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On the Activation Energy of Photographic Chemical Development

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In order to study the photographic chemical development from the standpoint of atomic physics, the activation energies of this phenomena were measured using various dry plates, and the following results were obtained;

(1) The activation energy for pure silver bromide emulsion is fairly similar to the activation energy for ionic conductivity of silver bromide crystal, but a little smaller.

(2) As the proportion of content of silver iodide in grains in emulsions grows the greater the activation energy becomes.

From these results, the mechanism of this reaction, especially the mechanism described by R. W. GURNEY and N. F. MOTT, is discussed.

§ 1. Introduction

The theoretical concept for the formation of latent image in photographic emulsion was given by GURNEY and MOTT¹⁾ and recently by J. W. MITCHELL.²⁾ According to their theories, the sensitive specks which have been made in the ripening process capture the photoconductive electrons in silver halide grains, and are neutralized by mobile positive ions, and the latent images are formed doing such process over and over again. All phenomena for sensitivities of emulsion seem qualitatively to be explained by means of their considerations.³⁾

As for the chemical development, they extended their sensitivity-theory as follows⁴⁾;

“At first the latent images are given the negative charges from developer-ions in developing solutions, and they are almost neutralized by migration of interstitial silver ions in silver halide grains. Perhaps neutralization by silver ions dissolved in the developer is, if there are, very slight.” It is said⁵⁾, however, that their theories for chemical development are inconsistent with a few experimental results; their representative one is that when one measures the ve-

locity of development using pure silver iodide emulsion, although a faster coagulation of image than in the case of pure silver bromide emulsion may be expected under their consideration, for ionic conductivity of silver iodide is considerably greater than that of silver bromide, one get generally the opposite results.

But the authors think if an experimental result for these two plates occurs as above, they must not always assert that GURNEY-MOTT-MITCHELL's theory is not probable, because there are many factors which influence the developing velocity in addition to ionic conduction, so these factors may mask the difference between the ionic conduction of two silver halides, even if interstitial silver ions in silver halide grains play a role in the process of development.

Besides their theories, on the other hand, many concepts for this phenomena have been proposed recently. In 1943, M. L. HUGGINS considered similarly the ionic migration of silver ions in grains as an important process, but his theory is slightly different from GURNEY-MOTT's theory. At about the same time, T. H. JAMES⁷⁾ indicated for this reaction another mechanism in which silver ions in developers almost form the images. Many photographic chemists are now accepting his theory as most reasonable for this reaction.⁸⁾ Certainly, his theory seems to be appropriate to explain, for example, the formation of filamental image.

However, strong reliable experimental support for his theory has never been offered,⁹⁾ and it seems to be very difficult to confirm his idea experimentally, as its mechanism is more complex than GURNEY-MOTT's. After all, the atomic mechanism for photographic chemical development is still uncertain. Measuring the activation energy for this reaction, which is indicated from the experimental relation between the temperature and the chemical activity, it has been studied, especially noticing the quantitative relation between the ionic conduction of silver halide grains and this reaction.

§ 2. Activation Energy for Chemical Development

Generally, the activation energy for a certain chemical reaction is an important value to estimate its mechanism in comparison with other well-known physical and chemical values. Therefore, the measurement of the activation energy for chemical development

also was taken up in order to study it. In this case, however, it is difficult to define the universal activation energy. For example, the temperature coefficient for this reaction which was given in the book by MEES¹⁰ represents a very complex mechanism. In it, perhaps, diffusion of developer ions through gelatins, its adsorption to the latent images, and coagulation of developing images etc., are considered. Presently, the last term alone needs to be measured, so the activation energy must be defined at the step where only image coagulation appears.

GURNEY and MOTT¹¹) have ever said that if their theory is probable, the time from the beginning of visible development of any single grains until its completion should vary with the temperature in the same way as its ionic conductivity. In other words, defining the activation energy for this reaction in the above sense, they expected it to coincide with the activation energy for ionic conductivity of silver halide grains.

However, it seems very difficult quantitatively to measure the coagulation of image in grain, so one must discuss such a problem having in mind an average velocity for groups of grains in an emulsion. Of course if one can observe the average velocity of coagulation at such a step in which progress of image coagulation is seen in all sensitive specks in all grains, he gets the same result as measuring in a grain. To catch such steps, generally, seems to be impossible, but the circumstance of development at the proper steps after macroscopic induction period seem to be approximated as above.

Recently URYU¹²) has measured the activation energy for development at its initial step with a certain commercial dry plate and metol developer and obtained for its value 0.66 ev which coincides very well with the activation energy for ionic conductivity of silver bromide crystal by LEHFELDT.¹³) If the step at which he measured the activation energy is the proper one, his result seems to offer good experimental support for the theory by GURNEY and MOTT, as he has stated.

However it should be noted that;

- (1) The commercial dry plate contains a small quantity of silver iodide.
- (2) The value of ionic conductivity of silver halide crystal

- may be not always same as that of silver halide grain.¹⁴⁾
- (3) The activation energies of the mechanism by JAMES and others may happen to give the same order as for ionic conductivity.¹⁵⁾

Considering these problems and influence due to the existence of induction period, the mechanism of development have been studied by measuring the activation energies with the experimental dry plates in which silver iodide is contained in various proportions and commercial dry plates. As the developers, metol and hydroquinone developer etc. was taken.

§ 3. Experimental Method

Through this study, the apparatus for giving the exposure has not been varied, with the exception of exposure durations and brightness of electric lamps. Therefore in part 4 of this paper, where the experimental results will be reported, these two factors will be indicated merely as exposure conditions for each plate. It must be also remarked that comparatively long exposure was generally given, because there was no apparatus to give a short exposure correctly. In addition, a green filter was used. The developers were contained in a slender glass cylinder of which the diameter and height are about 6 cm and 15 cm respectively. This cylinder, moreover, was put in a great cell which was, also, filled with water having a definite temperature. The exposed plates were fixed vertically in this cylinder, and developed for definite duration, when the developers were always stirred by a glass stick.

This disturbance was done in order to give a sort of agitation in developing process. The temperature of developers was varied between 0°C. and 35°C., and its accuracy is about in $\pm 0.1^\circ\text{C}$. at each temperature.

As for the fixing, ordinary oxidized fixing solutions—for example, Eastman F 5—were used and duration of fixing time was about ten minutes in room temperature for each plate with exception of that sort of plate, which contains a great amount of silver iodide and needs about an hour to complete fixation.

After being washed with water and dried, the blackness densities of these plates were measured for by an apparatus used photo-

tube and galvanometer. This apparatus is shown in Fig. 1.

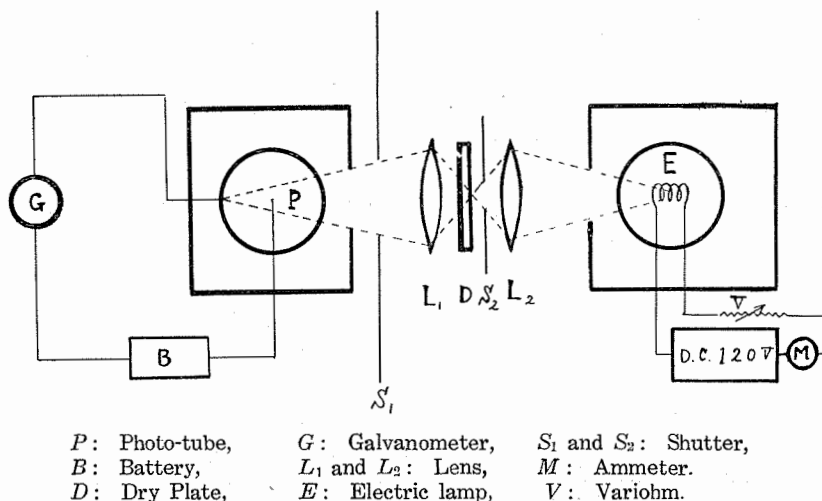


Fig. 1. The apparatus used for measuring the diffuse density of plates.

When D , by such method, is obtained as the value of density in the exposed region of a plate and D_f in non-exposed region—that is, D_f represents fog—, D should not be regarded as an important value in discussing the nature of latent image, but $D - D_f$. This is the reason why, even if two plates given the equal exposures are developed under same condition, their density is not always equal, but there is generally a small difference, for separate plates never have had the same distribution of sensitive specks.

On considering the latent image made by exposure, then, one must generally compare the value of $D - D_f$. The authors, however, think they must compare the value of D , not of $D - D_f$ in a discussion on chemical development, because chemical reactions involved in development are based upon the latent image, that is, upon a combination of sensitive speck and sensitive image. But if they do so, they must neglect the fluctuation of the nature of the emulsions, but the effect of that fluctuation will be perhaps small, with the exception of the cases for plates having accidental fog. Also, practically, the difference between activation energies calculated from the temperature dependence of D and that of $D - D_f$ is very small.¹⁶

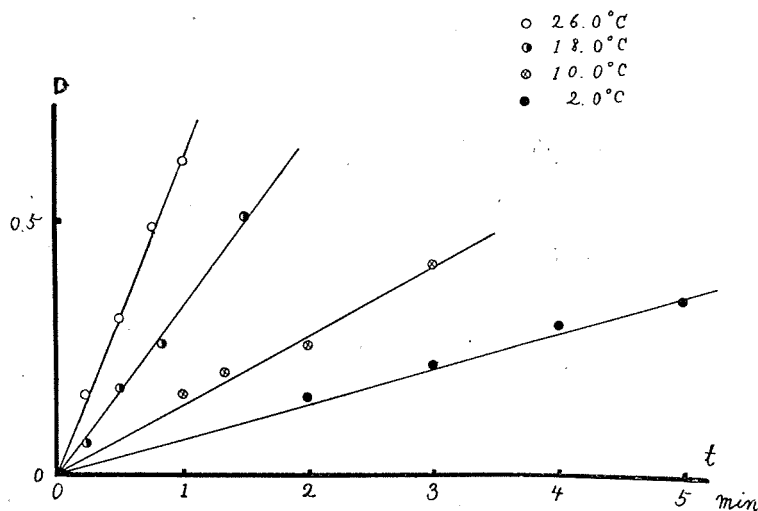


Fig. 2. The relation between D and t when used a commercial dry plate* and Metol developer.** Exposure conditions are; 10 watt, 0.1 amp. and 10 sec.

The linear relation between D and t was obtained at the initial step of reaction in this case. Therefore, if the reaction stated in part 2 can be assumed to happen in such step, one may measure the temperature dependence of developing duration needed for a certain progress of the reaction at any point in such step.

In this case, the step from $D=0.1$ to $D=0.4$ was taken. This relation is shown in Table 1, and Fig. 3.

TABLE I.

The relation between temperature T and duration of development needed for the progress of reaction from $D=0.4$ to $D=0.1$.

T	P	T	P
26.0 °C	28 sec	10.0 °C	136 sec
18.0	54	2.0	258

* Fuji A. I.

** Composition of this developer is as follow;

Metol 1 gr, Na_2SO_3 10 gr, Na_2CO_3 10 gr, Water 300 c.c.

*** These values mean that electrical lamp, of which brightness is 10 watt, is lighted with D.C. 120 volt, but electric current is always supported by 0.1 amp., and duration of exposure is 10 sec.

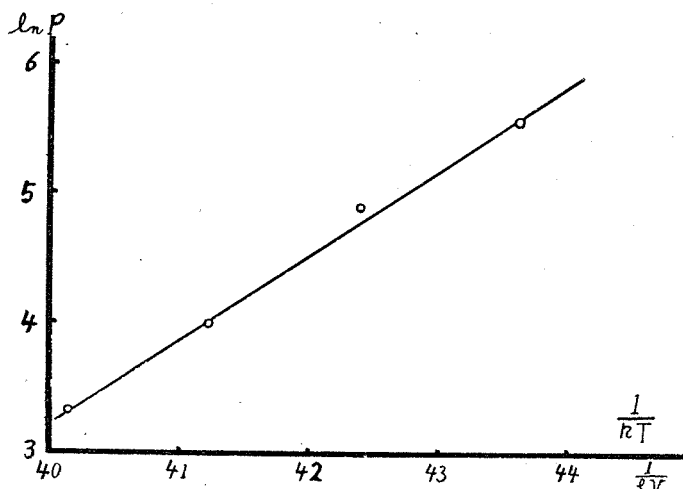


Fig. 3. The relation between $1/T$ and above-described P .

Using the same method, the activation energies for many cases can be calculated.

§ 4. Experimental Results

(I). Cases using commercial dry plates.

i). Development with metal developer in which KBr is not contained. The relation between D and t at each temperature has been shown already in Fig. 2.

This is a case having very short induction period, so the activation energy U can be calculated as below:

$$U = k \frac{\partial}{\partial \frac{1}{T}} \ln \left(\frac{\partial D}{\partial t} \right) \text{ at initial step}$$

Of course, however, the value of $\ln \frac{\partial D}{\partial t}$ at each temperature is not completely linear upon $1/T$. So calculating U from such relation, the method of least square must be used. From the relation in table 1, we can get

$$U = 0.64 \pm 0.02 \text{ ev}$$

The value of this activation energy is a little smaller than the activation energy for ionic conductivity of silver bromide reported by LEHFELDT,¹⁷⁾ and those for chemical development by URYU.

ii). Development with hydroquinone developer.

The characteristic curve of development by this developer shown in Fig. 4 represents clearly the existence of the induction period; then the temperature dependence cannot be discussed at initial step,

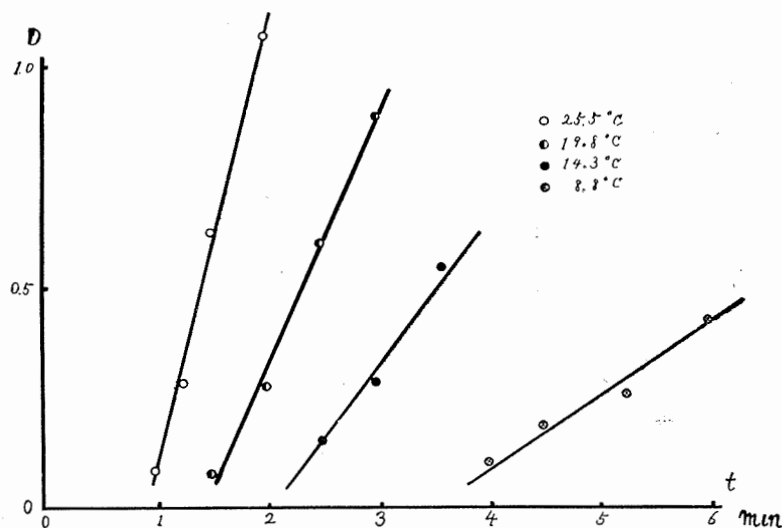


Fig. 4. The characteristic curve of development using a commercial dry plate* and hydroquinone developer.** Exposure condition is: 10 watt, 0.1 amp, 20 sec.

TABLE II.

The relation between T and P (to $D=0.5$ from $D=0.2$) in case with hydroquinone developer.

T	P
25.5 °C	19 sec
19.8	34
14.3	52
8.8	106

* Fuji A. I.

** Composition of this developer is:

Hydroquinone 2 gr, Na_2CO_3 10 gr,
 Na_2SO_2 10 gr, Water 300 c. c.

and so the activation energy was calculated at the proper step after macroscopic induction period in which the relation between D and t is about linear—for example, between $D=0.2$ and $D=0.5$. The result is shown in Table 2 and in Fig. 5.

From above result, U in this case is calculated,

$$U = 0.70 \pm 0.02 \text{ ev}$$

U in this case is a little greater than U in the case of metal developer; this is perhaps because the term due to the effect of induction period is contained, but the order of U is not different from the case of metal.

iii). Development with metal developer in which KBr is contained.

The characteristic curve of development by developers in which KBr is contained represents also the existence of induction period. In this case, there are the same circumstances about all phenomena as in case of the use of hydroquinone developer. So using the same method* the activation energy was measured. The results are shown in Table 3.

TABLE 3.

The relation between T and P (to $D=0.5$ from $D=0.2$) in case with metal developer in which KBr is contained.

T	P
24.5 °C	33 sec
19.0	53
14.3	83
9.5	177

From above table U is calculated as follow;

* In this case, Fuji A. I. and a developer of which composition is metal 2 gr, Na_2CO_3 10 gr, Na_2SO_3 10 gr, KBr 4 gr and water 300 c.c, are used. Exposure condition, also are the same as the case with hydroquinone.

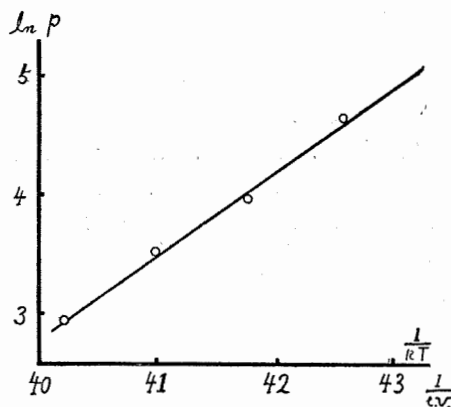


Fig. 5. The relation between $1/T$ and $\ln P$.

$$U = 0.70 \pm 0.02 \text{ ev}$$

(II) Cases using experimental dry plates

The experimental dry plates used here were manufactured by Fuji Photo. Film Co. The grains in these plates contain silver iodide in various proportions. These plates were developed by metal developer in which there is no content of KBr. The relations between D and t for each plate are not all presented here. As the special example, however, the case of a plate in which silver iodide is contained to the amount of 40 Mol % is shown in Fig. 6.

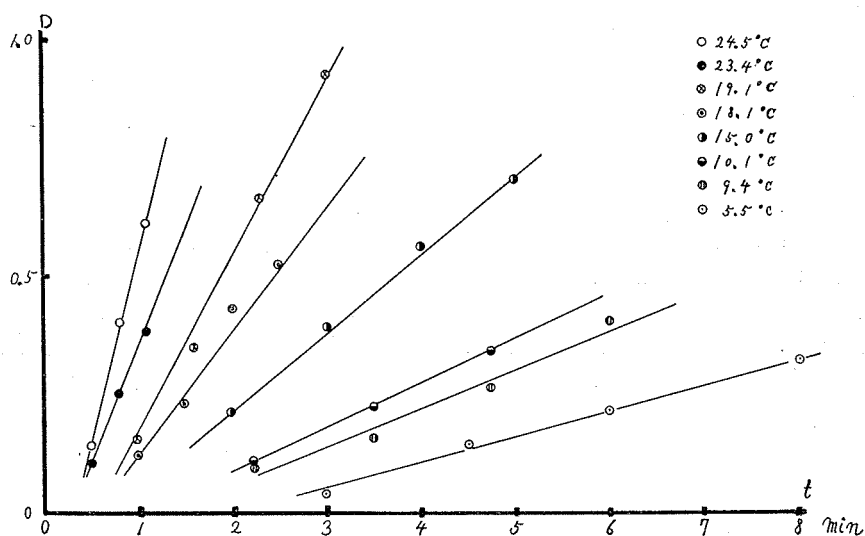


Fig. 6. The characteristic curve of development using plate in which silver iodide is contained by 40 Mol % and metal developer.

At a glance, the existence of the induction periods is evident in its curve, although the simple metal developers were used, then slopes of curve must not be measured at their initial step.

The velocities of development at each temperature in proper steps for four plates are summarized in Table 4. The experimental conditions used are also described in it.

TABLE 4.

Plate No.	experimental condition	T	P ($D=0.5 \sim D=0.2$)
1	1) Content of silver iodide 0 Mol %	25.0 °C	33 sec
		22.7	43
	2) Composition of developer used Metol 1 gr Na ₂ SO ₃ 10 gr Na ₂ CO ₃ 10 gr Water 300 c.c.	16.7	58
		15.2	72
		14.8	88
		10.8	123
	3) Exposure condition 60 watt 0.5 amp 20 sec.	5.8	178
		2.0	240
2	1) Content of silver iodide 2.5 Mol %	24.5 °C	14 sec
		19.3	22
	2) Composition of developer used Metol 1 gr Na ₂ SO ₃ 10 gr Na ₂ CO ₃ 10 gr Water 300 c.c.	16.6	28
		14.0	38
		12.5	48
		8.3	56
	3) Exposure condition 60 watt 0.4 amp 15 sec	3.1	97
3	1) Content of silver iodide 7 Mol %	25.0 °C	11 sec
		23.9	14
	2) Composition of developer used Metol 1 gr Na ₂ SO ₃ 10 gr Na ₂ CO ₃ 10 gr Water 300 c.c.	20.5	17
		18.5	20
		14.9	24
		12.2	37
	3) Exposure condition 60 watt 0.5 amp 15 sec	10.0	46
		7.2	71
	2.4	106	
4	1) Content of silver iodide 40 Mol %	24.4 °C	27 sec
		19.1	49
	2) Composition of developer used Metol 4 gr Na ₂ SO ₃ 3 gr Na ₂ CO ₃ 30 gr Water 600 c.c.	18.1	61
		15.0	110
		10.1	193
		9.4	220
	3) Exposure condition 100 watt 1 amp 2 min	5.5	305

From these results, the activation energies can be estimated as following table.

In TABLE 5 as the proportion of content of silver iodide in

TABLE 5.

Plate No.	activation energy
1	0.62 ± 0.02 ev
2	0.63 ± 0.02
3	0.66 ± 0.02
4	0.91 ± 0.02

grains in emulsions grows, the greater the activation energies become.

§ 5. Discussion

To summarize the final results of experiment are as follow;

- 1) In case of the use of pure silver bromide emulsion and simple metal developer, the activation energy of development is fairly similar to the one for ionic conductivity of silver bromide crystal, but a little smaller than the latter.
- 2) Using hydroquinone developer or the developers in which KBr is contained, the activation energy at any step of the reaction is more than about 0.1 ev. greater than in case of the use of metal developer.
- 3) As the proportion of content of silver iodide in grains in the emulsions increases the greater the activation energy becomes.

As for result 2), the conclusion can be given simply. When the developer having great induction period is used, the beginning of image coagulation in grains having great latent image differ very much from that of those having small latent image alone, then the activation energy measured at any step is affected by these factors.

In fact, it should be regarded to be reasonable to such consideration that the activation energy calculated from the relation between $D=0.1$ and $D=0.4$ is a little greater than that calculated between $D=0.2$ and $D=0.5$.¹⁸⁾ From 2), the authors rather intend to attach great importance to the unchangeability of order of activation energies for all cases no matter what developer is used; that is, the mechanism of coagulation of image is perhaps unchangeable with any developers.

From 1), it is remembered that even if GURNEY-MOTT's theory is probable the activation energy of the reaction may differ from that of ionic conductivity of silver bromide crystal on account of differences between the electric natures of crystal and grain.¹⁹⁾

Then if that is so, cannot a smaller value than that of crystal be expected from the data previously published?²⁰⁾ However, it seems that there are few reliable data on ionic conduction of silver halide grains.

The same circumstance must be repeated as respects 3). If there were reliable data for ionic conductivity of silver bromide grains in which silver iodide was contained in varying proportion, the authors could get on the important tracks of GURNEY-MOTT's theory as compared with the tendency of their own data.

Then if results can be obtained, similar to 1) and 3) above described, in a study of ionic conductivity of small grains in dry plates in which silver iodide is contained, from its direct measurement, or from indirect ones through study of the effect of temperature on the high intensity reciprocity law failure,²¹⁾ then the author's results may be considered to be of some value as experimental proof of GURNEY-MOTT's theory.

Now, some words about the effect of existence of induction period must be offered here.

Developing the plates in which great amount of silver iodide is contained, even with metol developer, the rather great induction periods appear as indicated in Fig. 6.

This result may be considered to indicate that when one use the silver iodide emulsion, the velocity of development is generally small.

On the other hand, from this result, it must be noted that even if the greater activation energy, over the experimental error, increases as the proportion of content of silver iodide in emulsion grows, the term due to the effect of induction period may be contained in it.

However, the value effected by the induction period, perhaps, is smaller than 0.1 ev even in case of plate containing the greatest proportion of silver iodide, because the value of induction period in case using a commercial plate and hydroquinone developer, when the term due to the effect of existence of induction period in

activation energy U is about 0.1 ev is greater than in case using this experimental plate and metal developer as shown in Fig. 7.

But, the increment of U due to inclusion of silver iodide in grains in case of this plate is about 0.3 ev, then the tendency of increase in U , if there is the term due to induction period in it, will be preserved.

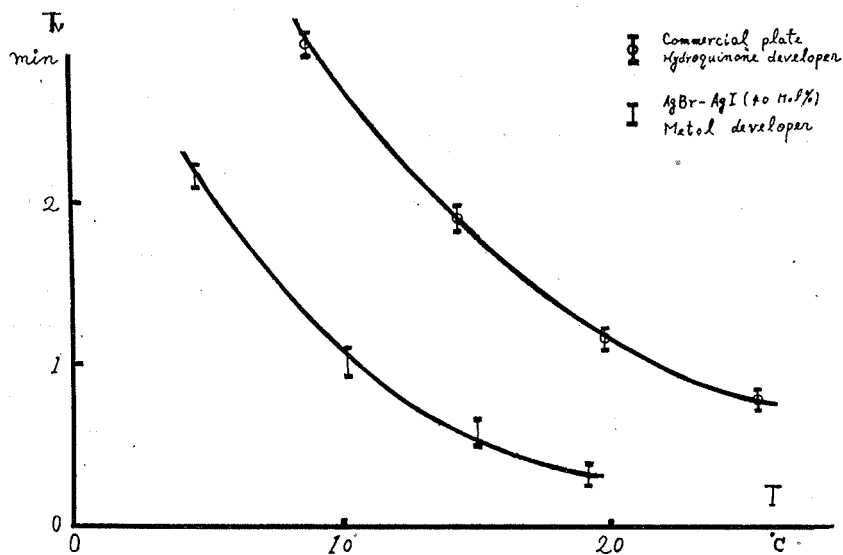


Fig. 7. Comparison of induction periods between the case using commercial dry plate and hydroquinone developer and that using experimental dry plate and metal developer.

More rigorous consideration about induction period will be entered into a succeeding paper.

§ 6. Final Remark

The authors wish to thank Mr. MIZUKI for supplying the experimental dry plates and for having suggested this work.

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