Then

$$\int_0^\infty Q(X)\,dX = 2\int_0^\infty \left[\int_0^\infty P(F+X)\,dX\right] P(F)\,dF$$
$$= 2\int_0^\infty [1-N(F)]\,P(F)\,dF$$
$$= 2-\Big[N^2(F)\Big]_0^\infty = 1.$$

The mean value of X, required for evaluating R, is

$$\langle X\rangle = \int_0^\infty XQ(X)\,dX$$
$$= 2\int_0^\infty \left[\int_0^\infty XP(F+X)\,dX\right] P(F)\,dF$$
$$= 2\int_0^\infty [\langle|F|\rangle - G(F) - F + FN(F)]\,P(F)\,dF$$
$$= 2[\langle|F|\rangle - \langle G(F)\rangle - \langle|F|\rangle + G(\infty)\,N(\infty) - \langle G(F)\rangle]$$
$$= 2\langle|F|\rangle - 4\langle G(F)\rangle. \qquad (5)$$

The reliability index is therefore

$$R = 2 - 4\frac{\langle G(F)\rangle}{\langle|F|\rangle}. \qquad (6)$$

Since $G(F)$ is necessarily positive, $R<2$ whatever the probability distribution of the structure amplitudes.

For the usual centric and acentric distribution functions $\langle G(F)\rangle$ can be evaluated in terms of Σ, the average value of $|F|^2$ (Wilson, 1949), and more precise numerical values can be assigned to the probable value of R.

In the centric case

$$(\bar{1})\ G(F) = \left(\frac{2}{\pi\Sigma}\right)^{\frac{1}{2}}\int_0^F F\exp\{-F^2/2\Sigma\}\,dF$$
$$= \left(\frac{2\Sigma}{\pi}\right)^{\frac{1}{2}}[1-\exp\{-F^2/2\Sigma\}],$$
$$\langle G(F)\rangle = \frac{2}{\pi}\int_0^\infty [1-\exp\{-F^2/2\Sigma\}]\exp\{-F^2/2\Sigma\}\,dF$$
$$= \left(\frac{\Sigma}{\pi}\right)^{\frac{1}{2}}[\sqrt{2}-1], \qquad (7)$$

$$(\bar{1})\ R = 2\sqrt{2}-2 \doteq 0{\cdot}828, \qquad (8)$$

since $\langle F\rangle = (2\Sigma/\pi)^{\frac{1}{2}}$.

In the acentric case

$$(1)\ G(F) = 2\Sigma^{-1}\int_0^F F^2\exp\{-F^2/\Sigma\}\,dF$$
$$= -F\exp\{-F^2/\Sigma\} + \tfrac{1}{2}(\pi\Sigma)^{\frac{1}{2}}\operatorname{erf}(F/\Sigma^{\frac{1}{2}}),$$
$$\langle G(F)\rangle = -2\Sigma^{-1}\int_0^\infty F^2\exp\{-2F^2/\Sigma\}\,dF$$
$$+\left(\frac{\pi}{\Sigma}\right)^{\frac{1}{2}}\int_0^\infty F\operatorname{erf}(F/\Sigma^{\frac{1}{2}})\exp\{-F^2/\Sigma\}\,dF,$$

which gives, on integration by parts,

$$\langle G(F)\rangle = \left(\frac{\pi\Sigma}{32}\right)^{\frac{1}{2}}. \qquad (9)$$

The value of R is therefore

$$(1)\ R = 2-\sqrt{2} \doteq 0{\cdot}586, \qquad (10)$$

since $\langle|F|\rangle = \frac{1}{2}(\pi\Sigma)^{\frac{1}{2}}$. Thus R for an entirely wrong centrosymmetric structure is $\sqrt{2}$ times as big as for a wrong non-centrosymmetric structure.

Opinions of crystallographers differ whether 0·586 and 0·828 are surprisingly small or about what would be expected for entirely incorrect structures, but the former view appears to be the more prevalent. Certainly it seems that even correct non-centrosymmetric structures and projections will give inherently lower values of R than centrosymmetric, merely because of the lower dispersion of the acentric distribution function. It is therefore necessary to achieve a greater measure of agreement between observed and calculated F's before a non-centrosymmetric structure can be regarded as established.

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Reliability index for centrosymmetric and non-centrosymmetric structures.

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In a discussion of the value of the reliability index for wrong structures (Wilson, 1950), it was suggested that R is inherently higher for reflexions with a centric distribution, even when the structure is nearly correct, merely because of the higher dispersion of the distribution function. Two other properties of the centric distribution tend in the same direction: the smaller value of $\langle|F|\rangle$, and the larger proportion of weak reflexions (and therefore ordinarily the larger proportion of accidental absences). The former reduces the denominator of R and the latter acts mainly by increasing the numerator, though it has a smaller effect on the denominator as well.

For simplicity R will be calculated for a group of reflexions with approximately the same value of $\sin\theta/\lambda$, so that variation of the f's and the temperature factor can be neglected. The variation of R with $\sin\theta/\lambda$ is mentioned briefly below. The effect of $\langle|F|\rangle$ on the denominator is then simple; $\langle|F|\rangle = 0{\cdot}798\Sigma^{\frac{1}{2}}$ for centric distributions and $0{\cdot}887\Sigma^{\frac{1}{2}}$ for acentric (Wilson, 1949). Other things being equal, therefore, R for centrosymmetric structures or projections will be about 10 % of its value larger than for non-centrosymmetric structures or projections.

The effect of accidentally absent reflexions is a little more complicated. If the photographic techniques are

similar, it may be assumed that the minimum structure amplitude observable (F_m) is the same for both distributions at the same $\sin\theta/\lambda$. The absent reflexions then (i) increase R by a direct contribution R', and (ii) increase the value of R that would otherwise be obtained by a fraction approximately R', where

$$R' = \frac{G(F_m)}{\langle |F| \rangle - G(F_m)}, \qquad (1)$$

and $G(F)$ is the function introduced in the preceding communication. In practice $\phi \equiv F_m/\Sigma^{\frac{1}{2}}$ is usually small compared with unity, so that series expansions for R' are more convenient than the explicit functions. For an acentric distribution

$$(1)\, R' = \frac{\operatorname{erf}\phi - 2\pi^{-\frac{1}{2}}\phi\exp(-\phi^2)}{1 + 2\pi^{-\frac{1}{2}}\phi\exp(-\phi^2) - \operatorname{erf}\phi} = \frac{4}{3\pi^{\frac{1}{2}}}\phi^3\left[1 - \frac{3\phi^2}{5} - \frac{4\phi^3}{3\pi^{\frac{1}{2}}} + \ldots\right], \qquad (2)$$

and for a centric distribution

$$(\bar{1})\, R' = \exp(\tfrac{1}{2}\phi^2) - 1 = \tfrac{1}{2}\phi^2[1 + \tfrac{1}{4}\phi^2 + \ldots]. \qquad (3)$$

In typical problems ϕ is 0·1–0·3, giving a contribution to R of 0·001–0·02 units for (1) and 0·005–0·05 units for $(\bar{1})$, and the same fractional increases. Both effects give a relatively larger R for centric distributions.

In general ϕ increases with $\sin\theta/\lambda$, though there may be a decrease again for θ close to $\frac{1}{2}\pi$. The increase in R through absent reflexions is therefore likely to be noticeable for the higher orders of reflexion, particularly for centric distributions. Further, the high-order reflexions form a larger fraction of the whole hkl array than of any zone, so that values of R calculated for all reflexions are likely to be higher than those calculated for zones. This effect may be overshadowed if a zone is centric but the general reflexions are acentric.

Differences of the order of 0·05 unit between the values of R for non-centrosymmetric and centrosymmetric projections have in fact been noticed. Fowweather & Hargreaves (1950) found $(1)\,R = 0{\cdot}13$ and $(\bar{1})\,R = 0{\cdot}17$ in *m*-tolidine dihydrochloride. There is a similar difference between the values of R calculated from the data of Crowfoot, Bunn, Rogers-Low & Turner-Jones (1949, p. 310) for the $(1)\,0kl$ and $(\bar{1})\,h0l$ zones of sodium benzylpenicillin, though the sparsely populated $(1)\,hk0$ zone is anomalous, approximating more closely in its statistical parameters to the $(\bar{1})\,h0l$ zone. Some preliminary work on the intensities of ephedrine hydrochloride (Phillips, unpublished) indicates, however, that the two factors discussed here are insufficient to account in detail for the differences between $(1)\,R$ and $(\bar{1})\,R$, and that the average value of $||F_{obs.}| - |F_{calc.}||$ is larger for $(\bar{1})$ than for (1). This may perhaps be another manifestation of the greater dispersion of the centric distribution, or due to a greater effect on $F_{calc.}$ of errors in the atomic parameters.

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Bemerkungen zur Struktur des Ammoniumtetrametaphosphates.

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Im Anschluss an die Bearbeitung des Natriumtetrametaphosphates (Andress & Fischer, 1949) wurde die Struktur des höhersymmetrischen Ammoniumtetrametaphosphates in Angriff genommen. Bis zum Erscheinen obiger Arbeit wurden unabhängig davon folgende Resultate gewonnen, welche die von MacGillavry & Romers (1949) vollauf bestätigen:

Habitus: rhombisch-holoedrische Bipyramiden.
$a = 10{,}35 \pm 0{,}02$, $b = 10{,}85 \pm 0{,}02$, $c = 12{,}50 \pm 0{,}03$ A.
$\rho_{exp.} = 1{,}77$ (15° C.), $\rho_x = 1{,}84$.
$Z = 4$ $(NH_4)_4[(PO_3)_4]$.
Raumsystem: D_{2h}^{18}–*Cmca*.
Struktur: P_4O_{12}-Ringe der Eigensymmetrie C_{2h}.

Besetzte Punktlagen (gleiche Bezeichnung wie in obiger Arbeit (MacGillivary & Romers, 1949)) und deren x-Parameter:

Atomart	Punktlage	x-Wert
P_I	8*f*	0
P_{II}	8*d*	0,209 ± 0,003
O_I	8*f*	0
O_{II}	8*f*	0
O_{III}	16*g*	0,279 ± 0,003
O_{IV}	16*g*	0,116 ± 0,001
N_I	8*f*	0
N_{II}	8*e*	0,250

Als Grundlagen der Punktlagenbesetzung dienten neben Raumerfüllungsbetrachtungen die am Natriumtetrametaphosphat (Abdress & Fischer, 1949) gewonnene Erkenntnis, dass es sich beim Anion um einen P_4O_{12}-Ring handelt.

Bei der Ermittlung der x-Parameter wurde wie folgt vorgegangen:

(1) O_{IV} ist als Ringglied des Anions in seinem x-Wert auf Grund des Ionenradius des Sauerstoffions für die Koordinationszahl 2 stark eingeschränkt:

$$0{,}11 < x(O_{IV}) < 0{\cdot}125.$$

(2) Da (12.0.0) zufällig ausgelöscht ist und die x-Koordinaten von P_I, O_I, O_{II}, N_I und N_{II} festgelegt sind, muss die Summe der Teilstrukturvektoren von P_{II}, O_{III}, O_{IV} gleich dem negativen Wert der Summe der Teilstrukturvektoren der übrigen fünf Atomarten sein. Dies schränkt die Möglichkeiten für $x(O_{IV})$ weiter ein:

$$0{,}116 < x(O_{IV}) < 0{,}134.$$

Insgesamt ist also $x(O_{IV})$ nur noch zwischen 0,116 und 0,125 variabel.

(3) $x(O_{IV})$ wurde nun systematisch variiert, und für jedes $x(O_{IV})$ wurde $x(O_{III})$ als Funktion von $x(P_{II})$ auf-