

On the formation of silver specks in silver halide crystals

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Abstract. This theoretical study summarizes ionic and electronic processes in AgBr crystals and the influence of its results on photographic process. It deals with the importance of surface generated interstitials which Gurney and Mott left untouched because of the non-availability of sufficient data at that time. The magnitude of various parameters, *e.g.*, mean intra-electron-ion distance in a latent image site, the rate of neutralization of Ag^+ ion with trapped electron and capture cross-section for combination of Ag^+ ion with the trapped electron, etc. (as desired for understanding the theory of photographic process) are calculated at different temperatures. The results when used in our earlier papers (Singh and Sharma, 1974 and 1975, and Singh 1975) for calculating charged particle track characteristics theoretically were found to give good agreement with the published experimental data (Della Corte *et al* 1953 and Dyer and Hechman 1967). A model for the mechanism of latent image formation (silver speck) is discussed.

Keywords. Photographic process ; silver halide crystals ; image formation.

1. Introduction

A knowledge of the concentration and mobility of point defects in the silver halides is essential for an understanding of the photographic process. It is generally believed on the basis of ionic conductivity studies and density measurement that pure silver halides have Frenkel defect disorder. It is also believed that in the silver halides the intrinsic ionic conduction process is the diffusion of thermally generated interstitial Ag^+ ions. Hamilton and Brady (1959, 1962) hypothesised, in connection with electrical measurements, that the unexposed microcrystals contain a high concentration of mobile interstitial Ag^+ ions whose concentration depends upon the conditions at the crystal surfaces. Kliewer (1966) has given a detailed theoretical discussion of the generation of mobile ionic defects in case of silver halides, from surface kink sites and from jogs on dislocations. It is assumed that the effective half-unit electrical charge is associated with a kink or jog, due to this fact the binding energy between the lattice and the ion located at such a site is less than that required for a normal lattice ion. It is, therefore, relatively easy for a silver ion situated at a positive kink or jog to jump into an interstitial site in the crystal and diffuse away. Similarly, relatively little energy is required for formation of a vacancy at a negative kink or jog. Thus interstitial silver ions and silver ion vacancies, although they may be formed in pairs from the normal lattice sites, are more easily generated individually from preferred sites on the

surface of a crystal or on imperfections in its volume (Hamilton and Brady 1959 and Hamilton 1966-69). Poeppele and Blakely (1969) developed the theory of the effect of surface sites upon interstitial silver ions in AgBr crystal and indicated the nature of these surface sites in small crystals for interstitial formation. Actually their model is based on the existence of a finite number of ionic surface sites which have a binding energy different from that of sites in the interior of the crystal. Recent experimental work of Baetzold and Hamilton (1972, 1973) and Baetzold (1974) on ionic conductivity of thin films of silver halides shows the type and concentration of the point defects near the surface. Baetzold (1974) made a comparison between the two silver halides (*i.e.*, AgBr and AgCl) and established that the AgBr has almost two orders of magnitude more interstitial silver ions in the bulk of the crystal than the AgCl at similar conditions. It has been shown that the ionic space charge layer consists of excess of interstitials in AgBr and AgCl (111) and also that films of former has one order of magnitude more interstitial silver ions than is present in the latter (Baetzold 1974, Blakely and Danyluk 1974).

These facts clearly establish the point that interstitial Ag^+ ions can occur within a micro-crystal of silver halide as a consequence of surface generation and that the formation energy for an interstitial is much less than that required for one half of a Frenkel pair.

This paper deals with the importance of surface generated interstitials a topic which Gurney and Mott (1938) did not consider because of the non-availability of sufficient data at that time. We have tried to make a theoretical study of the role of interstitials in electron trapping process and their ionic motion in neutralization process to form a silver speck or a group of silver atoms in order to understand the structure of particle tracks in emulsions.

2. Concentration and mobility of interstitial Ag^+ ions

The interstitial ions and vacancies within the bulk of the crystal of silver bromide are formed in equal concentration. However, at the surface of such a crystal there is a possibility of an excess of either of the defects since the interstitial Ag^+ ions and vacancies are not required to form simultaneously. The energy of surface formation of an interstitial silver ion is not expected to be the same as that of a vacancy, so that one type of these defects is formed at the surface in greater number than the other (Poeppele and Blakely 1969). When a point defect is formed at the surface, a charge compensating surface site is created. For example, an interstitial Ag^+ ion may be generated from a positive kink site. The effective charge of this site prior to the process is taken $+\frac{1}{2}$ (*i.e.*, a charge $e/2$ for every surface ion) and the effective charge after interstitial formation would then be $-\frac{1}{2}$.

The expressions for the concentration of interstitials (n_i) and vacancies (n_v) in case of surface charge layer, derived by assuming the potential (ϕ) which varies with distance, x from the surface towards the interior of the crystal according to Boltzmann distribution law (Tan and Hoyan 1972) are as follows:

$$n_i(x) = n_F \exp [-e\phi(x)/kT] \quad (1)$$

$$n_v(x) = n_F \exp [+e\phi(x)/kT] \quad (2)$$

where e is the electronic charge. The potential, ϕ in the bulk is taken as zero. n_F , the intrinsic carrier concentration (Frenkel defects) in the bulk is expressed as:

$$n_F = \sqrt{2} N \exp(-G_F/2kT) \quad (3)$$

where G_F is the free energy of formation for a Frenkel defect pair in the bulk and N is the number of AgBr ion-pairs per cm^3 .

The concentration of interstitials and vacancies at the surface ($x = 0$) as given by their free energies of formation is expressed as follows (Poeppl and Blakely 1969 and Tan and Hoyen 1972):

$$n_i(0) = 2N \exp(-G_i/kT) \quad (4a)$$

$$N_v(0) = N \exp(-G_v/kT) \quad (4b)$$

where the factor 2 in eq. (4a) comes from the fact that there are two interstitial sites for each lattice ion site (Kliewer 1966). G_i is the free energy of formation of an interstitial at the surface and G_v is the free energy of formation of a vacancy at the surface.

The average concentration of interstitial Ag^+ ions (N_i) can be found by adding eqs (3) and (5a) and dividing it by 2. Thus,

$$N_i = \frac{N}{\sqrt{2}} [\sqrt{2} \exp(-G_i/kT) + \exp(-G_F/2kT)]. \quad (5)$$

Because, according to the space charge theories, the interstitial concentration decreases on going from surface to bulk. Such behaviour can be observed in case of AgBr crystals in figure 1 of Baetzold and Hamilton (1972). n_i is maximum concentration at the surface and n_F is the minimum concentration in the bulk for crystals thickness ($0.135 \mu\text{m}$). This value of Debye thickness has been calculated by Trautweiler (1968). As we have considered G-5 emulsion grains having diameter $\sim 0.27 \mu\text{m}$, the present calculation of average concentration of interstitials N_i is valid. If, however, crystal thickness is less than the Debye thickness, the average concentration N_i will differ, as the minimum concentration is not equal to n_F (Frenkel defects).

According to Trautweiler (1968), $G_i \sim 0.32 \text{ eV}$ and $G_v \sim 0.60 \text{ eV}$. The number of AgBr ion-pairs (N) per cm^3 can be calculated from its crystal structure. AgBr is a cubic crystal of NaCl type and has a cell size equal to 5.775 \AA (Tani T, Priv. comm.) One cell contains four AgBr ion-pairs. Thus we find the value of $N = 2.1 \times 10^{22} \text{ cm}^{-3}$. The number of interstitial Ag^+ ions (Frenkel defects), n_F is equal to $8 \times 10^{14} \text{ cm}^{-3}$, which follows from Muller's figure 9 for room temperature (Muller 1965). According to Trautweiler (1968) this number of bulk defects, is equal to $5 \times 10^{14} \text{ cm}^{-3}$ in the pure crystal of silver bromide. Calculations from eq. (3) give the values of $N_F = 5.5 \times 10^{14} \text{ cm}^{-3}$ at 300°K which is consistent with the room temperature values of n_F reported by Muller (1965) and Trautweiler (1968). Baetzold and Hamilton (1972) computed the values of the concentration of interstitial Ag^+ ions for AgBr thin films by using Muller's values for the mobility and their measured values for conductivity. These values are shown in table 1. Our values computed with the help of eq. (5) are also shown in this table.

Table 1. Concentration of interstitial Ag⁺ ions in AgBr grains.

Temperature (° K)	n_i (cm ⁻³) (Baetzold and Hamilton 1972)	N_i (cm ⁻³) this paper	n_F (cm ⁻³) Frenkel defects (Muller 1965)
300	..	0.9×10^{17}	7.9×10^{14}
333	5.4×10^{17}	3.0×10^{17}	5.9×10^{16}
400	2.1×10^{18}	1.95×10^{18}	1.3×10^{17}

To summarize, the final results show that the mole fraction (n_F/N) of intrinsic Frenkel disorder in AgBr at room temperature is about 3×10^{-8} corresponding to a Frenkel density of around 10^{14} to 10^{15} . On the basis of eq. (4a) the surface density (n_i) of interstitials for AgBr crystal at room temperature comes out much larger—about 0.9×10^{17} cm⁻³. The mole fraction (n_i/N) of surface density of interstitials is $\sim 10^{-5}$.

Expressions for the mobility of interstitial silver ion, (μ_i) and for vacancy (μ_v) that follows from Muller's figure 9 for AgBr crystals are given by (Muller 1965):

$$\mu_i = \frac{1}{T} \exp \left(3.88 - \frac{0.15 \text{ eV}}{kT} \right) \left(\frac{\text{cm}^2}{\text{Volt Sec}} \right) \quad (6a)$$

and

$$\mu_v = \frac{1}{T} \exp \left(6.43 - \frac{0.34 \text{ eV}}{kT} \right) \left(\frac{\text{cm}^2}{\text{Volt Sec}} \right). \quad (6b)$$

In fact surface interstitial silver ion mobility is different from the bulk mobility because there are traps for the Ag⁺ such as kinks, jogs, etc., on the surface that are not present in the bulk perfect crystal. The magnitude of surface mobility of Ag⁺ ion has so far not been determined experimentally. If it is assumed that the difference between these two mobilities is negligible, then one can consider that the interstitial silver ion mobility at the surface is the same as in the bulk of the crystal (Baetzold and Hamilton 1972, and Baetzold 1974).

3. Time for ionic step in photographic process

In the scheme given below we will consider quantitatively the importance of the interstitials as well as their motion in the photographic process. Hamilton and Brady (1959, 1962) developed the techniques of the flash exposures in pulsed electric fields and studied the properties of the mobile silver ions and the photoelectric carriers in emulsion grains. They suggested that the principal ionic carriers are the mobile silver ions which are involved in the initial trapping of the photo electrons, and also in the ionic step during the growth of latent image centres in the grains.

(a) Mean intra-electron-ion distance in a latent image site

The mean distance \bar{x} , from the electron which is assumed to be trapped at random site on the surface to the nearest of the silver ions can be found by an approach similar to that of Hamilton and Brady (1962).

Let N_i be the concentration of silver ions per unit volume which is given by eq. (5), then the probability (P) that at least one of these silver ions lies within a hemispherical shell of volume ($V_s/2$) with radius r about the electron as a centre is given by (Singh, 1975):

$$p = 1 - \exp \left[-\frac{2\pi N_i r^3}{3} \right]. \quad (7)$$

The probability that the distance of the nearest ion from the trapped electron lies between r and $r + dr$ is the first derivative of this expression, with respect to r , which can be written as:

$$\frac{dP}{dr} = 2\pi N_i r^2 \exp \left[-\frac{2\pi N_i r^3}{3} \right]. \quad (8)$$

The value of the mean-intra-electron-ion distance \bar{x} , can be found by taking the integral of rdP between zero and infinity.

$$\bar{x} = \int_0^{\infty} 2\pi N_i r^3 \exp \left[-\frac{2\pi N_i r^3}{3} \right] dr. \quad (9)$$

Putting $x = r^{3/2}$, $q^2 = 3/4\pi N_i$ and $n = 1/3$, the equation reduces to

$$\bar{x} = q^{-2} \int_0^{\infty} x^{2n+1} \exp \left[-\frac{x^2}{2q^2} \right] dx. \quad (10)$$

This is a standard form for the moment of a Gaussian distribution of a Gamma function and therefore its value is given by

$$\bar{x} = 2^n q^{2n} \Gamma^\dagger(n+1) = 2^n q^{2n} n\Gamma(n) \text{ for } n > -1. \quad (11)$$

Substituting the values of n and q we have:

$$\bar{x} = \Gamma \left(\frac{4}{3} \right) \left[\frac{3}{2\pi N_i} \right]^{1/3}. \quad (12)$$

Substituting the value of N_i from eq. (5) we have:

$$\bar{x} = \Gamma \left(\frac{4}{3} \right) \left(\frac{3}{2\sqrt{2\pi N}} \right)^{1/3} \left[\frac{2}{\sqrt{2} \exp(-G_i/kT) + \exp(-G_F/2kT)} \right]^{1/3}. \quad (13)$$

(b) Mean time for ionic neutralization process

It is clear from eq. (13) that the motion (mobility) of Ag^+ ions does not contribute to the electron trapping process but rather the neutralization process is governed

† The value of $\Gamma(n+1)$ can be estimated by taking the more common notation

$$\Gamma(n+1) = n\Gamma(n)$$

and

$$\Gamma \left(n + \frac{1}{3} \right) = \frac{1.4.7.10 \dots (3n-2)}{3^n} \Gamma \left(\frac{1}{3} \right)$$

with

$$\Gamma \left(\frac{1}{3} \right) \approx 2.67893.$$

by the motion of interstitial Ag^+ ion near the trapped site of the electron where the latent image is formed. The mean time for the ionic step in latent image formation can be calculated by the following procedure.

Let τ_n be the time required by an interstitial Ag^+ ion to move the mean distance, \bar{x} , with a velocity v_i under the attractive influence of a net charge of $-e/2$ at the site where the electron is trapped. We also consider that dr is the small segment of length \bar{x} covered by the silver ion moving with velocity v_i in small interval of time dt . Thus

$$dr = v_i dt. \quad (14)$$

This equation in terms of the microscopic ion mobility (μ_i) and Coulombic force can be expressed as:

$$dr = \mu_i F dt. \quad (15)$$

The strength of the Coulomb's attractive force is given by

$$F = \frac{e}{2\epsilon r^2} \quad (16)$$

Here ϵ is the static dielectric constant of the AgBr crystal. Substituting the value of F from this eq. (16) in eq. (15) we have:

$$dr = \frac{\mu_i e}{2\epsilon r^2} dt. \quad (17)$$

Integrating the above expression within limits of the interval zero to \bar{x}

$$\int_0^{\bar{x}} r^2 dr = \int_0^{\tau_n} \frac{\mu_i e}{2\epsilon} dt$$

or

$$\tau_n = \frac{2\bar{x}^{-3}}{3\mu_i e}. \quad (18)$$

Substituting the value of \bar{x} from eq. (12) we have:

$$\tau_n = \frac{[\Gamma(4/3)]^3}{\Gamma\mu_i eN_i}. \quad (19)$$

Substituting the values of μ_i and N_i from eqs (6 a) and (5) in eq. (19) respectively, we have:

$$\tau_n = \frac{A_0 T \exp\left(-3.88 - \frac{0.15 \text{ eV}}{kT}\right)}{\sqrt{2} \exp(-G_i/kT) + \exp(-G_R/2kT)} \quad (20)$$

where

$$A_0 = \sqrt{2}\epsilon \left[\Gamma\left(\frac{4}{3}\right) \right]^3 / \pi N e.$$

4. Capture cross-section of Ag^+ ion

The ionic neutralization time τ_n in terms of the physical properties of the grain has the significance (Hamilton and Brady 1962).

$$\tau_n = 1/N_i v_i \sigma_i \quad (21)$$

in which σ_i is the capture cross-section of a Ag^+ ion at the electron trap, v_i is the thermal velocity of the Ag^+ ion, and N_i is concentration of interstitials per unit volume of AgBr grain. The magnitude of v_i is defined as:

$$v_i = \mu_i kT/ae \quad (22)$$

where a is the jump distance for interstitial Ag^+ ion and other symbols, have their usual significance.

The comparison of eqs (19) and (21) can be used for estimating the capture cross-section of an Ag^+ ion by a trapped electron. For this comparison, these two different expressions for τ_n , must have the same value. Under this condition, the magnitude of σ_i can be found from the following expression:

$$\sigma_i = \frac{\pi a e^2}{\mathcal{E} kT [\Gamma(4/3)]^3} = \frac{A_1}{kT} \quad (23)$$

$$A_1 = \frac{\pi a e^2}{\mathcal{E} [\Gamma(4/3)]^3}.$$

5. Calculations

The mean distance (\bar{x}) of the latent image site, the mean ionic neutralization time (τ_n) and the capture cross-section (σ_i) are calculated from eqs (20) and (23) respectively. The values of the constants used in these relations are taken as follows:

- (i) The dielectric constant, $\mathcal{E} = 13.1$ (Gurney and Mott 1938).
- (ii) The electronic charge, $e^2 = 1.44 \times 10^{13}$ MeV cm (Barkas 1963).
- (iii) Boltzmann's constant, $k = 0.8617 \times 10^{-4}$ eV/°K, and
- (iv) Number of AgBr ion-pairs, $N = 2.1 \times 10^{22}$ cm⁻³.

6. Mechanism of silver speck formation

The absorption of energy by a silver bromide (AgBr) grain from the ionizing particle or photon produces electron-hole pairs. A hole is trapped at a hole trap (some physical or chemical surface imperfections) and forms there a recombination centre so quickly that the passage of a charged particle in an emulsion can be considered equivalent to the formation of an electron and recombination centre pair with negligible delay. A trapped hole that does not form a recombination centre becomes a Br atom which is subsequently absorbed into the gelatin thereby eliminating it as a recombination centre. A free electron may recombine with hole at the recombination centre and thus restore the initial condition of the AgBr grain. Besides, an electron moves through the grain, and falling into traps where it may be held for a very small time (of the order of microseconds). During this time, a mobile interstitial silver ion moves up under the influence of the Coulomb field of the trapped electron and forms a silver atom. Consequently an additional electron which may be trapped at such a centre does not escape. In due time, the site acquires a second mobile interstitial silver ion to form a pair of silver atoms. The centre can trap a third electron, a third mobile interstitial ion, and so on, so that the speck grows indefinitely; the process for latent image or silver speck

formation is shown in figures 1 and 2. The values for the mean distance of the latent image site ($\sim 0.0248 \mu\text{m}$) and the ionic neutralization time ($\sim 4.8 \times 10^{-7}$ sec) using eqs (13) and (25) respectively are shown in figure 1 at room temperature (300°K). We also consider that these values remain constant during the process of the growth of the speck for a given temperature. We have not considered the mechanism for permanent disposal of holes by some impurities in the present model. It is assumed that the trapped electrons in the shallow traps may escape in a very short time and can recombine with holes at recombination centres till they are not joined by a mobile interstitial Ag^+ ions permanently. The model which we have assumed here for our considerations is somewhat similar to that considered by Bayer and Hamilton (1965).

7. Result and discussion

Figures 3 and 4 show the plots of theoretically calculated values from eqs (24), (25) and (26) for a temperature interval $233\text{--}325^\circ \text{K}$. It may be remarked that according to curve (a) of figure 3 the estimated values of ionic neutralization time (τ_n) decreases sharply up to a temperature of 273°K and beyond this region a slow decrease in these values is observed. Moreover the variation in the values of the mean intra-electron-ion distance (\bar{x}) in a latent image site is very small as compared to the variation in τ_n within this range of temperature which is clear from curve (b) of figure 3. This shows that a small change in \bar{x} produces a large change in τ_n at low temperatures. The values of \bar{x} , the mean intra-electron-ion distance from eq. (24) is of the order of 10^{-8}cm . This result is significant because it shows that the ions travel over distances which are much smaller than the size of the average emulsion grain. In all ordinary emulsions, therefore, the grain size itself will not influence the position of the bend-over point in the reciprocity failure curve (Berg 1940 and Tani 1974). From figure 3 it is also seen that at low enough temperatures

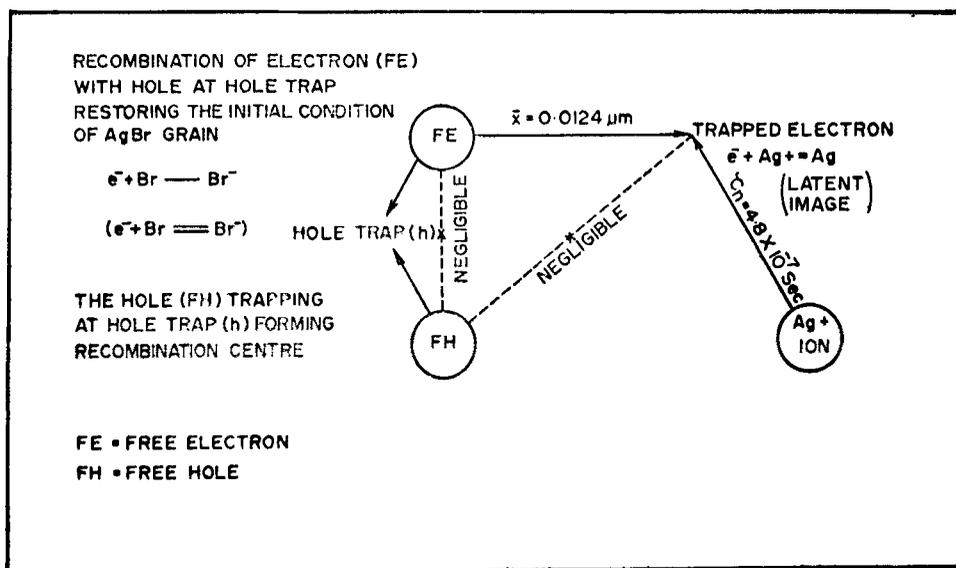


Figure 1. Ionic process on latent image formation at room temperature (300°K).

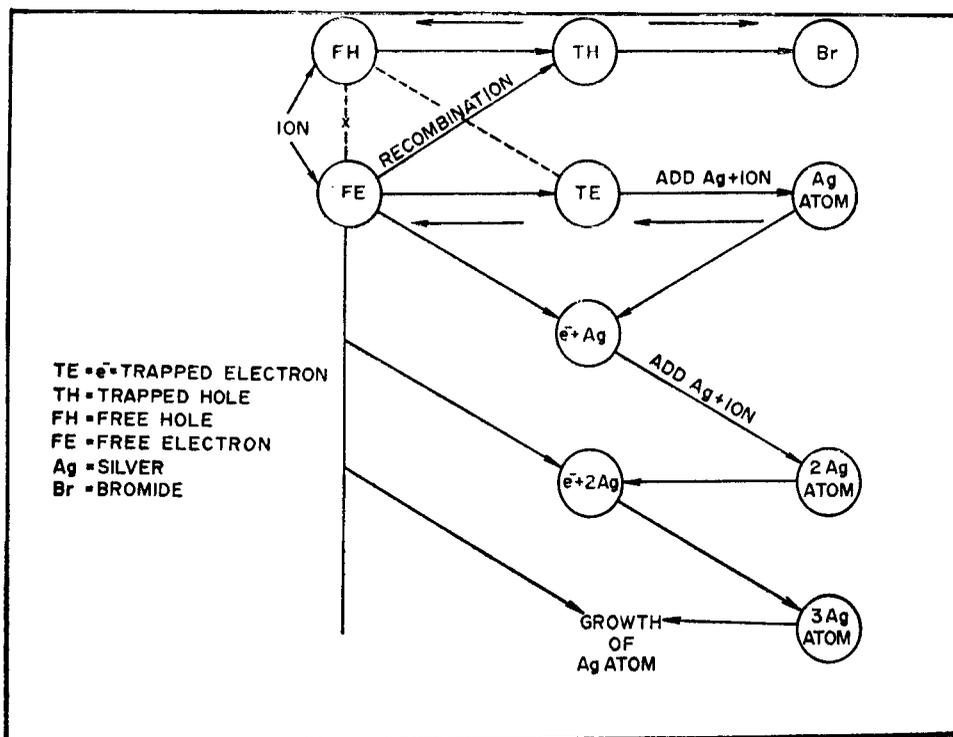


Figure 2. Schematic diagram of complete latent image model.

the time period for latent image formation in AgBr crystal is much longer compared to that at room temperature (300° K). This suggests that in the region of low temperatures the ionic process occurring in the latent image formation is reduced very much as compared to the process at room temperature.

Figure 4 shows the variation of the magnitude of capture cross-section (σ_i) as a function of temperature. This variation is considerably smaller ($\sim 1.4 \times 10^{-13}$ to 1.0×10^{-13} cm²) in the temperature interval 233–325° K. Thus, we conclude that the temperature effects do not markedly effect the capture cross-section of combination of Ag⁺ ion with electron. A limiting value of σ_i ($\sim 1.2 \times 10^{-13}$ cm²) may be considered a suitable average value to describe the results. The use of this limiting value of σ_i in eq. (21) for obtaining the magnitude of τ_n at any temperature does not change significantly the values of ionic neutralization time (τ_n). The value of τ_n obtained by using either of the eqs (21) and (25) at room temperature (300° K) is of the order of 4.8×10^{-7} sec which is quite small. This value is consistent with the value suggested by Bayer and Hamilton (1965). The fact that the values of τ_n are quite small (smaller than 10^{-8} sec.), seems to be in accord with the experimental fact indicating that high intensity reciprocity failure (HIRF) is not observed in chemically unsensitized silver bromide emulsion grains before 10^{-6} sec (ref. 26) after exposure. This also justifies the proposed model. Thus our model, based purely on theoretical considerations, suggests the magnitude of the various parameters, (\bar{x} , τ_n and σ_i) at any temperature appears quite satisfactory.

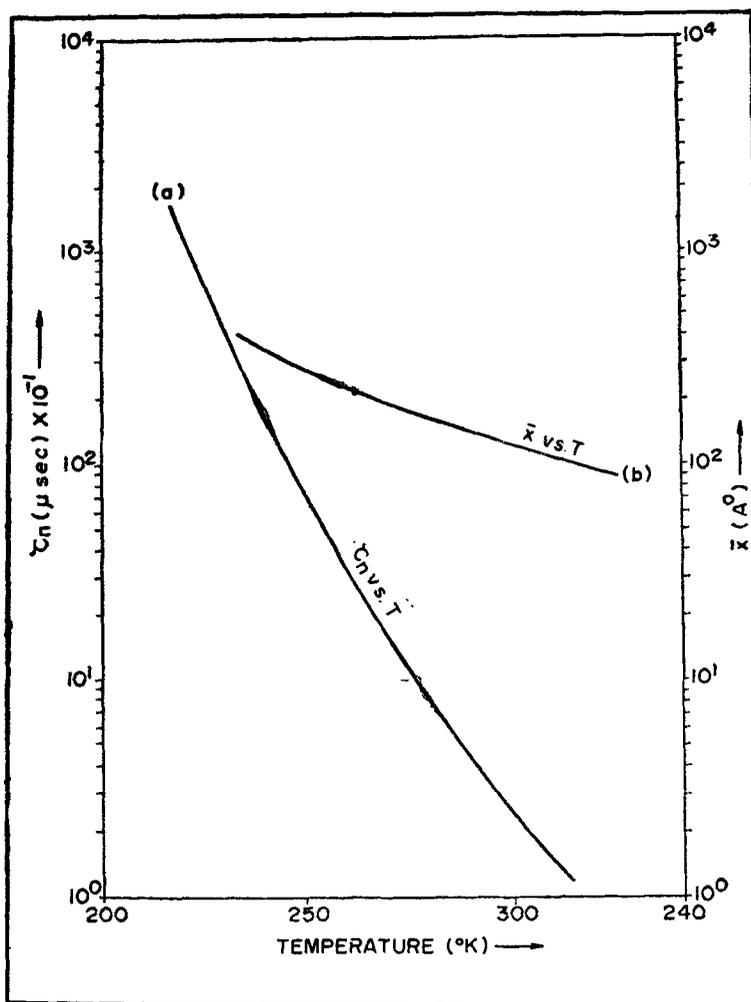


Figure 3. Variation of τ_n and \bar{x} with T .

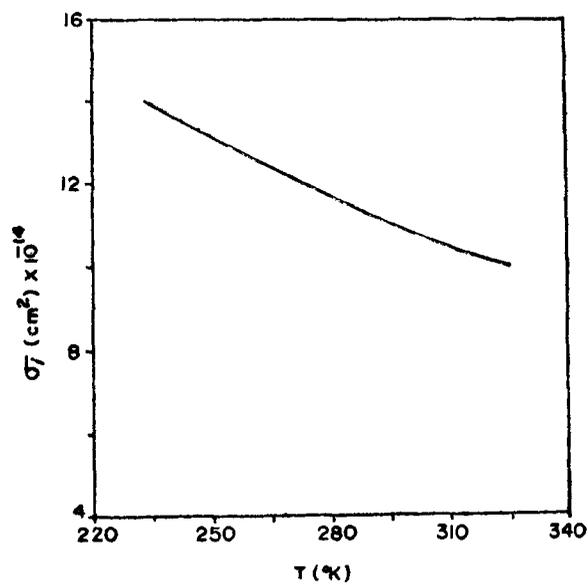


Figure 4. Variation of capture cross-section (σ_l) with temperature (T).

Finally we may comment on the application of these parameters. However, the property of ionic conduction of silver halide grains (and hence concentration of interstitial silver ions) varies with the variation of emulsion conditions, therefore, it is thought that the values of \bar{x} , τ_n , etc., may also vary depending upon emulsion conditions. However, we have not made the analysis of all such cases, therefore, one should be careful when these values are applied to the photographic process in some particular emulsions.

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