The Calibration of Photographic Emulsions for Electron Diffraction Investigations

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A procedure for calibrating photographic emulsions has been devised which measures the deviation from linearity of the curve relating electron exposure to optical density. The experimental application of this procedure is found to give results consistent with a very simple model of the exposure process. It is also noted that the sensitivity of a photographic plate increases with increasing distance from the center of the plate. Measurements of this effect are given.

IMPROVEMENTS in experimental technique and analysis of data in the field of electron diffraction by gas molecules, most notably in the development of the rotating sector-microphotometer method, have made possible both more reliable and more detailed information about the location of atoms in molecules. Since electron diffraction patterns are recorded on photographic emulsions, it is essential for the most precise work that the response characteristics of the emulsions to exposure by fast electrons be accurately known. It is necessary to have a simple procedure for routine calibration of emulsions to allow for possible fluctuations in photographic materials.

A calibration method has been devised by Karle and Karle[1] for measuring the variation of optical density with exposure to electrons which relies upon the assumption that two gas diffraction plates taken under identical conditions except for exposure time have radial intensity distributions of exactly the same shape. A closely related method has been developed at the University of Michigan which depends upon the same assumption but studies the deviation from linearity of the optical density versus exposure curve. The main advantages of the Michigan method are that errors are more easily recognized and uncertainties averaged out, that the

resulting calibration plot is as sensitive for small as for large optical densities, and that in many cases the conversion of density to exposure can be accomplished very simply analytically, much faster than by graphical procedures. This last advantage is especially important in converting the hundreds of individual values encountered in molecular structure determinations.

The calibration procedure is as follows: Two gas diffraction patterns a and b are prepared so that the exposure of a is twice or somewhat more than twice that of b. The optical density D of each pattern is measured as a function of the radius, r, by a recording microphotometer while the pattern is being spun rapidly about its center of symmetry to average out irregularities in the emulsion.[2] It is desired to find the relation between D and E/D, where E is the exposure, the product of intensity and time. If $F(D)=E/D$, it is seen that the departure of $F(D)$ from constancy is a measure of the deviation from linearity of the D vs E curve. Both D and E are functions of the parameter r. The condition that the radial intensity distributions of a and b are identical in shape is that $E_a(r)=RE_b(r)$, where R is the ratio of the total exposures of the patterns. Figure 1 shows how D_a, D_b, E_a, and E_b vary with r in a typical pair of sectored calibration patterns taken with argon gas. At small D, $D \propto E$ approximately. For convenience the arbitrary proportionality constant is taken to be unity; so to the first approximation $F_0(D)=1$. Since this is a better approximation for b than for a, D_b being less than D_a, an improved approximation $F_1(D)$ can be found by noting that $E_a(r)=RE_b(r)\simeq F_0(D_b)RD_b$ and substituting this information into the defining equation for $F(D)$. The result is that $F_1(D_a)=F_0(D_b)RD_b(r)/D_a(r)$. This procedure for improving $F(D)$ can be carried out indefinitely, for $F_n(D_a)=F_{n-1}(D_b)RD_b(r)/D_a(r)$. In practice this series of approximations converges about as rapidly as the geometric series $\sum_n R^{-n}$. F_∞ can be found graphically or, if F_1 can be fit by a simple function, analytically. For instance, if $RD_b/D_a=1+cD_a$, it follows that
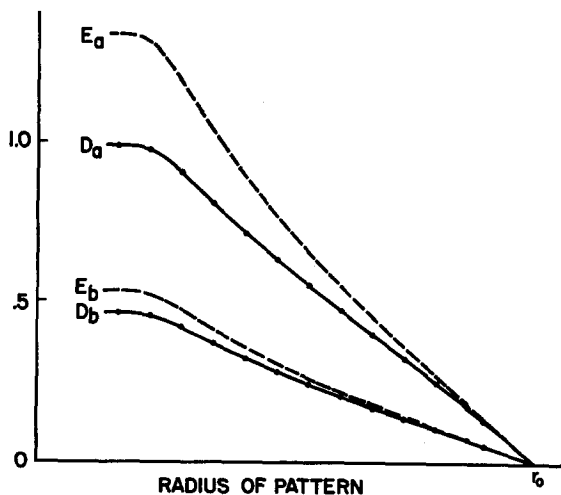

FIG. 1. The radial variation of optical density and exposure in a typical pair of calibration diffraction patterns.

$$\frac{E}{D}\cong 1+\frac{cR}{(R-1)}D+\frac{2c^2}{R^2}\left(\frac{R^2+1}{R-1}\right)D^2.$$

[1] J. Karle and I. L. Karle, J. Chem. Phys. **18**, 957 (1950).

[2] (a) Degard, Pierard, and van der Grinten, Nature **136**, 142 (1935). (b) Karle, Hoober, and Karle, J. Chem. Phys. **15**, 765 (1947).

Figure 2 shows how the $F_n(D)$ were found to vary with D for the patterns in Fig. 1. It is to be emphasized that it is not necessary to know the ratio R in advance. R can be found by extrapolating the experimental function $D_a(r)/D_b(r)$ to $D=0$, but even this is not necessary because it is only the shape of the function $F(D)$ in the range of D covered in the diffraction investigation that is important. Knowledge of the shape of $F(D)$ for D greater than D_m requires knowledge of $D_a(r)/D_b(r)$ from D_a greater than about $D_m/2$.

In order to determine $F(D)$ completely it is necessary that the density of both diffraction plates vary over a large range. On the other hand, it is desirable from photometric considerations regarding accuracy that the density of a pattern to be measured vary between as narrow limits as is possible. A carefully shaped rotating metal mask known as a rotating sector is therefore employed to modify in a known way the intensity of diffracted electrons reaching the photographic plate. The intensity of an unsectored electron diffraction pattern falls off roughly as $r^{-3.5}$, which is too rapid a drop to be suitable for calibration purposes, and the r^3 sector used at Michigan to record molecular diffraction patterns gives too flat a pattern. For these reasons a special calibration sector with an angular opening proportional to $r^3(r_0-r)$ has been constructed that can be easily placed over the regular sector. The diffraction patterns obtained with this sector have the convenient form illustrated in Fig. 1.

It is assumed in the procedure described by Karle and Karle[1] that $F(D)$ is constant from densities of zero to about 0.25 for contrast lantern slides. The method described above does not require this assumption, and the results obtained by it indicate that such an assumption will lead to an error of several percent in the calibration curve at optical densities less than 0.5. For contrast lantern slides it appears that $F(D)=1+cD$, with $c\sim0.3$, for optical densities up to 0.5. It is interesting that this is just the form that would be expected at small D for the following highly simplified model of the exposure process: (A) The photographic emulsion contains grain domains which are completely blackened by the impact of one fast electron and which are unaffected by further impact. (B) The impact of an incident electron affects only one domain. The optical density, which is proportional to the number of blackened grains per unit area, increases less rapidly than the number of electron impacts per area because of multiple impacts upon some of the grains. The relaxation of either condition A or B can result in a decreasing slope for $F(D)$ as D approaches zero. These considerations suggest the possibility of applying this type
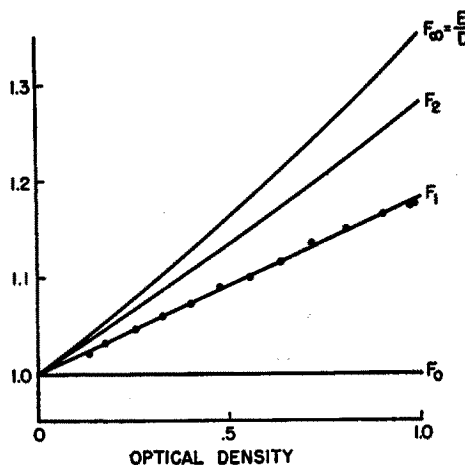

FIG. 2. The variation of $F_n(D)$ with optical density, The circles represent experimental values of RD_b/D_a computed from data plotted in Fig. 1.

of investigation to the study of the mechanism of exposure processes.

Another property of photographic plates that must be taken into account in intensity measurements is that the sensitivity of the emulsion varies with position on the plate. The edges of the plates are more sensitive than the centers. It is well known that mechanical disturbances can render an emulsion more sensitive; cutting and packing the plates with spacers at the edges may account for the variation. In order to get a measure of the magnitude of the effect, some Kodak $3\frac{1}{4}$ in. $\times$ 4 in. lantern slide plates were given uniform photon exposures varying from 0.2 to 1 in optical density and spun rapidly about their centers while being microphotometered on a Leeds and Northrup recording microphotometer. The traces were remarkably smooth but not flat. The variation of sensitivity with the radius r could be expressed by the same relationship for all of the exposures to within several parts per thousand for radii smaller than $3\frac{1}{2}$ cm. If this were not true, the calibration method just described would not be valid. The sensitivity was taken to be the ratio of the apparent exposure $E'(r)$ at r to the apparent exposure at $r=0$, where $E'(r)=D(r)F(D)$. The variation was approximately $E'(r)/E'(0)=1+0.004r^2$ with r in cm. For radii greater than $3\frac{1}{4}$ cm, $E'(r)/E'(0)$ increased more rapidly than $(1+0.004r^2)$, and the experimental points started to scatter.

Although this sensitivity variation is important in the study of scattering of electrons by atoms (to be published), fortunately it does not affect electron diffraction investigations of molecular structure, since such investigations are concerned with the ratio of molecular to atomic intensities rather than with direct intensities.