The Formulation of the Acidity Function J_0.

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The exact relationship between the acidity functions H_0 and J_0 is defined. The applicability of several approximate relations for the calculation of J_0 is examined by reference to recent photometric data on ionisation of alcohols in sulphuric acid.

The difference between the calculated approximate J_0 functions and the experimental scale is thought to arise from the variation of acidity coefficient terms with the composition of the aqueous acid. On this basis, the dependence upon composition of certain combinations of activity coefficients in aqueous sulphuric acid has been determined.

Equations of General Validity.—It is the object of the acidity function J_0 (Gold and Hawes, *J.*, 1951, 2102) to provide a quantitative scale for the acidity of a medium towards secondary bases, *i.e.*, bases which ionise according to the general equations

$$\mathrm{ROH} + \mathrm{HA} \rightleftharpoons \mathrm{R}^+ + \mathrm{A}^- + \mathrm{H_2O} \qquad (1)$$

or

$$\mathrm{ROH} + 2\mathrm{HA} \rightleftharpoons \mathrm{R}^+ + 2\mathrm{A}^- + \mathrm{H_3O}^+ \qquad (2)$$

This acidity depends on the composition of an acidic medium in a different manner from that which governs the ionisation of primary (or Brønsted) bases. A number of recent papers have dealt with applications of the J_0 function, and this interest has prompted the present re-examination of its formulation and the discussion of certain assumptions which were not considered in detail in the earlier paper.

The definition of the J_0 function is contained in equations (3), (4), and (5) :

$$[\mathrm{R}^+]/[\mathrm{ROH}] = j_0 K_{\mathrm{ROH}} \qquad (3)$$

$$J_0 = -\log_{10} j_0 \qquad (4)$$

$$J_0 = -\mathrm{p}K_{\mathrm{ROH}} + \log\,[\mathrm{ROH}]/[\mathrm{R}^+] \qquad (5)$$

with the condition

$$J_0 \longrightarrow H_0 \text{ as } H_0 \longrightarrow \mathrm{pH} \qquad (6)$$

K_{ROH} is a constant expressing the strength of the secondary base ROH. Equations (3)—(5) are analogous to the expressions defining the H_0 function

$$[BH^+]/[B] = h_0K_b^B \tag{7}$$

$$H_0 = -\log_{10}h_0 \tag{8}$$

$$H_0 = -pK_b^B + \log [B]/[BH^+] \tag{9}$$

Equations (3)—(6) are regarded as the ultimate definition of J_0. Like the definition of H_0, it is based on the experimental measurement of ionisation ratios of indicators. Measurements of this type have been carried out by Murray and Williams (*J.*, 1950, 3323), Bevan and Williams (*Chem. and Ind.*, 1955, 171), Gold and Hawes (*loc. cit.*), and Deno, Jaruzelski, and Schriesheim (*J. Org. Chem.*, 1954, **19**, 155), but the published data do not as yet suffice for a calculation of the J_0 function over the whole composition range of an acid–water system.

Let us formally consider the ionisation of secondary bases in terms of the equilibrium

$$H^+ + ROH \rightleftharpoons H_2O + R^+ \tag{10}$$

where the symbol H^+ denotes the proton in solution, as distinct from the hydroxonium ion H_3O^+. The equilibrium constant for (10) is given by

$$K = \frac{(H_2O)(R^+)}{(ROH)(H^+)} = \frac{[H_2O][R^+]\cdot f_{H_2O}\cdot f_{R^+}}{[ROH][H^+]\cdot f_{ROH}\cdot f_{H^+}} \tag{11}$$

[All equilibrium constants (K and $\boldsymbol{K}$) are defined in terms of activities, and activity coefficients (f) are referred to the standard state of an infinitely dilute aqueous solution.] Whenever necessary, we shall distinguish between concentrations (and activities) in molarity and mole-fraction units by affixing the subscripts C and N to the appropriately bracketed {[. .] or (. .)} chemical symbols. In (11), as in any other dimensionless ratio of concentrations or activities, the distinction is unnecessary. Activity coefficients are defined on a mole-fraction basis. Equation (11) may be rewritten as

$$K = \frac{[R^+]}{[ROH]}\cdot\frac{(H_2O)_N}{h_0}\left(\frac{f_B}{f_{BH^+}}\cdot\frac{f_{R^+}}{f_{ROH}}\right)\frac{55\cdot5}{\boldsymbol{K}_{H_3O^+}} \tag{12}$$

since

$$(H^+)_N = h_0\cdot\frac{\boldsymbol{K}_{H_3O^+}}{55\cdot5}\cdot\frac{f_{BH^+}}{f_B} \tag{13}$$

where f_B and f_{BH^+} are the activity coefficients relating to the acid–base pair BH^+,B used in the measurement of Hammett's acidity function H_0 over the particular range of solvent composition considered. $\boldsymbol{K}_{H_3O^+}$ is the acidity constant of the H_3O^+ ion, *i.e.*,

$$\boldsymbol{K}_{H_3O^+} = (H^+)_N(H_2O)/(H_3O^+) \tag{14}$$

(The constants $\boldsymbol{K}_{H_3O^+}$ and 55·5 appear in the above equation because, following Hammett's convention, $h_0 \longrightarrow [H_3O^+]_C$ at low concentrations of hydrogen ion.) Writing

$$K_{ROH} = K\boldsymbol{K}_{H_3O^+}/55\cdot5 \tag{15}$$

and taking logarithms, we find that equation (12) becomes

$$-pK_{ROH} + \log\frac{[ROH]}{[R^+]} = H_0 + \log (H_2O)_N + \log\frac{f_B\cdot f_{R^+}}{f_{BH^+}\cdot f_{ROH}} \tag{16}$$

and, by comparison with equation (5),

$$J_0 = H_0 + \log (H_2O)_N + \log\frac{f_B\cdot f_{R^+}}{f_{BH^+}\cdot f_{ROH}} \tag{17}$$

It was shown by Hammett that ratios of the form $f_{\mathrm{B}}/f_{\mathrm{BH^+}}$ were the same for several chemically different bases B. It *may* therefore be legitimate to equate

$$f_{\mathrm{B}}/f_{\mathrm{BH^+}} = f_{\mathrm{ROH}}/f_{\mathrm{ROH_2^+}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and hence derive

$$J_0 = H_0 + \log (\mathrm{H_2O})_N + \log f_{\mathrm{R^+}}/f_{\mathrm{ROH_2^+}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

From equation (14)

$$(\mathrm{H_2O})_N = \boldsymbol{K}_{\mathrm{H_3O^+}} \,.\, (\mathrm{H_3O^+})_N/(\mathrm{H^+})_N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and substitution of (20) in (11) leads to

$$K = \boldsymbol{K}_{\mathrm{H_3O^+}}\ (\mathrm{H_3O^+})_N(\mathrm{R^+})/(\mathrm{H^+})_N{}^2(\mathrm{ROH}) \quad . \quad . \quad . \quad . \quad . \quad (21)$$

which, by substitution for $(\mathrm{H^+})_N$ from (13), becomes

$$K = \frac{[\mathrm{R^+}]}{[\mathrm{ROH}]} \cdot \frac{[\mathrm{H_3O^+}]}{h_0{}^2}\left(\frac{f_{\mathrm{B}}{}^2}{f_{\mathrm{BH^+}}{}^2} \cdot \frac{f_{\mathrm{R^+}}}{f_{\mathrm{ROH}}} \cdot f_{\mathrm{H_3O^+}}\right)\frac{55{\cdot}5^2}{\boldsymbol{K}_{\mathrm{H_3O^+}}} \quad . \quad . \quad . \quad . \quad (22)$$

This equation may be rewritten in the form

$$-\mathrm{p}K_{\mathrm{ROH}} + \log \frac{[\mathrm{ROH}]}{[\mathrm{R^+}]} = 2H_0 + \log\,[\mathrm{H_3O^+}]_N + \log 55{\cdot}5 + \log\left(\frac{f_{\mathrm{B}}{}^2}{f_{\mathrm{BH^+}}{}^2} \cdot \frac{f_{\mathrm{R^+}}}{f_{\mathrm{ROH}}} \cdot f_{\mathrm{H_3O}}\right) \quad . \quad . \quad (23)$$

and, therefore, from (5)

$$J_0 = 2H_0 + \log\,[\mathrm{H_3O^+}]_N + \log\left(\frac{f_{\mathrm{B}}{}^2}{f_{\mathrm{BH^+}}{}^2} \cdot \frac{f_{\mathrm{R^+}}}{f_{\mathrm{ROH}}} \,.\, f_{\mathrm{H_3O^+}}\right) + 1{\cdot}74 \quad . \quad . \quad (24)$$

which, on the assumption contained in (18), becomes

$$J_0 = 2H_0 + \log\,[\mathrm{H_3O^+}]_N + \log f_{\mathrm{ROH}} \cdot f_{\mathrm{R}}{}^{+} \,.\, f_{\mathrm{H_3O^+}}/f_{\mathrm{ROH_2^+}}{}^2 + 1{\cdot}74 \quad . \quad . \quad (25)$$

Equations (17) and (24) are equally acceptable as rigorous thermodynamic formulations of J_0. They are not immediately useful for the purpose of predicting J_0 from the known properties of the solvent acid since both equations include terms involving unknown activity coefficients. It is therefore profitable to examine possible assumptions which eliminate the activity coefficients from the expression for J_0.

Approximate Expressions for J_0.—We shall examine in turn (i) the assumption that over the whole composition range considered

$$f_{\mathrm{B}} \cdot f_{\mathrm{R^+}}/f_{\mathrm{BH^+}} \cdot f_{\mathrm{ROH}} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

which leads to an approximate expression for J_0 :

$$J_0{}' = H_0 + \log (\mathrm{H_2O})_N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

[cf. Gold and Hawes, *loc. cit.*, equation (6)] ; (ii) the assumption

$$(f_{\mathrm{B}}{}^2 f_{\mathrm{R^+}} f_{\mathrm{H_3O^+}}/f_{\mathrm{BH^+}}{}^2 f_{\mathrm{ROH}}) = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

which leads to the alternative approximation to J_0 :

$$J_0{}'' = 2H_0 + \log\,[\mathrm{H_3O^+}]_N + 1{\cdot}74 \quad . \quad . \quad . \quad . \quad . \quad (29)$$

[cf. *idem, ibid.*, equations (9) and (10)] ; and (iii) the assumption

$$f_{\mathrm{B}} f_{\mathrm{R^+}} f_{\mathrm{H_3O}}/f_{\mathrm{BH^+}} f_{\mathrm{ROH}} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

which leads to the approximation

$$J_0{}''' = H_0 + \log\,[\mathrm{H_2O}]_N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Not much is known in detail about the behaviour of activity coefficients in strong aqueous acids and we shall therefore test the adequacy of the alternative approximations by applying them to the experimental data on the ionisation of triarylmethanol indicators in

52—90% aqueous sulphuric acid obtained by Bevan and Williams (*loc. cit.*), who, over that composition range, established a *relative* scale of J_0 values ($J_0^{\text{rel.}}$) which is expected to differ from the time scale (*i.e.*, the scale anchored by the limiting condition $J_0 \longrightarrow H_0$ as $H_0 \longrightarrow \text{pH}$) only by an additive term $J_0{}^*$, *i.e.*,

$$J_0 = J_0^{\text{rel.}} - J_0{}^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

It must be pointed out that the $J_0^{\text{rel.}}$ scale is in part based on measurements with secondary bases carrying positive charges. Strictly speaking, therefore, their ionisation should be governed by the functions J_+, J_{++}, and J_{+++}. By analogy with the small difference between the H_0 and H_+ functions (Brand, Horning, and Thornley, *J.*, 1952, 1374), it would now seem that, for present purposes, this distinction may be neglected. Furthermore, the $J_0^{\text{rel.}}$ scale applies at a temperature of 20° whereas H_0, J_0', J_0'', and J_0''' refer to 25°. For the comparisons given in this paper this difference is probably unimportant (Bevan and Williams, personal communication).

The function J_0' was calculated and tabulated in the earlier paper (Gold and Hawes, *loc. cit.*), where it was merely designated by the symbol J_0. The functions J_0'' and J_0''' may be calculated if the concentrations of the various molecular species in aqueous acids are known. Such information is provided for sulphuric acid–water by the intensities of Raman spectra measured by Young (" Record of Chemical Progress," Spring Issue, 1951, p. 81, and personal communication; cf. Redlich, *Chem. Rev.*, 1949, **44**, 1). The accuracy with which $[H_3O^+]$ is known from these measurements is not very high but adequate for the approximate calculation of J_0''; the values of $[H_2O]$ are known with a precision sufficient for the calculation of J_0''' only up to ~80% sulphuric acid. An alternative procedure for obtaining $[H_3O^+]$ and $[H_2O]$ in the region of high concentrations of sulphuric acid would be their calculation in terms of an assumed equilibrium constant of the reaction $H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$, as has been described in detail by Deno and Taft (*J. Amer. Chem. Soc.*, 1954, **76**, 244). However, at present the use of values derived from Raman spectra seems to be less open to objection and has been adopted in this work, but most of the conclusions remain unaffected if the alternative procedure is followed. At low acid concentrations all three approximation functions approach each other and go over into H_0.

A test of the functions is illustrated by Fig. 1, where H_0, J_0', J_0'', and J_0''' are plotted against $J_0^{\text{rel.}}$. It is seen that the J_0 approximations all agree with the experimental data very much better than H_0. J_0'' is more satisfactory than J_0' which, in turn, is superior to the approximation J_0'''. These results are thought to express the adequacy of the assumptions contained in equations (26), (28), and (30).

Behaviour of Activity Coefficients in the System Sulphuric Acid–Water.—The combination of the experimental $J_0^{\text{rel.}}$ values with the functions J_0', J_0'', and J_0''' permits some conclusions concerning the dependence of certain combinations of activity coefficients upon solvent composition in the range 52—90% sulphuric acid. From (17), (27), and (32)

$$J_0^{\text{rel.}} - J_0' = \log f_{\text{B}} f_{\text{R}^+} / f_{\text{BH}^+} f_{\text{ROH}} + J_0{}^* \quad . \quad . \quad . \quad . \quad . \quad (33)$$

from (24), (29), and (32)

$$J_0^{\text{rel.}} - J_0'' = \log f_{\text{B}}{}^2 f_{\text{R}^+} f_{\text{H}_3\text{O}^+} / f_{\text{BH}^+}{}^2 f_{\text{ROH}} + J_0{}^* \quad . \quad . \quad . \quad . \quad (34)$$

and from (17), (31), and (32),

$$J_0^{\text{rel.}} - J_0''' = \log f_{\text{B}} f_{\text{R}^+} f_{\text{H}_2\text{O}} / f_{\text{BH}^+} f_{\text{ROH}} + J_0{}^* \quad . \quad . \quad . \quad . \quad (35)$$

provided that the ratios $f_{\text{R}^+}/f_{\text{ROH}}$ and $f_{\text{B}}/f_{\text{BH}^+}$ may both be assumed to be independent of the nature of the bases employed in indicator studies over the range concerned. Furthermore, combination of the calculated functions J_0', J_0'', and J_0''' gives certain other combinations of activity coefficients over the composition range 0—90% sulphuric acid :

$$J_0'' - J_0' = \log f_{\text{B}} f_{\text{H}_3\text{O}^+} / f_{\text{BH}^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$J_0''' - J_0' = \log f_{\text{H}_2\text{O}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

and

$$J_0''' - J_0'' = \log f_{\text{B}} f_{\text{H}_3\text{O}^+} / f_{\text{BH}^+} f_{\text{H}_2\text{O}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Of course, the calculation of the activity coefficient ratios contained in equations (36)—(38) does not require the concept of the J_0 functions but can be thought to follow from the experimental values of concentrations of molecular species in the system. Deno and Taft (*loc. cit.*) carried out a calculation of $\log f_{H_2O}$ in this manner.

FIG. 1.

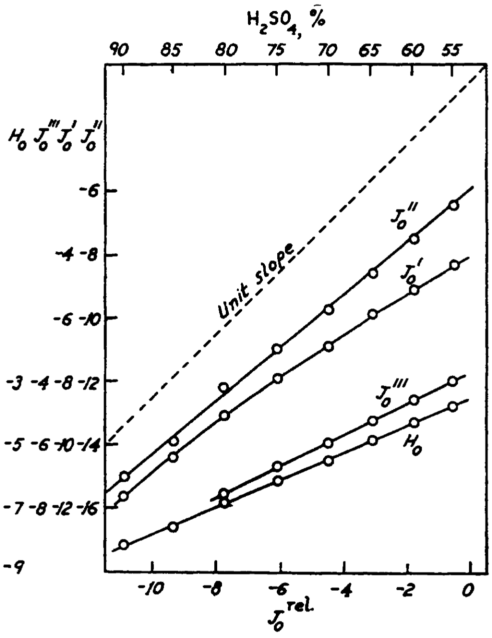


FIG. 3.

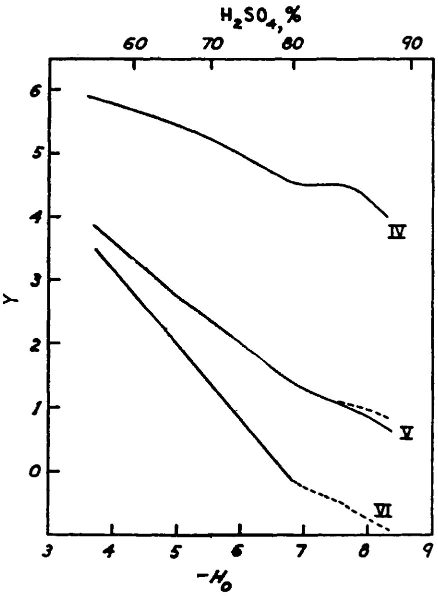
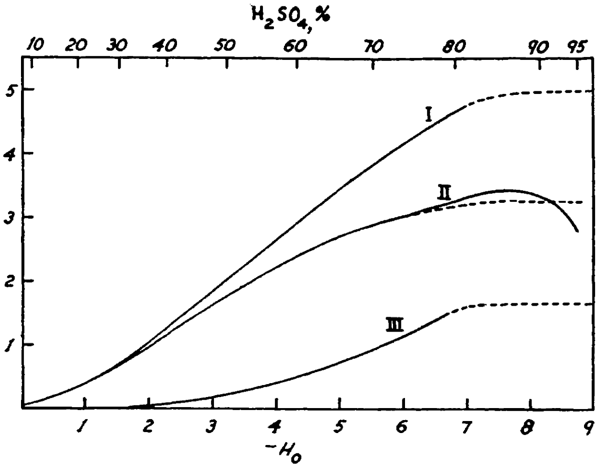


FIG. 2.



I; $Y = \log (f_{BH^+} f_{H_2O} / f_B f_{H_3O^+})$.
II; $Y = \log (f_{BH^+} / f_B f_{H_3O^+})$.
III; $Y = \log f_{H_2O}$.
IV; $Y = \log (f_B{}^2 f_{R^+} f_{H_3O^+} / f_{BH^+}{}^2 f_{ROH}) + J_0{}^*$.
V; $Y = \log (f_B f_{R^+} / f_{BH^+} f_{ROH}) + J_0{}^*$.
VI; $Y = \log (f_B f_{R^+} f_{H_2O} / f_{BH^+} f_{ROH}) + J_0{}^*$.

Equations (33)—(38) express the deviations of the approximate J_0 function from each other and from the experimental values, and the calculated terms are now more sensitive to the exact choice of the values of $(H_2O)_N$, $[H_3O^+]_N$, and $[H_2O]_N$. The curves given by us are again based on Young's data (*loc. cit.*) and values of $(H_2O)_N$ selected by Gold and Hawes, but we have indicated where the adoption of Deno and Taft's suggestions would lead to a qualitatively different result (broken lines in Figs. 2 and 3). The behaviour of some combinations of activity coefficients in sulphuric acid–water is shown in Figs. 2 and 3. The following features of the curves are noteworthy.

(1) The activity coefficient of water (curve III) remains virtually constant at unity up to a concentration of 30% sulphuric acid and thereafter its variation is slower than that of any other combination of activity coefficients examined.

(2) Curves IV and V do not support Deno and Taft's tentative suggestion that activity coefficients for any species in the region 83—100% sulphuric acid might approach constancy.

(3) The ratio $f_B{}^2 f_{R^+} f_{H_3O^+}/f_{BH^+}{}^2 f_{ROH}$ (curve IV) changes less rapidly with solvent composition than the ratio $f_B f_{R^+}/f_{BH^+} f_{ROH}$ (curve V). This result is not entirely unexpected. The velocities of certain acid-catalysed reactions are found to be proportional to $[H_3O^+]$ rather than to h_0 or to $h_0(H_2O)_N$ (Hammett, " Physical Organic Chemistry," New York, 1940, pp. 273—277; Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791; Long, Dunkle, and McDevit, *J. Phys. Chem.*, 1951, **55**, 829). Hammett pointed out that this result is intelligible if, over the acidity range studied, $f_K f_{H_3O^+}/f_{(K\cdot\cdot OH_3^+)}$ is constant, whereas the ratio $f_{KH^+}/f_{(K\cdot\cdot OH_3^+)}$ is not constant. Here K is the basic substrate undergoing reaction and $K\cdot\cdot OH_3^+$ denotes the molecular formula of the activated complex of the rate-determining step. Hammett advanced the tentative theory that the reason for the constancy of $f_K f_{H_3O^+}/f_{(K\cdot\cdot OH_3^+)}$ might lie in the fact that the two substances which appear in the numerator of the expression together make up the species which occurs in the denominator. The same relation between numerator and denominator exists in the case of the ratio $f_B{}^2 f_{R^+} f_{H_3O^+}/f_{BH^+}{}^2 f_{ROH}$ but not in the case of $f_B f_{R^+}/f_{BH^+} f_{ROH}$. However, this relation between the chemical species in a ratio of activity coefficients is evidently not a sufficient condition for that ratio to be independent of acid composition, as is illustrated by curves I and VI. Clearly, other factors must be taken into account.

(4) Curve IV has a considerable horizontal portion over which the ratio

$$f_B{}^2 f_{R^+} f_{H_3O^+}/f_{BH^+}{}^2 f_{ROH}$$

is accurately constant. This inflexion occurs near the composition of the monohydrate, where the ionic strength of the acid passes through a maximum. Curves V and VI also appear to be less steep in this region than at lower acidity. It may therefore be profitable to analyse activity coefficients in sulphuric acid on the basis that the ionic strength of the solution is a specific factor affecting the value of the activity coefficients even at very high concentrations of ions.

H_2SO_4, %	$J_0{}^{\text{rel.}}$ [1]	$J_0{}'$ [2]	$J_0{}''$	$J_0{}'''$	$J_0{}^{\text{rel.}} - J_0{}'$	$J_0{}^{\text{rel.}} - J_0{}''$	$J_0{}^{\text{rel.}} - J_0{}'''$	$J_0{}' - J_0{}''$	$J_0{}'' - J_0{}'$	$J_0{}''' - J_0{}''$
5	—	+0·23	+0·24	+0·24	—	—	—	0·01	0·01	0·00
10	—	−0·18	−0·27	−0·18	—	—	—	0·09	0·00	0·09
15	—	−0·58	−0·76	−0·57	—	—	—	0·18	0·01	0·19
20	—	−0·95	−1·26	−0·93	—	—	—	0·31	0·02	0·33
25	—	−1·30	−1·79	−1·28	—	—	—	0·49	0·02	0·51
30	—	−1·66	−2·35	−1·62	—	—	—	0·69	0·04	0·73
35	—	−2·07	−2·96	−2·00	—	—	—	0·89	0·07	0·96
40	—	−2·52	−3·68	−2·41	—	—	—	1·16	0·11	1·27
45	—	−3·05	−4·51	−2·87	—	—	—	1·46	0·18	1·64
50	—	−3·67	−5·44	−3·41	—	—	—	1·77	0·26	2·03
55	−0·59	−4·37	−6·46	−4·01	3·78	5·87	3·42	2·09	0·36	2·45
60	−1·81	−5·11	−7·50	−4·59	3·30	5·69	2·78	2·39	0·52	2·91
65	−3·12	−5·92	−8·60	−5·23	2·80	5·48	2·11	2·68	0·69	3·37
70	−4·52	−6·91	−9·76	−5·97	2·39	5·24	1·45	2·85	0·94	3·79
75	−6·10	−7·93	−10·98	−6·70	1·83	4·88	0·60	3·05	1·23	4·28
80	−7·75	−9·10	−12·24	−7·55	1·35	4·49	−0·20	3·14	1·55	4·69
85	−9·37	−10·41	−13·90	—	1·04	4·53	—	3·49	—	—
90	−10·92	−11·66	−15·04	—	0·74	4·12	—	3·38	—	—
95	—	−13·37	−16·22	—	—	—	—	2·85	—	—

[1] From Bevan and Williams (*loc. cit.*). [2] From Gold and Hawes (*loc. cit.*).

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