Effect of static charge on the tarnishing behaviour of silver in iodine atmosphere at low temperatures

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The kinetics of AgI film growth on silver under the action of applied static charge of both the polarities, as well as under normal iodination conditions in the temperature range of 294 to 338 K and in the iodine partial pressure range of 0.03 to 0.22 kPa, conform to parabolic rate law. Compared to normal iodination, an enhancement in rate under both positive and negative surface charge conditions at the Ag/AgI interface and a decrease in rate under either surface charge condition at the AgI/I_2 interface have been observed. The increased rate with negative charge at the Ag/AgI interface and the decreased rate with same kind of charge at the AgI/I_2 interface, compared to normal iodination, can be explained on the basis of positive hole transport, while the observed effects with positive charge at either of the interfaces receive reasonable support from cation migration as the rate limiting factor during the film growth process.

1. Introduction
Tarnishing studies of silver and silver alloys in different halogen atmospheres, at high as well as low temperatures, have been reported by several investigators and are reviewed in detail by Bose and Sircar [1-5] on Ag-Br_2, Ag-Cl_2 and Ag-I_2 systems. The only studies confined to thinner film range of silver halides at around room temperature in the cases of Ag/AgBr/Br_2 and Ag/AgCl/Cl_2 systems [1, 2] have established the validity of the cubic law mechanism of film growth as proposed by Mott [6], while the rest of the studies conducted in the thick film range confirmed the validity of Wagner's diffusion-controlled parabolic growth law mechanism [7, 8]. Furthermore, the studies in the less thick film range [2, 3] conforming to parabolic law did not show the theoretically expected square-root pressure dependence of rate constant. These rather exhibited a modified halogen pressure dependence relation, hinting at an unsteady state situation at the metal/halide interface.

An interesting study was reported by Eriksen and Hauffe [9] on the influence of local cell action on the bromination rate of silver at 250 to 400° C in P_{Br_2} = 0.23 atm showing not only a tremendous enhancement in rate compared to normal bromination but also demonstrating a change in mechanism from a hole transport- to a cation transport-controlled process under short-circuiting. Subsequently, the influence of impressed direct current and short-circuiting on the tarnishing behaviour of silver in iodine atmosphere at around room temperature has been reported from this laboratory [10]. However, analysis of earlier studies on the influence of direct current on Cu/Cu_2O/O_2 system [11, 12] at low temperatures, and recent results on Fe/FeO/CO + CO_2 [13, 14] and Cu/Cu_2O/O_2

[14-17] at high temperatures, have established that the kinetic results would become completely the opposite when the impressed current is applied continuously compared to those obtained with interrupted impressed current. These findings provided a clear insight into the differential responses of the two interfaces (metal/oxide and oxide/oxygen) to the impressed current when interrupted and uninterrupted, and hence a completely different picture of the interfacial concentration of defects. Therefore, disturbance of the interfaces, without passing a net current, might bring about a change in rate and thereby possibly a change in the mechanism of oxidation.

This idea prompted us to follow this direction of oxidation research, to establish that without passing a net electrical current the rate may either decrease or increase just by disturbing the interfaces with a static charge supply. To test this possibility, the Ag/AgI/I_2 system was chosen because even at room temperature and low partial pressure of iodine, AgI film growth follows Wagner's parabolic law, the least controversial of the oxidation mechanisms.

2. Experimental procedure
The silver used in this investigation was analysed on a spectrometer and revealed the following compositions (values in p.p.m.):

Fe	Cu	Ni	Al	Pb	Mg	Cd	Ag
< 10	25	< 5	< 10	500	< 50	–	rest

The silver specimens in the form of sheets of 35 × 15 × 1 mm were annealed at 1073 K for 2.7 ksec in a graphite crucible packed with charcoal powder. A hole of 1.0 mm diameter was drilled at one end of each specimen for hanging in the reaction chamber. The

surfaces of both sides of the specimens were prepared by mechanical polishing on 0,00,000 and 0000 grade emery papers in succession. The specimens were then thoroughly washed in distilled water followed by rinsing in acetone, and subsequently dried. The surface thus obtained was clean, shining, smooth and fairly reproducible.

For the samples selected for charge supply at the Ag/AgI interface during iodination, a platinum wire was tightly twisted through the hole of each specimen, and subsequently the joint was well covered with a small drop of araldite in order to safeguard the joint from iodination, as well as to prevent leakage of charge at the iodide/gas interface. Then an initial iodide layer of about 200 nm was allowed to develop on each specimen. When charge was applied at the AgI/I_2 interface, the sample with the initial iodide layer (~ 200 nm) was wrapped round with a platinum mesh, which in turn was hung in the reaction chamber by a platinum wire. For comparison, normal iodination of the specimen was also conducted with an initial iodide layer of ~ 200 nm.

Tarnishing of silver was carried out both in static and flow systems. In the static system a 221 glass dessicator was chosen as the reaction chamber, and for the flow system a conical flask (1.221 capacity) was used. In the flow system, the reaction chamber was connected with an iodine generation chamber (1.221) which was kept saturated with iodine vapour using iodine crystals. An air pump was used for blowing air through the system, the air being thoroughly dried by passing successively through a glass tube containing P_2O_5 followed by two bubblers containing H_2SO_4 (B.D.H., 'Analar') and finally through a column of silica gel. The iodine-generation chamber was heated to generate different partial pressures of iodine, and different temperatures of the reaction chamber were achieved by means of a tape heater. The gas emitted was analysed by the standard method to ascertain the partial pressure of iodine within the reaction chamber.

Each kind of charge was supplied to the sample by connecting only one of the terminals at a time to a capacitor (20 000 μF) which in turn was charged by a constant 100 V d.c. supply, while the other terminal was left floating.

3. Results and discussion

The effects of temperature and pressure on the kinetics of AgI film growth on silver were studied at 328 K in the pressure range of 0.14 to 0.22 kPa (1.43 × 10^{-3} to 2.20 × 10^{-3} atm) and also in fixed pressure of 0.14 kPa (1.43 × 10^{-3} atm) at 328 and 338 K in a dry gas flow (10 cc sec^{-1}) system at a total pressure of 101.325 kPa (1 atm). Tarnishing behaviour under normal iodination condition as well as under positive and negative charge supplied from a capacitor bank at the AgI/I_2 interface has been investigated (Figs 1–4). Similar studies have been carried out in a closed system at 294 K and in P_{I_2} = 0.029 kPa (P_{I_2} = 2.94 × 10^{-4} atm) under conditions of no charge and applied charge at the AgI/I_2 and Ag/AgI interfaces (Figs 5 and 6).

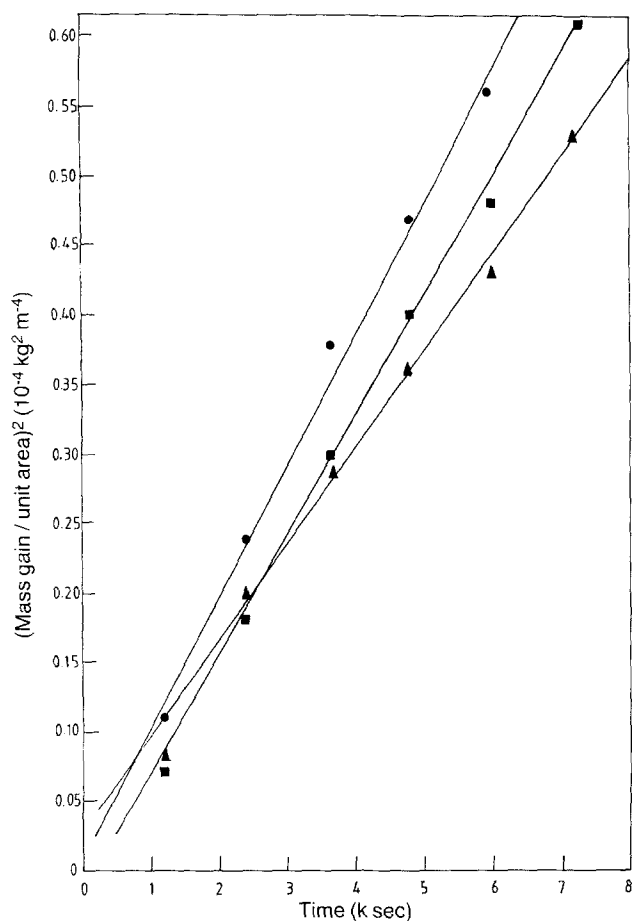The kinetic data of AgI film growth on silver in the above-mentioned iodine pressures and temperatures
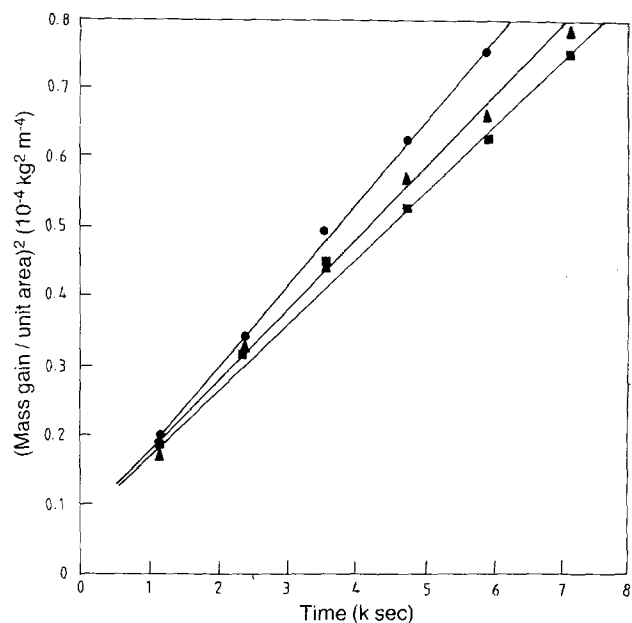

Figure 1 (Mass gain/unit area)^2 against time plots at 328 K in P_{I_2} = 0.14 kPa. ●, Normal iodination, k_p 0.09 × 10^{-7}; ■, negative charge, k_p 0.08 × 10^{-7}; ▲, positive charge, k_p 0.07 × 10^{-7}. (k_p in kg^2 m^{-4} sec^{-1}).

(in both flow and static systems) conform to the parabolic growth law for normal iodination as well as under positive and negative charge conditions.

The parabolic rate-constant value for normal iodination in 0.029 kPa pressure of iodine at 294 K is found to be 0.9 × 10^{-14} kg equivalents m^{-1} sec^{-1} as against 1.1 × 10^{-14} kg equivalents m^{-1} sec^{-1} reported by Weininger [18] at 298 K and in P_{I_2} = 0.041 kPa
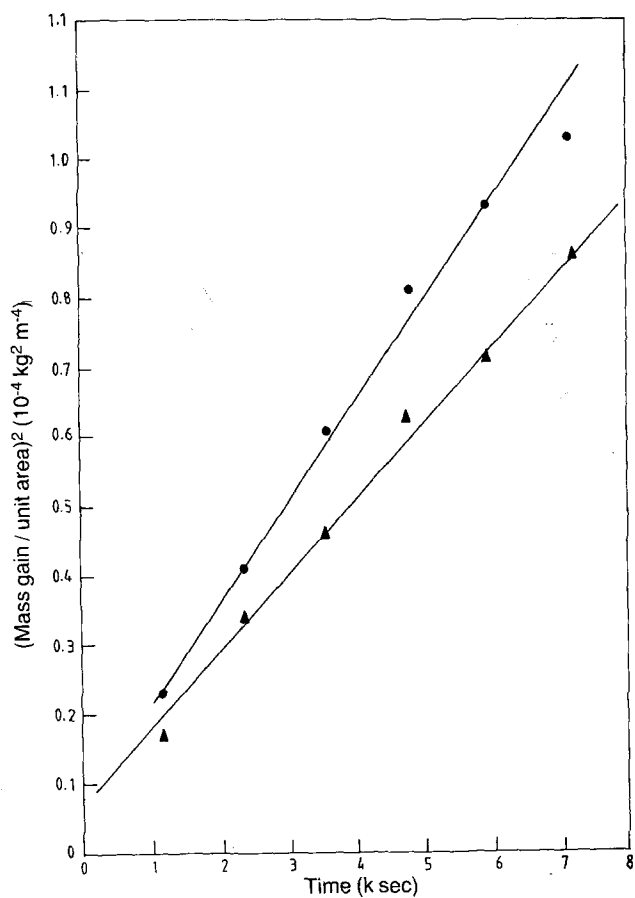

Figure 2 (Mass gain/unit area)^2 against time plots at 328 K in P_{I_2} = 0.20 kPa. ●, Normal iodination, k_p 0.116 × 10^{-7}; ▲, positive charge, k_p 0.102 × 10^{-7}; ■, negative charge, k_p 0.090 × 10^{-7}. (k_p in kg^2 m^{-4} sec^{-1}).
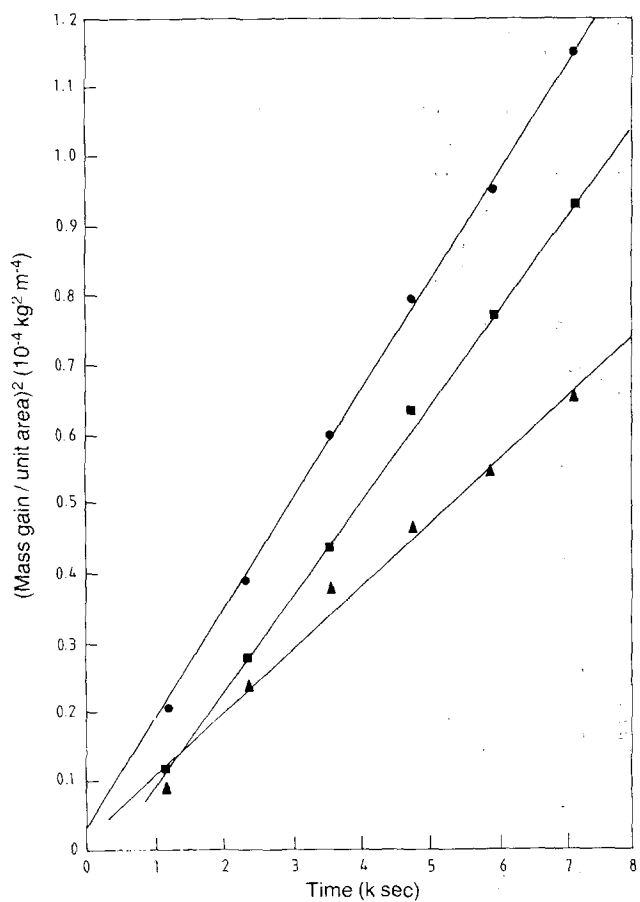
Figure 3 (Mass gain/unit rea)^2 against time plots at 328 K in $P_{I_2} = 0.22$ kPa. ●, Normal iodination, k_p 0.14 × 10^{-7}; ▲, positive charge, k_p 0.11 × 10^{-7}. (k_p in $kg^2 m^{-4} sec^{-1}$).
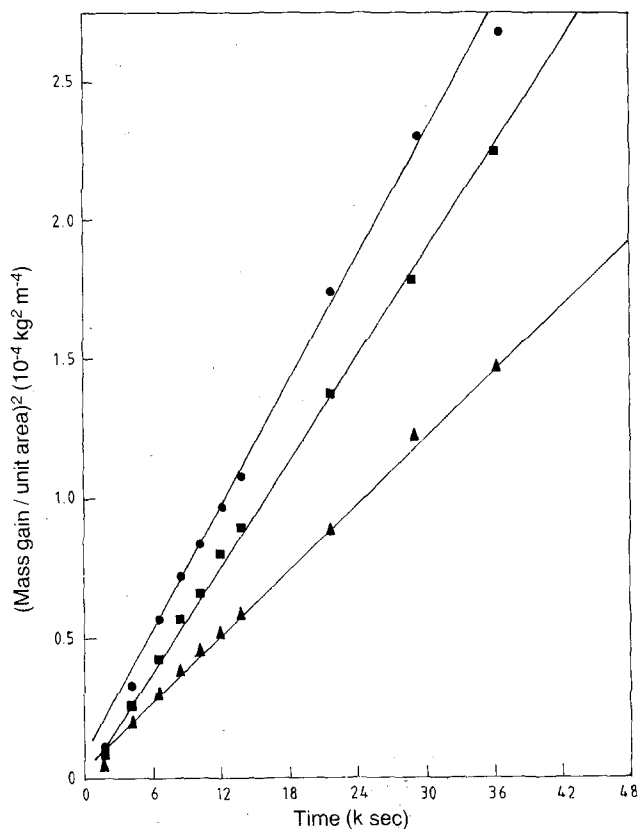

Figure 5 (Mass gain/unit area)^2 against time plots at 294 K in $P_{I_2} = 0.029$ kPa, (AgI/I$_2$ interface). ●, Normal iodination, k_p 0.074 × 10^{-7}; ▲, positive charge, k_p 0.040 × 10^{-7}; ■, negative charge, k_p 0.060 × 10^{-7}. (k_p in $kg^2 m^{-4} sec^{-1}$).

Figure 4 (Mass gain/unit area)^2 against time plots at 338 K in $P_{I_2} = 0.14$ kPa. ●, Normal iodination, k_p 0.16 × 10^{-7}; ▲, positive charge, k_p 0.09 × 10^{-7}; □, negative charge, k_p 0.14 × 10^{-7} (k_p in $kg^2 m^{-4} sec^{-1}$).
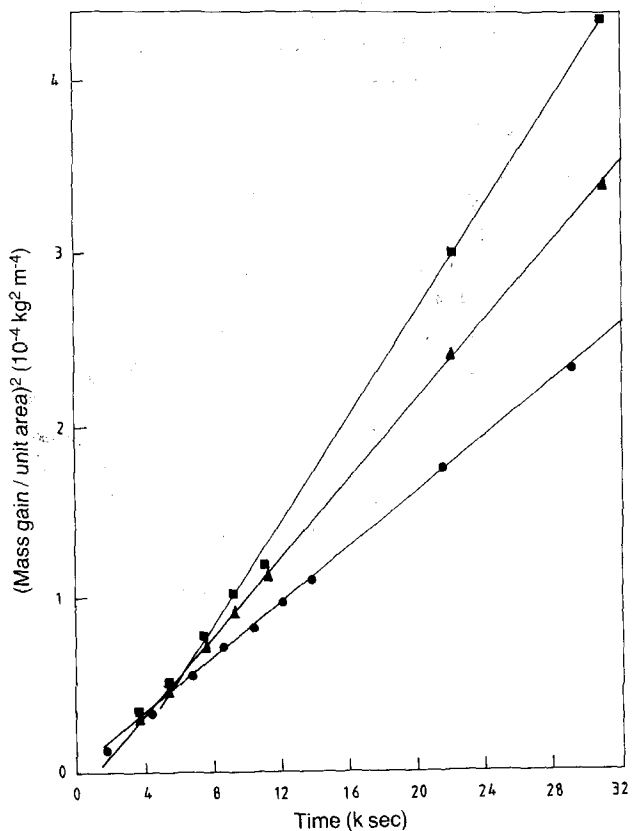

Figure 6 (Mass gain/unit area)^2 against time plots at 294 K in $P_{I_2} = 0.029$ kPa (Ag/AgI interface). ●, Normal iodination, k_p 0.074 × 10^{-7}; ▲, positive charge, k_p 0.110 × 10^{-7}; ■, negative charge, k_p 0.150 × 10^{-7}. (k_p in $kg^2 m^{-4} sec^{-1}$).

and 1.01×10^{-14} kg equivalents $m^{-1} sec^{-1}$ reported by Bose and Sircar [3] at 308 K and in $P_{I_2} = 0.033$ kPa. Similarly, the rate-constant values in the present investigation in $P_{I_2} = 0.14$ kPa at 328 and 338 K are found to be $4.8 \times 10^{-16} m^2 sec^{-1}$ and $8.51 \times 10^{-16} m^2 sec^{-1}$, respectively, which match fairly well with the value of $8.0 \times 10^{-16} m^2 sec^{-1}$ as reported by Smyth and Cutler [19] at 333 K and in $P_{I_2} = 0.13$ kPa $(1.32 \times 10^{-3} atm)$.

In the static system, a decrease in tarnishing rate was observed under both the surface charge conditions compared to that under normal iodination, the decrease in rate of tarnishing being $\sim 43\%$ and $\sim 14\%$ under positive and negative surface charge, respectively, at the AgI/I_2 interface.

Under similar conditions when charge was supplied at the Ag/AgI interface, the tarnishing rate was enhanced under either impressed charged condition at the inner interface, the corresponding increases in rate being $\sim 57\%$ and $\sim 114\%$ under positive and negative charge, respectively.

The general trend of decrease in tarnishing rate with positive and negative charges at the outer interface, compared to that with no charge is also maintained at higher temperatures and pressures selected in this study.

Since the initial thickness of AgI was comparatively high (~ 200 nm) and the kinetic data under all situations followed the parabolic rate expression, and after termination of the experiment the iodide layer on each sample appeared to be highly tenacious and compact, the observed parabolic growth can be attributed to Wagner's solid-state diffusional transport as the rate limiting process. Figure 7, representing the rate constant as a function of P_{I_2}, exhibits enhancement in rate with increase of P_{I_2} under all the conditions selected. It was also found that the plot of log k_p against log P_{I_2} gives the relation $k_p \propto P_{I_2}^n$ ($n \simeq 1.0$) under normal iodination and under iodination with positive surface charge, while k_p becomes approximately proportional to $P_{I_2}^{1/2}$ under iodination with negative surface charge.

Incorporation of the iodine atom into the AgI lattice at the outer surface takes place by the following reaction

$$\tfrac{1}{2}I_2 \rightleftharpoons AgI + V'_{Ag} + \oplus \qquad (1)$$
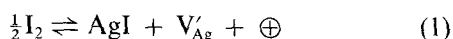
where V'_{Ag} = negatively charged silver vacancy and

$\oplus$ = positive holes in the valence band of AgI crystal. If the ideal mass action law is considered to be valid, then one can write the following equilibrium relation

$$\frac{[V'_{Ag}][\oplus]}{P_{I_2}^{1/2}} = K(T) = \text{equilibrium constant} \quad (2)$$

where square brackets represent concentration.

It is established that under normal iodination, positive hole migration decides the rate of film growth as a result of the almost constant concentration of V'_{Ag} in the above expression because of high inherent disorder in the AgI lattice. Hence, rate $\propto [\oplus] \propto P_{I_2}^{1/2}$. This is the expected pressure dependence relation according to Wagner's idea [8]. However, this relation is not found to be exactly valid under the present experimental conditions, under both normal iodination and under positive surface charge conditions. Under these these two conditions, when k_p is replotted against $(\sqrt{P_{I_2}} - \sqrt{P_{I_2}^0})$, a linear relation is found to become valid (Fig. 8), the line passing through the origin when $P_{I_2}^0 = 0.04$ kPa $(0.4 \times 10^{-3} atm)$ under normal iodination and $P_{I_2}^0 = 0.057$ kPa $(0.57 \times 10^{-3} atm)$ with a positive surface charge. These $P_{I_2}^0$ values at the Ag/AgI interface, however, much exceed the equilibrium $P_{I_2}^0$ at that interface which is $\sim 10^{-24}$ atm [20]. This type of observation has already been reported earlier for both $Cu/CuI/I_2$ [21, 22] and $Ag/AgI/I_2$ [3] systems and can be explained only on the basis of non-attainment of steady-state situation at the inner interface, as explained by other investigators and quoted previously [3, 21, 22]. Similar deviation from the equilibrium concentration of defects at the inner interface for copper oxidation have been reported by Cabrera and Mott [6] and Benard and Talbot [23] in the comparatively thinner oxide layer. It is then found from Fig. 8 that the computed $P_{I_2}^0$ is greater at the Ag/AgI interface when the outer surface is positively charged compared to that with no charge. A plausible explanation follows.

When the outer surface is disturbed by charge supply, because of the induced oppositve charge at the inner interface it is very likely that all the possible defect equilibria at the inner interface will be disturbed. When the outer surface is positively charged, the induced negative charge at the Ag/AgI interface
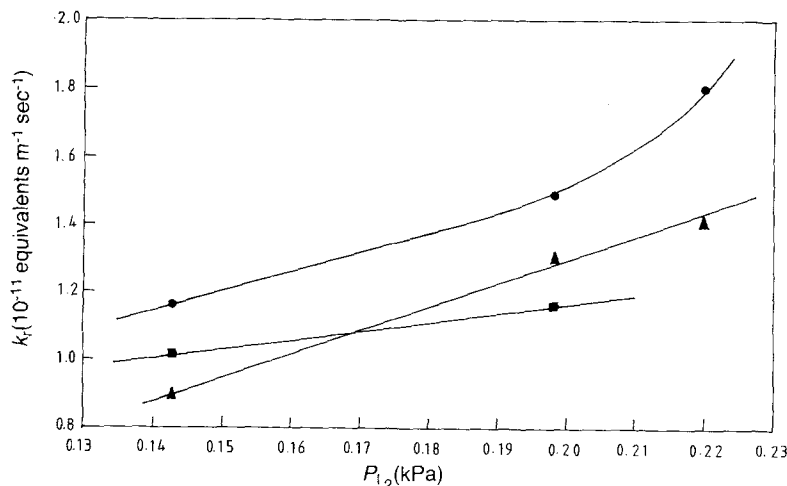

Figure 7 Plots of k_r against P_{I_2} at 328 K. ●, Normal iodination; ▲, positive charge; ■, negative charge.
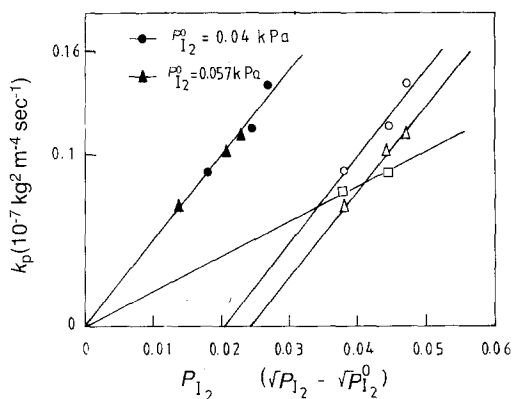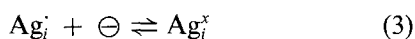
Figure 8 Plots of k_p against $\sqrt{P_{I_2}}$ (open symbols) and $(\sqrt{P_{I_2}} - \sqrt{P_{I_2}^0})$ (closed symbols) at 328 K. Circles, normal iodination; triangles, positive charge; squares, negative charge.

will tend to consume $Ag_i^.$ according to the following reaction

$$Ag_i^. + \ominus \rightleftharpoons Ag_i^x \qquad (3)$$

where $Ag_i^.$ and Ag_i^x represent singly charged and neutral interstitial silver, respectively. Therefore, the Frenkel defect equilibrium $[V_{Ag}'][Ag_i^.] = K_f$ will also be affected, which means that $[V_{Ag}']$ will tend to increase. It is also known that according to the following ionization reaction

$$V_{Ag}^x \rightleftharpoons V_{Ag}' + \oplus \qquad (4)$$

and the relation

$$K'(T) = \frac{[V_{Ag}'][\oplus]}{[V_{Ag}^x]} \qquad (5)$$

an increase of $[V_{Ag}']$ will tend to increase $[\oplus]$ in the AgI lattice in order to maintain charge neutrality. Hence, for maintaining $K'(T)$ constant, $[V_{Ag}^x]$ must increase. This will raise the value of P_{I_2} at the inner interface according to the reaction

$$\tfrac{1}{2}I_2 \rightleftharpoons V_{Ag}^x + AgI \qquad (6)$$
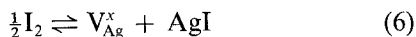
This probably explains the higher $P_{I_2}^0$ value, compared to that under normal iodination. Similarly, when the outer surface is negatively charged, induced positive charge at the Ag/AgI interface will tend to increase $[Ag_i^.]$, which means $[V_{Ag}']$ will drop. On the same count, with a decrease of $[V_{Ag}']$, the concentration of positive holes should decrease and hence $[V_{Ag}^x]$ has to decrease, that is, $P_{I_2}^0$ at the Ag/AgI interface must be smaller than that with no charge. Because of this reduced $P_{I_2}^0$ at the Ag/AgI interface, only the outer surface pressure of iodine out of the two pressure terms in the total expression of Wagner's equation [8] will become important for the pressure dependence of the rate constant. Thus it conforms to the $\sqrt{P_{I_2}}$ relation, as expected, instead of the modified $\sqrt{P_{I_2}}$ relation $(\sqrt{P_{I_2}} - \sqrt{P_{I_2}^0})$, as is found valid for normal iodination and iodination under a positive surface charge.

The decrease in rate constant values with both types of charge at the outer interface could be explained in the following way. When the outer AgI/I$_2$ interface is negatively charged, the normal diffusional field becomes steeper and favourable for ion migration, since the negative surface charge at the outer surface

will help the incorporation of excess iodine, with the creation of more cationic vacancies. This favours cation migration from the inner to the outer interface, and the rate should have shown an increase rather than a decrease. The alternative picture may be that due to excess negative charge at the outer surface, the concentration of positive holes will be drastically cut down. Furthermore, positive holes have to move through the AgI layer against the field, since they are likely to be pulled back by the negative surface charge and repelled by the induced positive charge at the inner interface (movement of holes takes place from the outer to the inner interface, that is, they are created at the AgI/I$_2$ interface and consumed at the Ag/AgI interface). Hence, lowering of the rate under a negative surface charge can only be explained on the basis of hole migration as a rate controlling step as under normal iodination for all silver halide systems.

When the outer surface is positively charged, the decrease in rate cannot be explained on the basis of hole migration, because now a favourable field is created for hole migration that should have been reflected in an increase rather than a decrease in rate. On the other hand, the positive charge at the outer surface and the induced negative charge at the inner interface will not only decrease the concentration of $Ag_i^.$ at the inner interface or concentration of V_{Ag}' at the outer interface, meaning the creation of a flatter gradient for ion migration, but the field has now become opposing for cation migration. Therefore, under such surface charge conditions, cation migration probably becomes the rate-limiting step.

Since for normal iodination and iodination under a negative surface charge, halide film growth is a hole diffusion controlled process, an attempt has been made to estimate the hole conductivity from tarnishing studies as reported earlier [24] utilizing Wagner's original expression of parabolic rate constant and following an inverse procedure by differentiating k_p (or k_r) with respect to P_{I_2}.

Wagner's original expression of the rational rate constant in the present Ag/AgI/I$_2$ system can be written in the form

$$k_r = \frac{1}{F^2 |Z_2|} \int_{\mu_I'}^{\mu_I''} (t_{Ag}^+ + t_I^-)\, t_\oplus\, \sigma\, d\mu_I \qquad (7)$$

where F = Faraday number; t_{Ag}^+, t_I^- and $t_\oplus$ = corresponding transport numbers, σ = total conductivity; μ_I' and μ_I'' = chemical potential of I$_2$ at the inner and outer interface, respectively; and Z_2 = valence of electronegative component. In the case of AgI, $t_{Ag^+} \simeq 1$, $t_I^- = 0$, $t_\oplus \ll 1$ and $t_\oplus \sigma = \sigma_\oplus$. Therefore, by differentiating the above equation at a fixed pressure at the outer surface and rearranging, we have

$$\sigma_\oplus = \frac{2F^2}{RT} P_{I_2} \text{ (at AgI/I}_2) \frac{dk_r}{dP_{I_2}}$$

$$= 6.83 \times 10^6\, P_{I_2} \frac{dk_r}{dP_{I_2}} \qquad (8)$$

Using the above relation, the estimated hole conductivity as a function of iodine pressure for normal

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P_{I_2} (kPa)	$\sigma_\oplus/10^{-8}$ ($S\,m^{-1}$)	
	Normal iodination	Negative surface charge
0.14	0.61	0.27
0.20	1.20	0.37
0.22	2.68	–

iodination and negative surface charge are given in Table I.

The data match fairly well with the hole conductivity data in various silver halide systems [25–28] and also to the previously reported values using tarnishing studies for this system [24].

Since under positive surface charge conditions, cation migration has been presumed to be rate limiting, Wagner's relation between k_r and the self-diffusion coefficient can be exploited for estimating the self-diffusion coefficient of cations from the knowledge of k_r as a function of P_{I_2}.

$$k_r = C_{equiv.} \int_{\mu_I^0}^{\mu_I^{''}} \left(D_1^* + D_2^* \left| \frac{Z_2}{Z_1} \right| \right) d \ln a_I$$

$$= \frac{C_{equiv.}}{2} \int_{P_{I_2}^0}^{P_{I_2}^{''}} (D_{Ag^+}^* + D_{I^-}^*) \, d \ln P_{I_2} \qquad (9)$$

The expression for the self diffusivity of Ag^+ ions in the growing AgI film under positive surface charge conditions can be written as

$$D_{Ag^+}^* = \frac{2 \times 234.8}{5.67} \frac{dk_r}{dP_{I_2}} \cdot P_{I_2} \qquad (10)$$

Hence,

$$D_{Ag^+}^* \text{ (at } P_{I_2} = 0.20 \,\text{kPa)} = 1.35 \times 10^{-15} \,\text{m}^2 \,\text{sec}^{-1}$$

The self-diffusivity data on AgI crystal are lacking. However, self diffusivity in AgBr and AgCl are reported to lie between 10^{-14} and $10^{-17}\,\text{m}^2\,\text{sec}^{-1}$ [29, 30]. Considering the strong dependence of diffusivity on the purity of the crystal, the above estimated diffusivity value is likely.

When the inner interface is supplied with a negative charge, the rate increase can only happen if positive hole migration remains rate-determining because, under this situation, cation migration will be hindered by the oppositve type of surface charge. Similarly, when the Ag/AgI interface is positively charged, the enhancement in rate can not be explained on the basis of hole migration, but by cation migration which will be favoured by a favourable surface charge.

4. Conclusions

1. The rate of AgI film growth on Ag under either positive or negative charge supply at the AgI/I_2 interface is found to be lower than that under normal iodination.

2. The kinetics of film growth are faster compared to normal iodination, when the Ag/AgI interface is disturbed by charge of either type.

3. Iodine pressure dependence of the parabolic rate constant under negative surface charge at the AgI/I_2

interface is found to follow the $\sqrt{P_{I_2}}$ relation as expected theoretically from the defect formation reaction and the corresponding applicability of the ideal mass action law. In contrast, a modified $\sqrt{P_{I_2}}$ relation is found to apply with normal iodination as well as with positive charge supply at the AgI/I_2 interface.

4. The decreased rate with negative charge at the AgI/I_2 interface and the enhanced rate with negative charge at the Ag/AgI interface have been explained on the basis of positive hole migration as rate limiting. On the other hand, the decreased rate with positive charge at AgI/I_2 and the enhanced rate with positive charge at Ag/AgI can be attributed to a change in mechanism from the hole-transport- to the cation-transport-controlled process of film growth.

5. The estimated positive hole conductivity values and self-diffusivity of Ag^+ through growing AgI lattice using Wagner's theoretical relation of parabolic rate expression match fairly well to the available data in the literature.

6. Detailed studies are in progress on $Cu/CuI/I_2$ and $Cu/Cu_2O/O_2$ systems, which will hopefully cast more light on the changed mechanism of film growth with film interfaces disturbed by static charge.

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