# Studies in Photographic Sensitivity, Part V.

## Effects of Heat on the Absorption Spectrum and Photoelectric Conductivity of Silver Bromide, and their Relation to the Photographic Action

By

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### Abstract

The present experiments were carried out to examine the effect of heat on the absorption spectrum and photoelectric conductivity of silver bromide, and also to find their relation to the photographic action. The following were the results:– (1) The red end of the absorption spectrum was displaced to the red side by the raising of the temperature of the sample, and those of other silver halides behaved in a similar way. (2) The maximum point in the photoelectric conductivity curve of silver bromide was also displaced towards the same side on its temperature being raised.

Thus heat affects the absorption and photoelectric conductivity of silver bromide in the similar way as it affects the photographic action, indicating that there is some close connection between these three phenomena. This seems to support the photoelectric conductivity theory of photographic action.

## Introduction

In a course of the present investigation the writer noticed[1] that the sensitivity of certain photographic plates (i.e. panchromatic, and ordinary slow plates) was increased by the raising of their temperature, but that of ordinary and isochromatic plates of high speed emulsion was decreased by the same treatment, and that in all cases the maximum point of the sensitivity curve was shifted towards the longer wave length side of the

1 These Memoirs; **12**, 1 (1929)

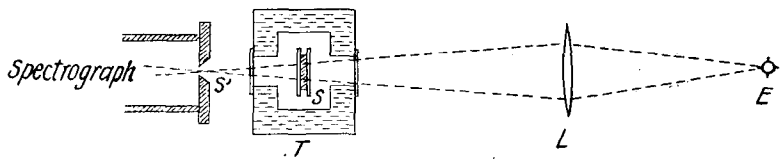
spectrum. The amount of this shift was about 0.8 Å per degree of temperature. The present experiments were carried out to study the effects of heat on the absorption spectrum of silver bromide and also on its photoelectric conductivity, and to see whether or not there is any connection between photographic action, absorption, and photoelectric conductivity of silver bromide.

## Effect of Heat on Absorption Spectra of Silver Halides

A small amount of silver bromide was melted on a thin glass plate by holding it over the flame of an alcohol lamp, and a thin film of it was made by squeezing it between this and another glass plate. The thin film of silver bromide thus prepared was placed in a thermostat, and this was placed before the slit of a grating spectrograph as shown in Fig. 1.

Fig. 1

Apparatus to take the absorption spectrum of silver halide.




*E*: light source *L*: lens
*T*: thermostat *S'*: slit
*S*: thin film of silver halide

This thermostat has double walls, the space between them being filled with water, its temperature being controlled by means of an autoregulator within $\pm 0.5$°C. The temperature inside the thermostat can be raised to a required one by means of an electric heater which was placed outside the thermostat.

A 250-watt tungsten lamp with a condensed filament was used as the source of a continuous spectrum. Two spectra, one of which was filtered through the thin film of silver bromide, at a certain temperature, the other being unfiltered, were photographed on one plate, with a spectrum of tin for comparison.

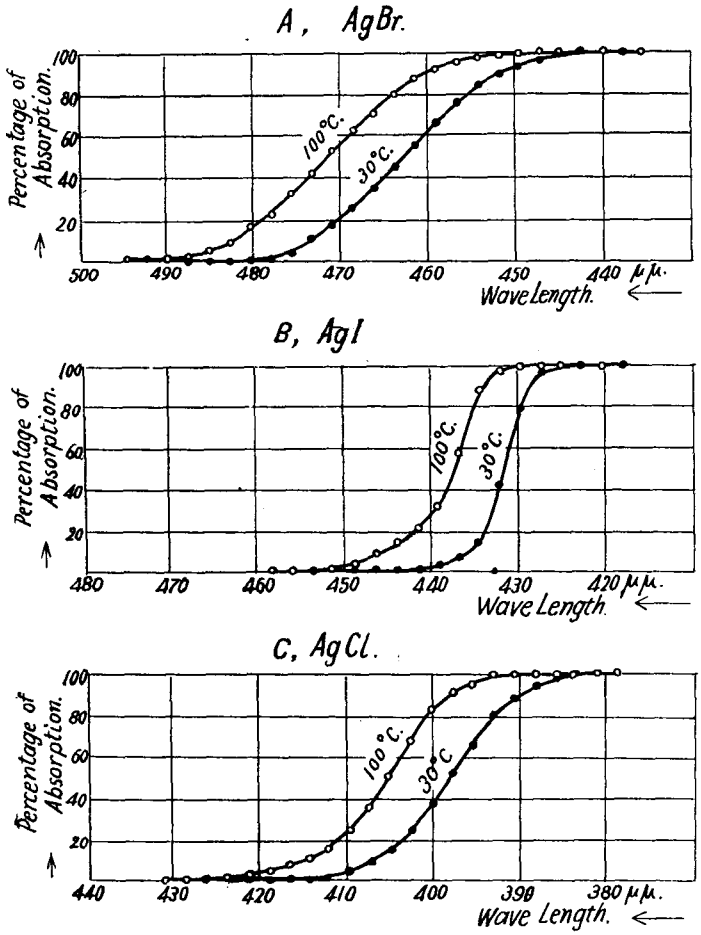
The density of the negative photographic plate was measured by means of a microphotometer with a photoelectric cell, the photoelectric current being once amplified by a triodbulb, and this was measured by a Leads and Northrup's No. 2500-*B* galvanometer, according to the method

devised by Toy, Edgerton and Vick.[1]

The result was as illustrated in Fig. 2, *A*. Fig. 2, *B* and *C* represent similar curves taken with silver iodide and chloride.

Fig. 2

Absorption spectra of silver halides.




The ordinates of the curves represent the percentage of the absorption due to silver halides calculated in the following way.

The intensity of the light at a certain wave length is given by

$$I_0 = k \log \frac{D_\infty}{D_\infty - D_0}$$

1 Phil. Mag.; **6**, 324 (1928)

for the light when unfiltered, and by

$$I = k \log \frac{D_\infty}{D_\infty - D}$$

for the light filtered by silver halide, where $D_0$ and $D$ represent the densities of the negative plates taken with direct and filtered lights at that spectral region, and $D$ the maximum density of that plate. Therefore, the percentage of the absorption is given by

$$\frac{I_0 - I}{I_0} \times 100 = \left\{ 1 - \frac{\log D_\infty - \log(D_\infty - D)}{\log D_\infty - \log(D_\infty - D_0)} \right\} \times 100.$$

The absorption of a thin film of silver bromide commences at about $\lambda$ 4900 Å and continues to the ultra-violet region. The longer wave length end of the absorption spectrum was thus shifted to the red side by the raising of its temperature. A shift of about 80 Å was found when the temperature was raised from 30° to 100°C, which is equivalent to 1.1 Å per degree.

Similar amounts of shift were found for silver iodide and silver chloride.

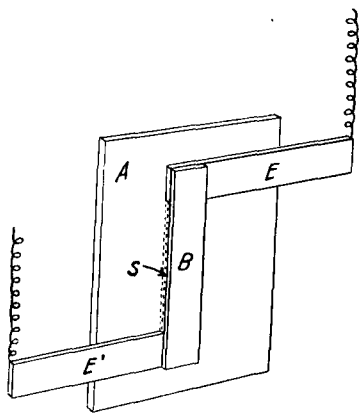
## Photoelectric Conductivity of Silver Bromide

Coblentz[1] found that the photoelectric conductivity of silver bromide commences at about $\lambda$ 5000 Å and becomes sharp maximum at about $\lambda$ 4650 Å. The present writer investigated the change in the position of the maximum of the photoelectric conductivity curve of silver bromide when the temperature of the sample is varied.

The method of the experiment was similar to that used by Coblentz, with a slight modification as described below.

The sample to be tested was first melted upon a glass or quartz plate, and then the molten material was squeezed by another strip of glass or quartz having a size of about $2 \times 25$ mm$^2$. The electrodes

Fig. 3
Sample




*A*, *B*: glass or quartz plate.
*E*, *E'*: silver electrodes.
*S*: thin film of silver bromide.

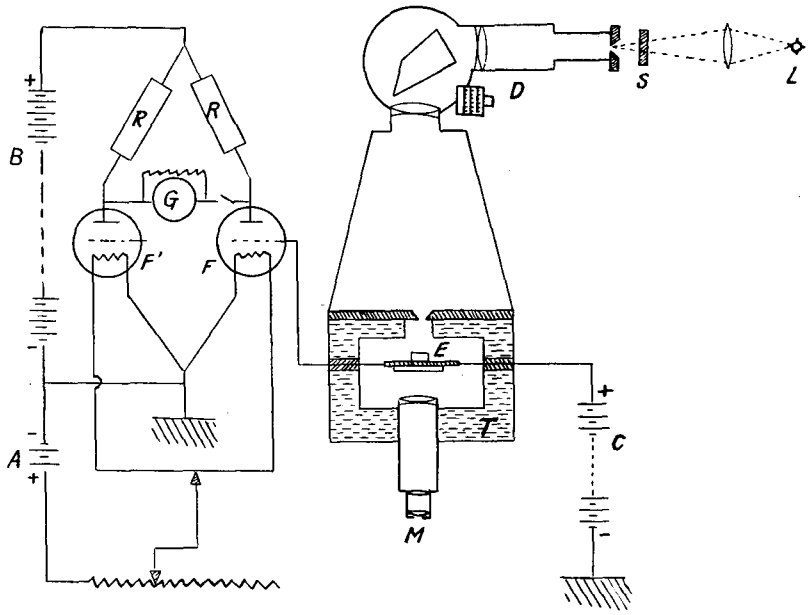
1 Bureau of Standards, Sci. Paper; No. 456. (1922)

consisted of pieces of silver plates of the thickness of about 0.3 mm., placed between two plates as shown in Fig. 3, the thickness of the film being thus made the same as that of the silver electrodes. The distance between the electrodes was about 15 mm. This sample was placed in the same thermostat as that described above. This thermostat was placed just behind a monochromator reconstructed from a Hilger's constant deviation spectrograph, the width of the slit in the focal plane being 1 mm., and the sample to be tested was placed to face the slit at a distance of about 1 cm. from it. One of the electrodes was connected to the anode of a 48 volt battery, the cathode of which was earthed, and the other electrode connected to the grid of an amplifying triodbulb.

An increase in the electric current produced by the illumination was measured by the method devised by Wynn Williams[1], the connection circuit

Fig.4

Apparatus for the measurement of photoelectric conductivity.

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|---|---|---|---|
| *L* : | 1000 watt tungsten lamp. | *A* : | 4 volt battery. |
| *S* : | shutter. | *B* : | 75 volt battery. |
| *D* : | constant deviation monochromator. | *C* : | 48 volt battery. |
| *E* : | thin film of silver bromide. | *F* : | amplifying bulb. |
| *F'* : | compensating bulb. | *T* : | thermostat with an autoregulator. |
| *R* : | adjustable resistance. | | |
| *M* : | microscope to test the condition of illumination. | | |

1 Phil. Mag.; **6**, 324 (1928)

for the measurement being shown in Fig. 4.

Telefunken's *R. E.* 78 bulbs were used as amplifiers, and Leads and Northrup's No. 2500–*B* galvanometer was used for the measurement of currents. The system was initially adjusted so as to give no deflection of the galvanometer when the sample was not illuminated, and the deflections produced by opening the shutter for 5 seconds were recorded for various wave lengths. Other precautions given by Coblentz and Williams were followed in this experiment.

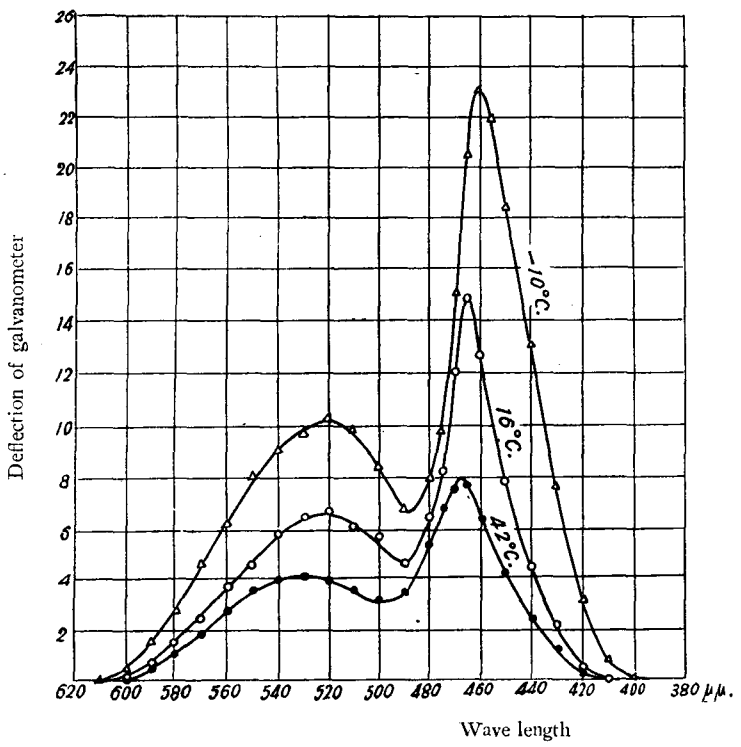
The photoelectric conductivity produced by the illumination became very small and unstable when the sample was heated above 50°C, so that the measurements were made at 42°C, 16°C and −10°C, the last one being obtained by cooling the thermostat with a freezing mixture of ice and common salt.

The curves given in Fig. 5 show the mean of 8 observations taken at three temperatures.

The photoelectric conductivity curve of silver bromide obtained by the

Fig.5

Photoelectric conductivity curve of silver bromide.



present writer has two maxima. The maximum at about $\lambda$ 4600 Å coincides with that found by Coblentz, indicating that this is due to pure silver bromide, but the other was not found by Coblentz. A further experiment is required to determine the origin of this second maximum.

Generally, the photoelectric conductivity of silver bromide was decreased by the raising of its temperature, and the maximum point of the photoelectric conductivity curve always shifted towards the longer wave length side of the spectrum. The amount of this shift was about 75 Å for a rise of 52°C i.e. about 1.4 Å per degree.

## The Relation between the Photoelectric Conductivity and the Photographic Action

In the first part of these studies[1], it was found that the maximum points of the sensitivity curve of a photographic plate was shifted towards the longer wave length side by heating, and that the sensitivity of high speed plates was decreased, but that of panchromatic and slow plates was increased by the same treatment. It was also found that the sensitivity of panchromatic and slow plates was increased by drying, but that of high speed emulsion remained almost the same, the maxima of the sensitivity curves in both cases remaining unchanged by the same treatment.

Comparing these two effects, it may be considered that the sensitizing effect of heat on slow plates may perhaps be due to extreme drying of the plate, but the desensitizing effect of heat on rapid plates and the shifting of the maxima for all plates can not be understood as due to the same reason. From these facts we considered that the decrease in sensitivity and the shift of the maximum points in the sensitivity curve, as is seen for such plates as Apem Non Screened, Ilford Special Rapid, and Eastman Universal plates, must be considered to be really due to the effects of heat. (See Fig. 5 ; *C*, *D* and *E* in Part 1 of these studies)

Generally, the amounts of this shift for many plates were found to be about 50 Å for a rise of 65°C i.e. 0.8 Å per degree.

In the present experiments it was found that the red ends of the absorption spectra of silver halides shifted towards the red side when their temperature was raised, and that the photoelectric conductivity of silver bromide was decreased and that the maximum of the photoelectric conductivity curve was shifted towards the same side by the same procedure.

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1 These Memoirs; **12**, 1 (1926)

The amount of this shift in the former case was about 1.1 Å. per degree, and that in the latter case was about 1.4 Å per degree.

Thus, it may be osberved that there is a close connection between photographic action, absorption and photoelectric conductivity, as indicated by the similar effects produced by heat on these three phenomena.

This supports the photoelectric conductivity theory of photographic action.

In conclusion, the writer wishes to express his sincere thanks to Prof. M. Kimura, under whose guidance the present experiments were carried out.