A statistical treatment of the effect of thermal parameter errors on the value of the residual.

By E. STANLEY,* *College of Science and Technology, Manchester, England*

Introduction

Errors in calculated structure factors can be considered as arising from two sources, the errors in the position of the atoms and errors in the assumed electron-density distribution in the atoms (*i.e.* the f curves). The effect of the former has been treated by Luzzati (1952) and by Stanley (1964). The latter source of error will contain many variables and is not susceptible to a full treatment. There is, however, one error which can be considered. This is the error due to the uncertainty in the thermal parameters.

The distribution of the errors in a structure factor

The structure factor for a centrosymmetric structure can be written as

$$F = \sum_j f_j \cos (2\pi \mathbf{r}_j . \mathbf{s}) \exp (-B_j s^2) . \quad (1)$$

If ΔB_j is the error in B_j, the temperature factor of the jth atom, the calculated value of the structure factor will be

$$F + \Delta F = \sum_j f_j \cos (2\pi \mathbf{r}_j . \mathbf{s}) \exp -(B_j + \Delta B_j) s^2$$

and the error in the structure factor

$$\Delta F = \sum_j f_j \cos (2\pi \mathbf{r}_j . \mathbf{s}) \exp (-B_j s^2) \{\exp (-\Delta B_j s^2) - 1\} . \quad (2)$$

The contribution to the error, ΔF, in the structure factors, by a single atom is

$$\Delta a_j = f_j \cos (2\pi \mathbf{r}_j . \mathbf{s}) \exp (-B_j s^2) \{\exp (-\Delta B_j s^2) - 1\} \quad (3)$$

which has a mean value

$$\langle \Delta a_j \rangle = f_j \cos (2\pi \mathbf{r}_j . \mathbf{s}) \exp (-B_j s^2) \langle \exp (-\Delta B_j s^2) - 1 \rangle . \quad (4)$$

If we call

$$\langle \exp (-\Delta B_j s^2) \rangle = \beta(s)$$

then

$$\langle \Delta a_j \rangle = f_j \cos (2\pi \mathbf{r}_j . \mathbf{s}) \exp (-B_j s^2) (\beta(s) - 1) \quad (5)$$

and the mean square deviation from the mean is given by

$$\langle (\Delta a_j - \langle \Delta a_j \rangle)^2 \rangle$$
$$= \langle f_j^2 \cos^2 (2\pi \mathbf{r}_j . \mathbf{s}) \exp (-2B_j s^2) (\exp (-\Delta B_j s^2) - \beta(s))^2 \rangle$$
$$= \tfrac{1}{2} f_j^2 \exp (-2B_j s^2) (\beta(\sqrt{2}s) - \beta^2(s))$$
$$+ \tfrac{1}{2} f_j^2 \exp (-2B_j s^2) (\beta(\sqrt{2}s) - \beta^2(s)) \cos (4\pi \mathbf{r}_j . \mathbf{s}). \quad (6)$$

The mean value of the error in F will be given by

$$\langle \Delta F \rangle = \sum_j \langle \Delta a_j \rangle = F(\beta(s) - 1) , \quad (7)$$

---

* Present address: Department of Physics, University of Saskatchewan, Regina Campus, Regina, Saskatchewan, Canada.

and the mean square deviation from the mean error in a structure factor is

$$\langle (\Delta F - \langle \Delta F \rangle)^2 \rangle = \sum_j \langle (\Delta a_j - \langle \Delta a_j \rangle)^2 \rangle$$
$$= \tfrac{1}{2} (\beta(\sqrt{2}s) - \beta^2(s)) \{ \sum_j f_j^2 \exp (-2B_j s^2)$$
$$+ \sum_j f_j^2 \exp (-2B_j s^2) \cos (4\pi \mathbf{r}_j . \mathbf{s}) \} . \quad (8)$$

For an infinite number of randomly distributed atoms the second term is zero; for a finite number of atoms, N, it will differ from zero by the order $1/N$. For a reasonably complex structure, then, we can write

$$\langle (\Delta F - \langle \Delta F \rangle)^2 \rangle = \tfrac{1}{2} (\beta(\sqrt{2}s) - \beta^2(s)) \sum_j f_j^2 \exp (-2B_j s^2) . \quad (9)$$

From the central limit theorem (Cramer, 1946) the probability of an error in F between ΔF and $\Delta F + d(\Delta F)$ is

$$P(\Delta F) d(\Delta F) = \{ \pi \Sigma (\beta(\sqrt{2}s) - \beta^2(s)) \}^{1/2}$$
$$\exp \left\{ -\frac{[\Delta F - F(\beta(s) - 1)]^2}{\Sigma (\beta(\sqrt{2}s) - \beta^2(s))} \right\} d(\Delta F) , \quad (10)$$

where $\Sigma = \sum_j f_j^2 \exp (-2B_j s^2)$ (Wilson, 1949).

The value of $\beta(s)$ and $\beta(\sqrt{2}s)$

If $P(\Delta B) d(\Delta B)$ is the probability of an error in temperature coefficient between ΔB and $\Delta B + d(\Delta B)$

$$\beta(s) = \int_{-\infty}^{+\infty} \exp (-\Delta B_j s^2) P(\Delta B) d(\Delta B) . \quad (11)$$

If ΔB is distributed normally with a standard deviation $\sigma(B)$

$$P(\Delta B) d\Delta B = 1/(\sqrt{(2\pi)}\sigma(B)) \int_{-\infty}^{+\infty} \exp (-\Delta B^2/2\sigma^2(B)) d(\Delta B) \quad (12)$$

and

$$\beta(s) = 1/(\sqrt{(2\pi)}\sigma(B)) \int_{-\infty}^{+\infty} \exp (-\Delta B^2/2\sigma^2(B) + \Delta B s^2) d(\Delta B)$$
$$= \exp (\tfrac{1}{2}\sigma^2 s^4) . \quad (13)$$

The corresponding value of $\beta(\sqrt{2}s)$ is given by

$$\beta(\sqrt{2}s) = \exp (2\sigma^2 s^4) = \beta^4(s) . \quad (14)$$

The residual

The residual is a function of both $\sigma(B)$ and s. At a fixed value of $\sigma(B)$ and s the value of

$$R(\sigma, s) = \langle ||F + \Delta F| - |F|| \rangle / \langle |F| \rangle . \quad (15)$$

Unlike errors of position, errors in the temperature coefficients of reasonable magnitude are unlikely to change the sign of a structure factor and little error will be introduced by assuming that

$$R(\sigma, s) = \frac{\langle |\Delta F| \rangle}{\langle |F| \rangle} = \frac{\int_0^{\infty} P(F) \int_{-\infty}^{+\infty} \Delta F P(\Delta F) d(\Delta F) dF}{\int_0^{\infty} F P(F) dF} \quad . \quad (16)$$

The value of the denominator has been evaluated by Wilson (1949) as $\sqrt{(2\Sigma/\pi)}$. Then

$$R(\sigma, s) = \frac{1}{\sqrt{(2\Sigma/\pi)}} \int_0^{\infty} P(F) \int_{-\infty}^{+\infty} \frac{\Delta F}{(\pi \Sigma (\beta^4(s) - \beta^2(s)))^{1/2}}$$

$$\times \exp \left\{ -\frac{[\Delta F - F(\beta(s) - 1)]^2}{\Sigma(\beta^4(s) - \beta^2(s))} \right\} d(\Delta F) dF = \beta(s) - 1 , \quad (17)$$

a result which could have been inferred from (7).

If all the atoms are of the same type the residual can be obtained from

$$R_2 = \frac{\int_0^{s_{max}} 2\pi s R(\sigma, s) f \exp(-Bs^2) ds}{\int_0^{s_{max}} 2\pi s f \exp(-Bs^2) ds} ,$$

and

$$R_3 = \frac{\int_0^{s_{max}} 4\pi s^2 R(\sigma, s) f \exp(-Bs^2) ds}{\int_0^{s_{max}} 4\pi s^2 f \exp(-Bs^2) ds} .$$

in two and three dimensions respectively.

Assuming carbon atoms of the type suggested by Vand, Eiland & Pepinsky (1957) the expressions for R_2 and R_3 have been evaluated over limited ranges of values of $\sigma(B)$ and B within the limits of s given by the Cu $K\alpha$ sphere of reflexion and the results are given in Tables 1 and 2.

Table 1. *Values of the residual R_2 for two dimensions*

$\sigma(B)$ \ B	0·0	2·0	4·0	6·0	8·0	10·0
0·00	0·000	0·000	0·000	0·000	0·000	0·000
0·02	0·016	0·012	0·008	0·006	0·004	0·003
0·04	0·064	0·047	0·033	0·024	0·017	0·012
0·06	0·144	0·105	0·075	0·053	0·038	0·028
0·08	0·256	0·187	0·134	0·095	0·068	0·050
0·10	0·401	0·293	0·209	0·149	0·107	0·078
0·12	0·579	0·423	0·302	0·215	0·154	0·112
0·14	0·790	0·577	0·412	0·292	0·210	0·153
0·16	1·034	0·755	0·539	0·383	0·274	0·200
0·18	1·313	0·958	0·684	0·486	0·348	0·254
0·20	1·627	1·187	0·847	0·601	0·430	0·314
0·25	2·575	1·876	1·437	0·948	0·678	0·494
0·30	3·749	2·729	1·942	1·375	0·982	0·714
0·35	5·188	3·771	2·680	1·894	1·350	0·981
0·40	6·893	5·001	3·548	2·503	1·781	1·292
0·45	8·914	6·455	4·575	3·217	2·285	1·654
0·50	11·257	8·136	5·748	4·036	2·859	2·065

Table 2. *Values of the residual R_3 for three dimensions*

$\sigma(B)$ \ B	0·0	2·0	4·0	6·0	8·0	10·0
0·00	0·000	0·000	0·000	0·000	0·000	0·000
0·02	0·024	0·019	0·015	0·011	0·008	0·006
0·04	0·094	0·075	0·058	0·044	0·033	0·025
0·06	0·212	0·169	0·131	0·099	0·075	0·056
0·08	0·377	0·301	0·233	0·177	0·133	0·100
0·10	0·591	0·472	0·365	0·277	0·208	0·157
0·12	0·852	0·681	0·527	0·400	0·300	0·226
0·14	1·163	0·929	0·719	0·545	0·409	0·308
0·16	1·524	1·217	0·942	0·713	0·535	0·402
0·18	1·935	1·545	1·195	0·905	0·679	0·510
0·20	2·398	1·914	1·480	1·121	0·840	0·631
0·25	3·797	3·027	2·339	1·769	1·326	0·995
0·30	5·534	4·408	3·402	2·570	1·923	1·442
0·35	7·667	6·099	4·702	3·547	2·649	1·983
0·40	10·200	8·102	6·236	4·696	3·502	2·617
0·45	13·209	10·476	8·048	6·049	4·502	3·357
0·50	16·710	13·229	10·143	7·607	5·649	4·203

Comparison with experimental results

The method of refinement proposed and used by Bhuiya & Stanley (1963), in which the thermal parameters associated with each atom are varied in turn about their supposed value in search of a new value giving a lower residual, provides results for comparison.

During the refinement of the individual temperature factors of triphenyl phosphate (Davies & Stanley, 1962) it was observed that, during the first cycle, the root mean square change in B was 0·20. If we regard this as the value of $\sigma(B)$ the corresponding value of R_2 from Table 1, using the observed general temperature coefficient $B = 4\cdot5$, is 0·78%. In fact during this cycle the residual fell from 11·91 to 11·23%, a fall of 0·68%. During the next cycle the root-mean-square change in B was 0·16. The residual fell to 10·86%, a drop of 0·37. The calculated value, from Table 1 was 0·50%.

Since the residual here considered contains 11% of errors arising presumably, from the errors in the observed structure factors, in the f scattering curves and thermal anisotropy, this agreement can only be regarded as confirmation of the order of magnitude of the effect of these errors on the residual.

References

BHUIYA, A. K. & STANLEY, E. (1963). *Acta Cryst.* **16**, 98.
CRAMER, H. (1946). *Mathematical Methods of Statistics.* Princeton Univ. Press.
DAVIES, W. O. & STANLEY, E. (1962). *Acta Cryst.* **15**, 1092.
LUZZATI, V. (1952). *Acta Cryst.* **5**, 802.
STANLEY, E. (1964). *Acta Cryst.* **17**, 1028.
VAND, V., EILAND, P. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303.
WILSON, A. J. C. (1949). **2**, 318.