NaNO <sub>3</sub> -KNO <sub>3</sub>	17.42	22.09	30.84	18.30	21.30 (22.40)	29.35 (27.9)
NaNO <sub>3</sub> -Ba(NO <sub>3</sub> ) <sub>2</sub> (94.2:5.8)	17.34	21.97	29.54	18.21	26.26	36.12
KNO <sub>3</sub> -Ba(NO <sub>3</sub> ) <sub>2</sub> (89:11)	16.96	20.65	27.25	19.15	24.05	32.83
LiClO <sub>4</sub> -NaClO <sub>4</sub> (75:25)	18.70	25.09	33.01	19.3	26.3	39.6

Values in parentheses are taken from ref. 7.

TABLE 2 — FREE ENERGIES AND HEATS OF SOLVATION FOR SILVER HALIDES

Solvent	$-\Delta G_{\text{solv}}^{\circ}$ (kcal/mole)			$-\Delta H_{\text{solv}}^{\circ}$ (kcal/mole)		
	AgCl	AgBr	AgI	AgCl	AgBr	AgI
Water	188.0	180.0	172.3	201.7	193.6	183.2
NaNO <sub>3</sub> -KNO <sub>3</sub>	188.6	179.4	168.1	199.5	193.07 (191.97)	183.68 (185.1)
NaNO <sub>3</sub> -Ba(NO <sub>3</sub> ) <sub>2</sub> (94.2:5.8)	188.7	179.5	169.4	199.6	188.11	176.9
KNO <sub>3</sub> -Ba(NO <sub>3</sub> ) <sub>2</sub> (89:11)	189.1	180.8	171.7	198.7	190.3	180.2
LiClO <sub>4</sub> -NaClO <sub>4</sub> (75:25)	187.3	176.4	166.0	198.5	188.1	173.4

Values in parentheses are from ref. 7.

temperature difference. Thus, using Eq. (1) and the experimentally determined values for enthalpy of solution<sup>2-4,7,8</sup>, the enthalpy of solvation ( $\Delta H_{\text{solv}}$ ) in NaNO<sub>3</sub>-KNO<sub>3</sub>, NaNO<sub>3</sub>-Ba(NO<sub>3</sub>)<sub>2</sub>, KNO<sub>3</sub>-Ba(NO<sub>3</sub>)<sub>2</sub> and LiClO<sub>4</sub>-NaClO<sub>4</sub> melts have been calculated and are recorded in Table 2.  $\Delta H_{\text{solv}}$  in aqueous solutions<sup>9</sup> have been included for comparison.

Free energies of solvation ( $\Delta G_{\text{solv}}^{\circ}$ ) for silver halides in ionic solvents have also been evaluated from lattice-free energies and experimental values for the free-energies of solution ( $\Delta G_{\text{soln}}^{\circ}$ ). Lattice-free energies were obtained from the data of free energies of solvation and free energies of solution in water<sup>9</sup>. Computed  $\Delta G_{\text{solv}}^{\circ}$  values are given in Table 2.

According to Born's theory of solvation, if the ions are assumed to be spherical, the free energy of solvation could be expressed as:

$$-\Delta G^{\circ} = \frac{N(Ze)^2}{2r_i} \left(1 - \frac{1}{D}\right) \quad \dots(2)$$

in which  $r_i$  is the radius of the ion carrying a charge of  $Ze$  units and  $D$ , the dielectric constant of the medium. Since, in ionic solvents, the crystalline structure is maintained (at least near melting point), it can be assumed that the ionic radii in melt would be equal to the crystal radii. In the light of theories based on dielectric saturation under very high fields<sup>10,11</sup>, the dielectric constant value in the immediate vicinity of the 'solute ion' could be taken equal to that of the bulk ( $D = 6$ ), in ionic melts. Thus, Eq. (2) was employed in estimating the individual ion contributions to the total free energy of solvation. These computed values for the free energies of solvation for the ions, Ag<sup>+</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> are found to be -109.81, -76.44, -70.69 and -64.06 kcal/g ion respectively.

The similarity between the values of  $\Delta H_{\text{solv}}^{\circ}$  and  $\Delta G_{\text{solv}}^{\circ}$  for silver halides in molten salt solvents and water reflects that the neutralization of the electrical field of the ions by water is about the same as for the 'solute-ions' in the molten solvent. It is apparent from Table 2, that the change in solvent cation has only a small influence on the  $\Delta H_{\text{solv}}$  and  $\Delta G_{\text{solv}}$  values; however, a change of anion from nitrate to perchlorate has a marked effect. This could be attributed to the large size and lower polarizability of the perchlorate ion as compared to the nitrate ion. Also, both the parameters vary almost linearly as the solute anion is changed from Cl<sup>-</sup> to I<sup>-</sup>. Progressive decrease in the magnitude of  $\Delta G_{\text{solv}}$  and  $\Delta H_{\text{solv}}$  in going from AgCl to AgI in all the melts can be anticipated, when Cl<sup>-</sup> is replaced by more polarizable bromide and iodide ion.

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### Evidence for Oriented Adsorption in the Monolayers of Glassy Silica Gel & Fibrous Silica Gel (Santocel C)

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Studies on the adsorption of secondary amines and ketones on fibrous silica gel (Santocel C) and glassy silica gel reveal that these sorbate molecules are adsorbed perpendicular to the surface in the case of the former and both perpendicular and parallel to the surface in the case of the latter.

INVESTIGATIONS on sorption and desorption in glassy silica gel and fibrous silica gel (Santocel C) of normal aliphatic alcohols<sup>1</sup>, normal aliphatic amines and normal aliphatic aldehydes<sup>2</sup> have shown that these straight chain linear molecules are held in the adsorbed layer perpendicular to the surface. It was felt that a study of sorption-desorption with sorbates having two hydrocarbon chains, as in secondary amines and ketones, would throw further light on the nature of orientation of adsorbed molecules on the surface of silica gels. With this in view sorption and desorption of diethylamine, di-*n*-propylamine, acetone, diethyl ketone and di-*n*-propylketone have been studied and the results are presented in this paper.

Glassy silica gel was prepared according to the method described earlier<sup>1</sup>. Fibrous silica gel (Santocel C) was obtained as a gift sample from M/s Monsanto Co., USA. The sorbates used were: diethylamine (Riedel), redistilled, b.p. 56.0°; di-*n*-propylamine (Koch-Light), redistilled, b.p. 110.7°; acetone (BDH), redistilled, b.p. 56.1°; diethyl ketone (E. Merck), redistilled, b.p. 101.7°; and di-*n*-propylketone (Fluka), redistilled, b.p. 144.2°.

Sorptions and desorptions were studied at 35° in an air thermostat employing McBain-Bakr spring balance<sup>3</sup>. Silica gels were activated at 450° for 4 hr before use. Duplicate experiments were conducted and the results of one set of experiments are presented. In each system the 1st, 2nd and 3rd sorption-desorption hysteresis loops were drawn. For calculations, the 2nd cycles have been taken into consideration. Equilibrium values were recorded every three hourly, though complete equilibrium had been attained after 1.5 hr.

Applying the BET equation the monolayer capacities have been calculated and the values are presented in Table 1. The specific surface areas

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of glassy silica gel and fibrous silica gel have been calculated assuming the secondary amine and ketone molecules as spheres<sup>4</sup>. The detailed procedure of calculations have been given earlier<sup>1</sup>. Table 2 gives the values of surface areas along with the molecular cross-section.

It is observed that the values of specific surface area are not constant either for glassy silica gel or fibrous silica gel. Therefore, the assumption that the secondary amine and ketone molecules are spheres is incorrect. As in the case of normal aliphatic alcohols<sup>1</sup>, normal aldehydes and amines<sup>2</sup>, the linear shape of the secondary amine and ketone molecules is to be taken into consideration in calculating the surface area. The secondary amine and ketone molecules contain two hydrocarbon chains attached to a polar group, either >NH or >CO. Like normal aliphatic alcohols, amines or aldehydes the adsorbed molecule of the secondary amine or ketone can be held on the surface of the sorbent at its polar end, either perpendicular or parallel to surface. In the parallel position there are two possibilities: the double chain strip-like molecule may be oriented with one chain resting on the surface or both chains resting on the surface. In these three possible modes of adsorption, the cross-sectional areas occupied by the molecules, and hence the surface areas, will be different. Now, the cross-sectional area of a single hydrocarbon chain is 20.7 Å<sup>2</sup> (ref. 4). As the secondary amines and ketones have two hydrocarbon chains, the cross sectional areas of these molecules may be assumed to be twice the value for a single chain, i.e. 41.4 Å<sup>2</sup>. Assuming this value for the cross-sectional area of the secondary amines and ketones and knowing their monolayer capacities, the surface areas of glassy and fibrous silica gel have been calculated for perpendicular mode of adsorption. For calculating

TABLE 1 — MONOLAYER CAPACITIES FOR GLASSY SILICA GEL AND FIBROUS SILICA GEL

Sorbate	Monolayer capacity (g/g of sorbent)	
	Glassy silica gel	Fibrous silica gel
Diethylamine	0.173	0.0178
Di- <i>n</i> -propylamine	0.174	0.0221
Acetone	0.144	0.0126
Diethyl ketone	0.169	0.0187
Di- <i>n</i> -propyl ketone	0.179	0.0241

TABLE 2 — SPECIFIC SURFACE AREAS OF GLASSY SILICA GEL AND FIBROUS SILICA GEL CONSIDERING THE MOLECULES AS SPHERES

Sorbate	Molecular cross-section Å <sup>2</sup>	Specific surface area (m <sup>2</sup> .g <sup>-1</sup> )	
		Glassy silica gel	Fibrous silica gel
Diethylamine	30.51	437	44.7
Di- <i>n</i> -propylamine	36.90	382	48.7
Acetone	24.38	364	31.9
Diethyl ketone	31.03	366	40.7
Di- <i>n</i> -propyl ketone	37.41	353	47.5