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Scale Errors in Experimental Scattering Curves for Sulphur

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Megaw's (1958) suggestion that the accumulation of experimental scattering curves may be a means of checking the adequacy of theoretical *f*-curves requires that the scale of experimental data used for deriving scattering curves be on a strictly absolute basis. This is considered in terms of two curves for S derived from structure analyses of thiophthen, $C_6H_4S_2$, and orthorhombic sulphur, S_8. A simple test shows that, in both cases, the scale of the data must have differed considerably from the absolute basis. Other aspects of the derivation from S_8 are discussed, and used in estimating the scale error by means of a suitably-weighted *f*-curve analysis. This scale error is found to be approximately twenty-five per cent. Essentially the same error applies to the thiophthen data. The greater difficulty of scattering-curve derivation in this heteroatomic system is illustrated by the difference in scale estimate given by analysis of the scattering curve for C also derived from thiophthen.

After correction for scaling effects in the curve from S_8, the experimental results compare satisfactorily with temperature-modified (by $\exp[-B\sin^2\theta/\lambda^2]$) poly-detor ($B=3\cdot70$ Å^2) and James & Brindley ($B=3\cdot59$ Å^2) *f*-curves over the range of $\sin\theta/\lambda$ chosen for the scale analysis. The low-angle region of the experimental curve is discussed in terms of Megaw's suggestion, and the high-angle region considered in terms of the likelihood that the atomic coordinates of S_8 determined by use of this curve may be in error.

Introduction

In reporting new atomic scattering factors (*f*-curves) for the second-row members Cl, Cl$^-$, S and S$^-$ (Dawson, 1960) (hereafter D) the potential deficiencies in *f*-curves based either directly or by interpolation on models which neglect electron correlation effects (e.g. Hartree (H)-type models) were discussed, and the magnitudes of these deficiencies in the James & Brindley (1931) (hereafter JB) values for Cl, Cl$^-$ and S shown to be considerable (Fig. 1 of D). In principle, experimental scattering curves derived from long-spacing structures in centrosymmetric space groups should bypass any such deficiencies in existing *f*-curves. The derivations will refer to atoms in the solid state but, in most cases, any large differences between experimental results and theoretical *f*-curves should be relatable primarily to inadequacies in the isolated-atom models upon which the latter are based. The usefulness of experimental procedures in this regard has been noted by Megaw (1958).

In practice, experimental derivations from the F_o data given by a structure will depend, among other things, on the scale of the F_o's being adjusted to a strictly absolute basis. The two scattering curves for S to be discussed here, from orthorhombic sulphur, S_8 (Abrahams, 1955) (hereafter A), and thiophthen, $C_6H_4S_2$ (Cox, Gillot & Jeffrey, 1949) (hereafter CGJ), provide striking examples of how scale errors in the data can affect the detection and correction of deficiencies in existing *f*-curves, which in these cases were the JB or Viervoll & Øgrim (1949) curves.

The experimental scattering curves for S

The curves derived from these structures both referred to S under thermal motion. The high-angle regions of the two curves differed slightly due to different temperature factors, but otherwise the results were essentially the same (see Fig. 3 of A). Only one curve, and the structure analysis leading to it, need therefore be considered in detail, and we choose here the later investigation of S_8 since this is free of any complications in scattering-curve derivation arising from the presence of other atoms of different scattering power. However, any modifications of these considerations in the case of thiophthen will be noted where necessary.

No numerical values of the experimental curve obtained from S_8 (to be denoted as f_{exp}) were recorded by A, but these may be estimated from his Fig. 3. There, f_{exp} is compared with the temperature-modified JB curve ($B=3\cdot25$ Å^2 in $\exp(-Bs^2)$, where $s=\sin\theta/\lambda$), and the curve of the numerical results obtained for S in thiophthen (Table 3 of CGJ). Values of f_{exp} as estimated with the aid of these reference curves are given in Table 1. The derivation of f_{exp} was based on three-dimensional data collected with Mo $K\alpha$-radiation, and it was noted that part of the considerable difference between f_{exp} and the above JB curve might reflect uncertainty, quoted as possibly 5%, in the scale of the data used in the derivation.

Preliminary estimate of scale accuracy in the S_8 *data*

A rough test of scale accuracy can be obtained from the fact that, although the values of an experimental scattering curve will be generally higher than those of a deficient f-curve, they must be smaller than those of any f-curve for the atom next but one up in atomic number. The test can be made more restrictive if an accurate f-curve is available for the adjacent atom of higher atomic number, although considerable latitude in scale estimate must still remain if the test is satisfied in this case. Only f-curves in the normal spherically-averaged approximation need be considered since this approximation is usually imposed on an experimental derivation to make best use of the low-angle data available.

Fig. 1(a) shows this test applied to the values of f_{exp} in Table 1, by comparing them with accurate f-curves for chlorine and argon suitably modified by temperature factors (with $B=2{\cdot}90$ and $3{\cdot}00$ Å^2 respectively) to bring their high-angle regions into approximate coincidence with each other and with f_{exp}. The chlorine curve is from the poly-detor (PD) model used by D, and the argon curve from the Hartree–Fock (HF) model used by Berghuis *et al.* (1955), so that the test here for f_{exp} is in the form most likely to be satisfied. However, both curves are markedly exceeded, and no essential change occurs on reducing the values of f_{exp} by 5%. Consequently, the error in the scale of the S_8 data associated with the experimental derivation must be considerable.

Table 1. *The experimental scattering curve* f_{exp} *from orthorhombic* S_8

$\sin\theta/\lambda$ (Å^{-1})	f_{exp}	$\sin\theta/\lambda$	f_{exp}
0·00	(16·0)	0·45	4·5
0·05	15·6	0·50	$3{\cdot}6_5$
0·10	$14{\cdot}8_5$	0·55	$2{\cdot}8_5$
0·15	13·8	0·60	$2{\cdot}2_5$
0·20	$12{\cdot}3_5$	0·65	$1{\cdot}7_5$
0·25	$10{\cdot}5_5$	0·70	1·4
0·30	$8{\cdot}7_5$	0·75	1·1
0·35	7·0	0·80	$0{\cdot}8_5$
0·40	5·6		

The failure of this test shows that f_{exp}, viewed as an experimental scattering curve for S, is without physical meaning and therefore has no value in terms of Megaw's (1958) suggestion. The low-angle values of f_{exp} must represent only the bias to the atomic number ($Z=16$) at $s=0$ that may be assumed because of the overall neutrality of the S_8 system. This bias will not influence the values of f_{exp} at higher angles, however, so that relating them to the PD f-curve in D should permit reliable estimation of the actual scale error in the S_8 data, provided that it can be assumed that only the effects of some isotropic thermal motion are present in f_{exp}. The validity of such a scale estimation must therefore depend on whether Abraham's analysis of the S_8 structure was such as to produce f_{exp} values independent of the 'structural' details associated with atomic positions and individual thermal motion.

The structure analysis of S_8

The influence of atomic positions, thermal motion and scaling in the F_o data associated with the S_8 structure can be expressed, using a discrete-atom relation, by

$$KF_o(hkl) = \sum_i f_i^o(hkl)T_i(hkl)\cos 2\pi(hx_i+ky_i+lz_i)\,, \quad (1a)$$

where K is the scale factor, $f_i^o(hkl)$ is the at-rest scattering power of each atom for the (hkl)th reflexion, and $T_i(hkl)$ is the modification of this scattering power produced by thermal motion about the point, with fractional coordinates x_i, y_i, z_i, which defines the atom position, i.e. the position of the time-averaged maximum of the electron-density distribution of the atom. The basis for assessing f_{exp} in Abraham's analysis of S_8 is then obtained from equation (1a) by: (i) ignoring the presence of any intrinsic asymmetry in each f_i^o; (ii) assuming that all S atoms then have the same at-rest spherically-averaged scattering power $\bar{f}^o$; (iii) regarding the individual temperature factors T_i in the form $T_i=\overline{T}\,.\,\Delta T_i$, where $\overline{T}$ is an average isotropic temperature factor for all S atoms and the ΔT_i are residual temperature factors for the individual atoms. Equation (1a) then becomes

$$KF_o(hkl) = f(s_{hkl})\sum_i \Delta T_i(hkl)\cos 2\pi(hx_i+ky_i+lz_i)\,, \quad (1b)$$

where $f(s)=\bar{f}^o(s)\overline{T}(s)$, with $\overline{T}(s)=\exp(-\overline{B}s^2)$: assuming ellipsoidal vibration of each atom, the residual temperature factors will have the general form

$$\Delta T_i(hkl)=\exp(-\alpha_i h^2-\beta_i k^2-\gamma_i l^2-\delta_i hk-\eta_i hl-\varepsilon_i kl).$$

Provided K, the x_i *etc.* and the ΔT_i are known, the determination of $f(s)$ will be independent of structural details in S_8, since negligible error should exist in replacing the true Fourier transform relation between this structure and its F_o data by the discrete-atom relation (1a).

The approach used by Abrahams in obtaining f_{exp} was rather different from that demanded by the form of equation (1b). He assumed that the ΔT_i were zero, and, using Warren & Burwell's (1935) results for S_8, then refined atomic coordinates, x_{ic} *etc.*, in terms of the equation

$$F_c(hkl)=f_{\text{exp}}(s_{hkl})\sum_i \cos 2\pi(hx_{ic}+ky_{ic}+lz_{ic})\,. \quad (2)$$

Successive versions of f_{exp} were employed, these being derived by dividing the observed structure factors ($KF_o(hkl)$) by the trigonometric parts of equation (2), grouping the results obtained over small ranges of $\sin\theta$, averaging them, and then drawing a smooth curve through the averaged results: apart from the use of different x_{ic} *etc.*, the final f_{exp} (Table 1) differed from the earlier versions in that the scale of the experimental data was reduced by 5%. (For details on the initial choice of scale and this modification see

§ 5 of A.) The initial assumption that the ΔT_i were zero was taken as justified when subsequent use of f_{exp} to determine the $\alpha_i, \beta_i, \gamma_i$ components (the remaining cross-terms were neglected) gave results of trivial magnitude (§ 7 of A).

Since Abrahams's derivation procedure for f_{exp} cannot define the influence of K and yet will be biased to $Z=16$ at $s=0$, the process of refining the x_{ic} and the experimental curves in this mutual fashion is rather circular, as errors in the one will affect the other. Also, if the ΔT_i are not negligible, their neglect in equation (2) may result in their inclusion, to some extent, in the experimental curves so derived. Subsequent use of such a curve to detect α_i *etc.* is, thus, again a circular process, so that Abrahams's demonstration of the trivial nature of the axial components of the ΔT_i must be of dubious value. Both coordinate and individual thermal motion effects will be greatest in the high-angle values of f_{exp} so that these, like the low-angle values, are not suitable for estimating K, and only the middle range of values can be taken as useful in this regard.

The scale error in the S_8 *data*

As a practical compromise, the range $0{\cdot}30 \le s \le 0{\cdot}60$ Å^{-1} was chosen for estimating K from f_{exp}. In this range, $\bar{f}^o$ in f of equation (1*b*) will be closely satisfied by the ground-state PD curve f^o_{PD}, so that we can write $f(s)=f^o_{\text{PD}}(s)\exp(-Bs^2)$. Then assuming that f', the experimental approximation to f, is given by $f'(s)=kf_{\text{exp}}(s)$, we can determine k and B by least squares, using the relation

$$kf_{\text{exp}}(s)=f^o_{\text{PD}}(s)\exp(-Bs^2) \qquad (3)$$

in the form $X(s)=A-Bs^2$, where $X=\ln[f_{\text{exp}}/f^o_{\text{PD}}]$ and $A=\ln k^{-1}$. The quantity minimized will be

$$R=\sum_s \{w(s)\ln[f(s)/f'(s)]\}^2$$

according to the weights $w(s)$ assigned to the observational equations at the s-intervals chosen for the calculation. The value of k (and B) will vary with $w(s)$, and proximity to the desired K (and $\bar{B}$) will then depend on the suitability of the $w(s)$ scheme used.

There are two requirements that the weights must attempt to satisfy. Firstly, the proximity to K of k, which is derived from an f-curve analysis, will depend on $w(s)$ simulating the relative frequencies with which the various $f(s)$ values occur in different s-ranges of the F_o data. For example, in complete three-dimensional data the scheme $w(s)=s^2$ would be appropriate, but for S_8 this scheme is not suitable owing to the accidental absences present among the data. A count of the numbers $N(x)$ of measured F_o's (Table 9 of A) in s-ranges of 0·1 Å^{-1} centred about $s=x$ gives 11(0·1), 41(0·2), 86(0·3), 132(0·4), 177(0·5), 165(0·6), 55(0·7) and 2(0·8)—totalling the 669 reflexions measured. (Ignoring the last two ranges, the potential numbers are 12, 44, 91, 170, 259, 368.) Thus here the two simple schemes $w(s)=1$ and $w(s)=s$ will straddle the actual count in the range $0{\cdot}30 \le s \le 0{\cdot}60$ Å^{-1} used for k, with the latter scheme being the more appropriate. The second requirement of the weights is that they must ensure the validity of k itself. This validity depends on the assumption $f'(s)=kf_{\text{exp}}(s)$ being true over the least-squares range, and is related to whether all high-angle 'structural' detail in f_{exp} has become negligible at the upper end of this range. Minimizing the influence on k of any failure in this assumption thus requires that reduced weight be given to the values of f_{exp} at this end of the range. These two opposing weighting requirements therefore suggest that k for $w(s)=1$ will be a more reliable estimate of K than k for $w(s)=s$, even though the differences between the k's are small.

Using unit weights and taking values of X at intervals of 0·05 in s (the necessary f^o_{PD} being obtained directly or by interpolation from Table 2 of D), the least-squares results are $k=0{\cdot}759$ and $B=3{\cdot}70$ Å^2. Since k and K are unity for absolute scaling, the departure from this value shows that the scale of the S_8 data used in extracting f_{exp} was some 25% too high. (Extension of the range to include X at $s=0{\cdot}20$ and 0·25 Å^{-1} modifies the results only fractionally, to $k=0{\cdot}764$ and $B=3{\cdot}68$ Å^2, but this extension of the f-curve analysis is not valid as f_{exp} at $s=0{\cdot}20$ Å^{-1} is affected by the low-angle bias mentioned earlier). The effect of weighting scheme on this scale estimate is shown by replacing $w(s)=1$ by $w(s)=s$: $k=0{\cdot}776$ and $B=3{\cdot}61$ Å^2 are then obtained.

The scale error in the thiophthen data

A similar result is obtained here from the scattering curve for S in Table 3 of CGJ, although the average temperature factor is somewhat different. Using unit weights over the range $0{\cdot}3 \le s \le 0{\cdot}6$ Å^{-1} the values of k and B are 0·76 and 3·34 Å^2. Unit weights are taken here since, with the upper limit of CGJ's Table 3 the same as the upper limit of the range for k, greater use is being made of that region of the experimental curve most susceptible to coordinate and ΔT_i effects. The influence of these effects will therefore be minimized but, as no F_o-table is available for an $N(x)$ count in thiophthen, the scale estimate given by k must be regarded as less reliable than that obtained for S_8.

A further reason for the lower reliability lies in the difficulty of deriving a satisfactory scattering curve when other atoms of different scattering power are present. This is shown by the unfavourably different value of k which applies to the curve for C also derived from thiophthen. If the HF f-curve of Berghuis *et al.* (1955) is used as reference over the above range the value of k (and B) is then 0·72 (and 3·52 Å^2). Variation of the range affects the two values of k (and B) to a minor degree, but k for C is always smaller than k for S; and the differences become slightly greater if the HF curve is replaced by McWeeny's (1951) valence-state curve or the effective scattering curves, f_e^o, of McWeeny (1954). Although these differences will be affected by rounding-off errors in the values listed by CGJ to the first decimal place, the fact that k for C should be *larger* than the above k for S, which ignores the influence of anomalous-dispersion effects in the experimental results (see below), provides some confirmation of the greater difficulties of derivation in heteroatomic systems and hence of the lower reliability of these curves as a means of estimating the actual scale error in the thiophthen data.

Discussion

Fig. 1(b) compares the values of f_{exp}, before and after scaling with $k=0{\cdot}759$, with the PD curve for $B=3{\cdot}70$ Å^2 and the JB curve for $B=3{\cdot}59$ Å^2. The Δf differences ($f_{\text{JB}}-f_{\text{PD}}$) in these two curves are shown on an enlarged (ten times) vertical scale in Fig. 1(c), together with the at-rest differences ($f_{\text{JB}}^o-f_{\text{PD}}^o$): the latter Δf-curve is as in D, apart from the shorter s-range here. Fig. 1(b) also shows an empirical scattering curve (Dawson, 1956, unpublished), with $B=3{\cdot}59$ Å^2, to illustrate the usefulness of considering potential deficiencies in existing f-curves as a means of assessing the validity of experimental curves more critically than is possible by comparison with an accurate f-curve for the atom of next highest atomic number (i.e. Fig. 1(a)). The empirical curve was obtained by increasing the values of the JB curve in the region $0<s<0{\cdot}4$ Å^{-1} by slightly more than the difference between the HF and H results for Cl$^-$: it was used in most stages of the analysis of tosyl-L-prolyl-L-hydroxyproline monohydrate (Beecham, Fridrichsons & Mathieson, 1958; and to be published).

The general agreement between experimental and theoretical f-values in Fig. 1(b) over the range used for establishing k confirms that the main source of error in f_{exp} was the scale of the S$_8$ data. The details of the agreement in this range are sensitive to the value of k associated with f_{exp}, so that Fig. 1(b) must reflect both the weighting scheme used and any uncertainties in the values of Table 1, such as those of estimation from A's Fig. 3 or those of 'structural' origin discussed earlier. Fractionally, such uncertainties (particularly of estimation) will be more important in the higher parts of the least-squares range, but their influence on k will affect more strongly the magnitudes of the details in the lower parts of this range. Since these details must also reflect any errors associated with the actual grouping and averaging procedure used in extracting f_{exp} from the data (see earlier), their general smallness can be regarded as confirming Abrahams's assessment (§ 3) that the measurement-reliability of the data was quite satisfactory. It is unlikely that the details in this range are in any way related to bonding effects not included in the PD curve. McWeeny's (1954) examination of the light-atom cases more favourable for detecting bonding details shows that, even in the most advantageous at-rest condition, spherically-averaged scattering curves for isolated atoms (in their ground or valence states) and bonded atoms differ only slightly.

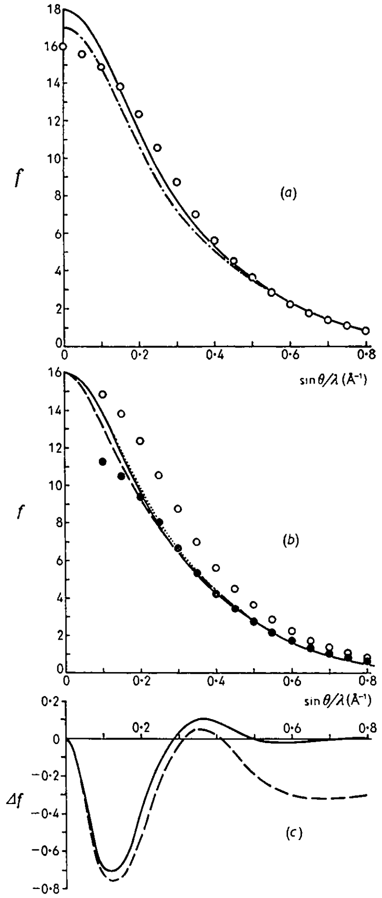

Fig. 1. (a) Comparison of f_{exp} (open circles) with f-curves of Cl (chain line) and Ar (full line) modified by isotropic temperature factors with $B=2{\cdot}9$ and $3{\cdot}0$ Å^2 respectively. (b) The result (closed circles) of scaling f_{exp} (open circles) by $k=0{\cdot}759$. The full line is the poly-detor f-curve of S for $B=3{\cdot}70$ Å^2, the broken line the JB f-curve for $B=3{\cdot}59$ Å^2 and the dotted line an empirical scattering curve for $B=3{\cdot}59$ Å^2. (c) Departures Δf of the JB f-curve from the poly-detor f-curve. The dotted line applies to conditions of zero thermal motion, and the full line to the thermal conditions relevant to (b).

The requirement of absolute scaling in experimental procedures aimed at defining and correcting deficiencies in f-curves based on inadequate models (i.e. Megaw, 1958) is shown strikingly by the failure of f_{exp} over the inner range of Fig. 1(b). From the Δf-curves of the JB scattering factor for S in Fig. 1(c), it is seen that, in general, only the low-angle deficiencies of an inaccurate f-curve will be amenable to experimental detection. Those at higher angles will be minimized by temperature-factor adjustment, and their detection thereby rendered more difficult, or, in cases of strong thermal motion, virtually impossible. Thus it is mainly the low-angle data that are of potential value in deriving experimental curves. Their exploitation for this purpose will depend on the establishment of absolute scaling since otherwise any assumptions regarding the state of ionization will influence the credence placed on the experimental results. In S_8, where some fifty to one hundred terms are potentially valuable, Fig. 1(*b*) shows that the bias to $Z=16$ at $s=0$ must have led to the discarding of most of the useful experimental information. The alternative, that the low-angle region of Abrahams's curve represents the effects of inaccuracies in the S_8 data here, is hardly consistent with the evidence of measurement-reliability obtained at higher angles. This example of scale effects is an extreme one, however, as even small departures from the absolute basis can affect the proper detection of low-angle deficiencies. The influence of these errors, which may arise, for instance, from the use of internal scaling procedures based on the inadequate *f*-curves whose subsequent correction is contemplated, will be considered separately. Equally stringent scaling requirements obviously apply to those cases where low-angle data may be used, in association with *f*-curves adequate except for the state of ionization they represent, to determine the actual conditions of ionization present.

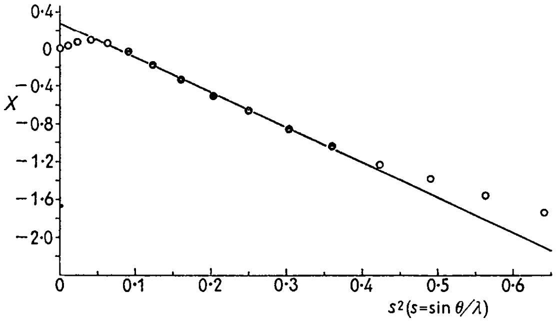

Fig. 2. The plot of $X(s)$ versus s^2 and comparison with the straight line for $k=0{\cdot}759$ and $B=3{\cdot}70$ Å, to illustrate the 'structural' detail in the high-angle region of f_{exp}. Hatched circles are the values of X used to determine k and B.

The results of A's use of equation (2), leading to the omission of the high-angle region of f_{exp} from the analysis for k, are shown in Fig. 2. Here $\ln[f_{\text{exp}}/f^o_{\text{PD}}]$ for all values of s in Table 1 are plotted against s^2, and compared with the straight line for $k=0{\cdot}759$ and $B=3{\cdot}70$ Å^2. This comparison is related to that in Fig. 1(*b*): it shows the failure of the low-angle region of f_{exp} and the good agreement over the range used for the scale analysis, although neither of these features, and particularly the former with its implications for Megaw's (1958) suggestion, are as apparent as in Fig. 1(*b*). However, Fig. 2 does show clearly that incorporation of the high-angle values of f_{exp} in the scale determination would result in a rapid worsening of the agreement obtained in the middle range of s. Hence, unless the measurement-reliability of the data deteriorates suddenly when $s>0{\cdot}6$ Å^{-1} or unless this region of A's Fig. 3 does not correspond to the values of f_{exp} actually obtained, the increasing deviation in Fig. 2 of the points at $s=0{\cdot}65$, 0·70 and 0·75 Å^{-1} (that at 0·80 Å^{-1} is dubious because of the $N(x)$ count) must cast doubt on whether the final x_{ic} *etc.* obtained with equation (2) are the best that the data can produce, for any of the $w(hkl)$ schemes tested by A (§ 7). The other possibility is that these deviations may represent only some build-up in f_{exp} of the α_i *etc.* components of the ΔT_i in equation (1*b*) due to the distribution of missing reflexions in this region of the data: in this case the failure of A's use of f_{exp} to detect significant thermal anisotropy in the individual atoms is understandable. It is more likely, however, that both these 'structural' influences are reflected in this region of f_{exp}. In view of the importance of the S–S bond length in S_8 (§ 12 of A), it is therefore desirable that the atomic coordinates and individual thermal motion be determined with a reliable *f*-curve.

Conclusion

The approximations to K given by the analyses for k are modified slightly when anomalous dispersion effects are considered. However, these effects have no influence on the details of the agreement in Fig. 1(*b*) or Fig. 2 discussed above. The result of replacing f^o in equation (3) by $|f|^o$ (James, 1948) can be shown by writing

$$|f|^o(s)=(1+\delta k)f^o(s)\exp(+\delta B s^2)\,. \qquad (4)$$

Using $\Delta f'_K=+0{\cdot}12$ and $\Delta f''_K=+0{\cdot}10$ for S with Mo-radiation (see James, 1948), and solving for δk and δB by least squares, using unit weights and 0·05 intervals in the range $0{\cdot}05\le s\le 0{\cdot}80$ Å^{-1}, we obtain $\delta k=+0{\cdot}0099$ and $\delta B=+0{\cdot}0243$ Å^2. Inserting these in equation (4), the difference (RHS − LHS) has a maximum value of only −0·04 electrons at $s=0$, falls rapidly to zero at $s\approx 0{\cdot}22$, rises to just over +0·01 electrons at $s\approx 0{\cdot}36$, and then diminishes: these results show that neglect of the 'point-atom' contribution of small K-electron anomalous scattering can be compensated almost entirely by slight scale and temperature-factor adjustments. In monatomic S_8 the effect of this scale change is virtually negligible, and, for Fig. 1(*b*), the replacement of k, B and f^o by the more correct $(k+\delta k)$, $(B+\delta B)$ and $|f|^o$ will have no effect on the magnitudes of the details there, since these are for strong thermal motion which reduces greatly, except for $s=0$, the differences between f^o and $|f|^o$ given above.

In the case of thiophthen where Cu $K\alpha$-radiation was used by CGJ, the compensation of the larger anomalous dispersion contribution by scale and temperature factor adjustment to f^o is not quite so adequate. For $\Delta f'_K=+0{\cdot}3$ and $\Delta f''_K=+0{\cdot}5$ (see James, 1948) and use of the range $0{\cdot}05\le s\le 0{\cdot}65$ Å^{-1}, the values of δk and δB are $+0{\cdot}024$ and $+0{\cdot}074$ Å^2: their use in equation (4) gives differences of essentially the same pattern as quoted above, but slightly more than twice the magnitude. This value of δk is still sufficiently small not to affect seriously the estimate of K in thiophthen given by the earlier analysis of the S curve. However, the replacement of k for S there by the more correct $(k+\delta k)$ worsens rather than improves the agreement with k obtained from the C curve. Hence, it follows that the influence on scaling of even small dispersion effects (for the case of larger effects see Clark, Templeton & MacGillavry, 1958) needs consideration in any detailed structure analysis of a heteroatomic compound, particularly if experimental f-curve derivation is intended (Jellinek, 1958).

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X-ray Crystal Analysis of the Substrates of Aconitase.*
I. Rubidium Dihydrogen Citrate

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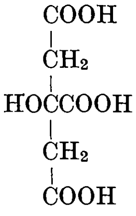
Rubidium dihydrogen citrate crystallizes in the space group $P2_1/a$ with 12 molecules in a cell of dimensions

$$a=14{\cdot}924,\quad b=9{\cdot}710,\quad c=19{\cdot}145\ \text{Å}\ (\pm0{\cdot}2\%),\quad \beta=108{\cdot}63^\circ\ (\pm0{\cdot}10^\circ)\,.$$

Reflections hkl with $l \neq 3n$ are very much weaker than those for $l=3n$. An approximate analysis was made on the basis of a cell for which $c=19{\cdot}145/3=6{\cdot}382$ Å. The structure was refined by difference Fourier methods on the $hk0$ and $h0l$ projections. A general description of the relative orientation of the groups within the citrate ion is given and the hydrogen bonding between ions is discussed. The rubidium ion is coordinated with nine oxygens and all oxygens take part in the coordination.

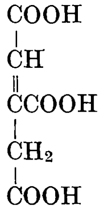
Introduction

It has been demonstrated (cf. e.g. Ochoa, 1951) that the enzyme aconitase catalyzes the establishment of equilibrium between the ions of citric acid (I), *cis*-aconitic acid (II), and *d*-isocitric acid (III). A particularly interesting aspect of this process lies in the fact that only one of the four possible optical isomers of the isocitrate ion is made from optically inactive citrate. Although it has been generally supposed that a single enzyme is responsible for this equilibrium there is evidence (Neilson, 1955) that in some organisms two enzymes may be involved. The transformation of citrate to isocitrate catalyzed by aconitase



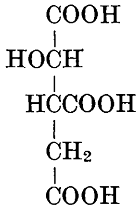
$$\begin{array}{c}\mathrm{COOH}\\ | \\ \mathrm{CH_2}\\ | \\ \mathrm{HOCCOOH}\\ | \\ \mathrm{CH_2}\\ | \\ \mathrm{COOH}\end{array}$$

I



$$\begin{array}{c}\mathrm{COOH}\\ | \\ \mathrm{CH}\\ \| \\ \mathrm{CCOOH}\\ | \\ \mathrm{CH_2}\\ | \\ \mathrm{COOH}\end{array}$$

II



$$\begin{array}{c}\mathrm{COOH}\\ | \\ \mathrm{HOCH}\\ | \\ \mathrm{HCCOOH}\\ | \\ \mathrm{CH_2}\\ | \\ \mathrm{COOH}\end{array}$$

III

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