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## Limits of Infra-Red Sensitizing\*

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The competition between the thermal reaction and the photochemical reaction will set a natural limit to the extension of photographic methods into the infra-red region. From plausible assumptions concerning the velocity of the spontaneous reaction of molecules containing an excess of energy, it is concluded that this limit will be found at a wave-length of  $2\mu$ .

THE extension of photographic technique into the infra-red region can be extremely helpful in the investigation of vibrational bands, and for this purpose the passing of the long wave limit beyond its present value is very important. There does not seem any doubt that this end will be reached in the very near future, since the synthesis of the polymethine dyes, used as sensitizers, progresses steadily.<sup>1</sup> However, the polymethines are rather unstable substances, and their synthesis becomes increasingly difficult with their absorption spectrum shifting to longer wave-lengths. Thus, progress in this field is necessarily slow, since it has to fight against heavy odds.

It may be of some interest, therefore, to consider the theoretical boundaries of this progress—the limit which cannot be surpassed even by the ingenious methods of organic synthesis. Some years ago Czerny<sup>2</sup> pointed out that in the infra-red region space radiation increases rapidly with the wave-length. Calculating for different infra-red regions the number of quanta incident per  $\text{cm}^2$  per second at room temperature, he found the number  $4.0 \times 10^{10}$  for the region between  $1.5$  and  $2\mu$ , and the number  $2.4 \times 10^{15}$  for the region between  $3$  and  $4\mu$ . The first number he showed to be equal to the infra-red radiation of the same region emitted by a Nernst burner at thirty meters distance, whereas the distance from the Nernst burner would have to be only twelve centimeters for the second number. It is doubtful whether the intensity in the first case would be sufficient to produce an appreciable density even

during a long time—since the law of reciprocity is not valid for photographic exposure. There certainly can be no doubt, however, about the second case, so that the region between  $3$  and  $4\mu$  seems inaccessible for infra-red photography because of the competitive influence of thermal radiation.

Besides the thermal radiation, however, there is yet another possibility, also mentioned by Czerny: the reaction of molecules to which an energy corresponding to infra-red radiation has been imparted in thermal equilibrium. It remains to be seen whether the limit of infra-red sensitizing will not be shifted even nearer to shorter wave-lengths by this reaction than by the influence of space radiation. To answer the question, the velocity of this reaction must be compared with the reaction velocity produced by exposure.

To arrive at this last value it will be assumed that a developable image is obtained after an exposure of a few seconds, so that the plate would already show an appreciable density if exposed to the same radiation for one second. By using the data which Leszynski<sup>3</sup> obtained for exposure of a sensitized plate, the rate of the corresponding primary reaction can be determined. He found that of 150 quanta one was absorbed, and the number of incident quanta per  $\text{cm}^2$  per second (using an energy of  $2.5 HK$ ) could be determined by this formula (p. 266) to be  $9 \times 10^{14}$ , so that  $6 \times 10^{12} = 10^{12.8}$  quanta were absorbed per  $\text{cm}^2$  per second. This actually is the velocity which, according to the assumption, produces a developable density on the plate in one second. It is further assumed that the same number of quanta would be necessary in the

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<sup>1</sup>L. G. S. Brooker and G. H. Keyes, *J. Frank. Inst.* **219**, 255 (1935); W. Dieterle and O. Riester, *Zeits. f. wiss. Phot.* **36**, 68, 141 (1937).

<sup>2</sup>M. Czerny, *Zeits. f. Physik* **53**, 1 (1929).

<sup>3</sup>W. Leszynski, *Zeits. f. wiss. Phot.* **24**, 261 (1927).

infra-red region, which means that the absorption of the sensitizers for their specific regions is taken to be equal, as a first approximation. (This assumption may be wrong by an order of ten, especially as the increase of quanta per energy unit has not been taken into account.)

The velocity of the thermal reaction, on the other hand, can be calculated from the following expression:

$$10^{-Q/4.57T} \cdot v \cdot t \cdot n,$$

where  $Q$  is the energy of the quantum in question, expressed in calories,  $T$ , the absolute temperature,  $v$ , the velocity of the spontaneous reaction,  $t$ , the time in seconds, and  $n$ , the number of sensitizer molecules per  $\text{cm}^2$  surface. The value  $Q$  varies according to the frequency,  $T$  is taken to be room temperature ( $300^\circ$  abs.), and  $n$  is supposed to be  $10^{14}$  for optimum sensitizing, according to Leermakers, Carroll and Staud.<sup>4</sup>

The velocity of the spontaneous reaction,  $v$ , remains to be found. In an early paper, Polanyi and Wigner<sup>5</sup> had assumed that a molecule containing a certain surplus amount of energy would need  $10^{-13}$  seconds for concentrating this energy on a single bond where it could be used as critical activation energy. This rule was found to hold good in many cases, although some exceptions have been pointed out since that time. In a recent paper H. Sachsse<sup>6</sup> expressed the opinion that this time might be much longer for large molecules, and there is a special reason, moreover, to assume this time to be longer in this case—of the order of  $10^{-7}$  to  $10^{-8}$  seconds: the electronic state of the sensitizing dye is changed in the primary reaction, and for this change the energy transfer will be less easy than for the change in a vibrational bond. Volmer and Froehlich<sup>7</sup> found the unusually large value of  $2 \times 10^{-8}$  seconds for the predissociation of  $\text{N}_2\text{O}$ , and G. Herzberg<sup>8</sup> showed that for this molecule predissociation occurred by the crossing of two electronic states.

On inserting the various values for  $v$  in the

<sup>4</sup> J. A. Leermakers, B. H. Carroll and C. J. Staud, *J. Chem. Phys.* **5**, 878 (1937).

<sup>5</sup> M. Polanyi and F. Wigner, *Zeits. f. physik. Chemie* **A139**, 439 (1928).

<sup>6</sup> H. Sachsse, *Zeits. f. physik. Chemie* **B32**, 87 (1936).

<sup>7</sup> M. Volmer and H. Froehlich, *Zeits. f. physik. Chemie* **B19**, 85 (1932).

<sup>8</sup> G. Herzberg, *Zeits. f. physik. Chemie* **B17**, 68 (1932).

formula given above, it becomes obvious that the value  $v = 10^{-13} \text{ sec.}^{-1}$  is much too large. For, if the formula is applied to the wave-length  $1.356\mu$ , the limit which actually has been reached so far in infra-red photography, the velocity of the thermal reaction (the corresponding value for  $Q$  being 20970 cal.) turns out to be

$$10^{-15.3} \times 10^{13} \times 10^{14} = 10^{11.7}$$

reacting molecules per second, only ten times less than the velocity obtained by exposure. This means that within ten seconds of contact with the sensitizer the plate should already obtain an appreciable developable density—which would make it utterly useless for practical purposes. But with  $v = 10^7 \text{ sec.}^{-1}$ , the velocity is

$$10^{-15.3} \times 10^7 \times 10^{14} = 10^{5.7}$$

reacting molecules per second, which corresponds to such a small intensity of exposure that, even with an assumed reciprocity law, the plate would only be affected after a few months; according to the reciprocity law failure, however, no effect should be expected at all.

In the same way the expression for  $1.5\mu$  is found to be

$$10^{-13.8} \times 10^7 \times 10^{14} = 10^{7.2}$$

reacting molecules per second, which is the  $10^{5.6}$  part of the velocity obtained by exposure. Again the reciprocity law failure makes any effect improbable.

For  $2.0\mu$ , however, with  $Q = 14210$  cal., the thermal velocity will be

$$10^{-10.0} \times 10^7 \times 10^{14} = 10^{11}$$

reacting molecules per second, so that within one or two minutes the plate should be affected.

According to this reasoning, infra-red sensitizing should be impractical even at  $2\mu$  where space radiation does not seriously interfere. At slightly shorter wave-lengths, with the plates kept in solid carbon dioxide most of the time, exposure might be used to give a solarized image. The only possibility left for efficient sensitizing at  $\lambda = 2\mu$  and at longer wave-lengths would lie in the existence of dyes with a spontaneous reaction velocity much smaller than  $10^7 \text{ sec.}^{-1}$ . This, however, seems very improbable.