799. *The Distribution of Water in Cation-exchange Resins*

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The water contents of some cation-exchange resins in their hydrated M(I), M(II), and M(III) forms after reaching equilibrium in an atmosphere of known temperature and water activity have been determined, and the hydration of resins containing mixtures of two different ions has also been studied. For ions that form only aquo-complexes $[M^{n+}(H_2O)_z]$, at a fixed water activity and temperature, the water in the resin is divided between the anionic sites and the cations present; the amount attached to the sites is constant and independent of the cations present, and the cation hydration (at least at high water activity) is proportional to the heat of hydration of the ion divided by its charge, $\Delta H/n$. There is no evidence for the existence of swelling water, *i.e.*, water absorbed with zero free energy.

THE absorption of water by resins has been studied by Glueckauf and Kitt,[1] and by Redinha and Kitchener,[2] who reached certain conclusions referred to below. The present related work involves a different experimental technique, and, in general, supports the view that the bulk of the water in a cation exchange resin is divided between the cations and anionic sites—a somewhat higher proportion being assigned to the latter than found by Glueckauf and Kitt.

EXPERIMENTAL

Four different sulphonated polystyrene resins in bead form were used: (A) Zeo-Karb 225, 14—52 mesh, D.V.B. content unstated. (B) Zeo-Karb 225, 50 particle size, 4·5% D.V.B. (F) Zeo-Karb 225, 14—52 mesh, 1·0% D.V.B. (G) Zeo-Karb 225, 52—100 mesh, 8·0% D.V.B. The capacity was determined on the H-form in the usual way, and when a form other than the H-form was required, the latter was washed repeatedly with a warm solution of the desired cation, usually as the chloride, nitrate, or acetate. When incomplete replacement of an ion (X) by ion (Y) was required, the (X)-form received a restricted number of washes with the (Y)-solution. All preparations were finally washed with water, and surface-dried by contact with filter paper. The preparations were then confined in weighing bottles (3—6 g., in each) and allowed to equilibrate in an atmosphere of constant humidity at 30°, by confining saturated solutions of the substances listed in Table 1 in large (10—14 in.) desiccators, which were stored in an incubator at 30°. The bottles and their contents were weighed from time to time, and when their weights were constant (4—5 weeks) the residual quantity of water in the resin was found by drying the bottles for 6 hr. at 120°, followed by overnight storage (unstoppered) in a vacuum desiccator (P_2O_5). The bottles were then stoppered, weighed, and the drying, etc., continued until the weights became constant. Three to four weighings were usually sufficient to ensure constancy. The results of this procedure were found to correspond closely with those obtained by the method of Pepper *et al.*,[3] which involves drying *in vacuo* at a lower temperature. Finally, the cation content of the resin was found by the usual analytical methods. All determinations were carried out in duplicate, although extra determinations were occasionally required in order to verify results.

In Table 1, the column headed a_w gives the published data [4] on water activity at 30°; no data are available for mixtures yielding values in the lower range at this temperature. Accordingly, a hair hygrometer reading to 1% R.H. (Gallenkamp, model HV 450) was calibrated at 30° from the published data, and this was then used to determine the unknown values of a_w. In order to check variation, the humidity of the atmosphere in a desiccator was always determined after equilibration by using this instrument; the column headed a_w found shows such

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[1] E. Glueckauf and G. P. Kitt, *Proc. Roy. Soc.*, 1955, **228**, 322.

[2] J. S. Redhina and J. A. Kitchener, *Trans. Faraday Soc.*, 1963, **59**, 515.

[3] K. W. Pepper, D. Reichenberg, and D. K. Hale, *J.*, 1952, 3129.

[4] R. H. Stokes and R. A. Robinson, *Ind. Eng. Chem.*, 1949, **41**, 2013; D. S. Carr and B. L. Harris, *ibid.*, p. 2014; "International Critical Tables," McGraw-Hill Book Co., Inc., 1926, **1**, 67; "Handbook of Chemistry and Physics, 42nd edn., Chemical Rubber Publishing Co., New York, 1960, p. 2499; "Handbook of Chemistry," Lange, 9th edn., Handbook Publishers, Inc., Ohio, 1956, p. 1420.

TABLE 1

Water activities from constant-humidity mixtures at 30°

Substance	a_w	a_w found			
P_2O_5	0·00	0·00			
$NaOH,H_2O$	—	0·05	0·05	0·05	0·05
$LiCl,H_2O$	—	0·10	0·10	0·10	0·10
CH_3CO_2K	—	0·16	0·17	0·175	0·19
$CaCl_2,6H_2O$	—	0·30	0·30	0·30	0·30
$K_2CO_3,2H_2O$	—	0·40	0·40	0·40	0·40
$Mg(NO_3)_2,6H_2O$	—	0·50	0·50	—	—
$Na_2Cr_2O_7,2H_2O$	0·542	0·53	0·55	—	—
$NaNO_2$	0·63	0·62	0·62	—	—
$Na_2CrO_4,4H_2O$	0·646 (30·2°)	0·65	0·65	0·65	—
$NaNO_3$	0·728	0·73	—	—	—
NaCl	0·749 (30·2°)	0·74	0·75	—	—
$(NH_4)_2SO_4$	0·811	0·81	0·81	0·81	0·81
$Na_2CO_3,10H_2O$	—	0·85	—	—	—
$NH_4H_2PO_4$	0·929	0·90	0·93	0·93	—
$Pb(NO_3)_2$	—	0·97	0·97	—	—
H_2O	1·00	1·00	1·00	1·00	1·00

successive readings—the a_w values that appear in Tables 2—7 and 9. The fluctuations observed were undoubtedly due to small local temperature changes in the incubator combined with instrumental errors of the hygrometer; as it was impossible to separate these, the uncorrected readings were taken as the a_w values. Since the precise determination of the a_w values is not required in the calculation shown below, the uncorrected readings suffice. For example, the four determinations given in Table 2 for the water associated with the four different cationic forms of resin (A) at a_w read as 0·175 were all obtained from identical conditions of atmosphere, whatever the exact composition of this may have been.

RESULTS AND DISCUSSION

The results are contained in Tables 2—9 inclusive. The first five columns of Table 2, and the first three columns of Tables 3—5, give the water content in moles per equivalent at 30°, at several water activities and in various cation forms, for the four resins described above. The symbol W_{ion}, *i.e.*, W_H, W_{Cu}, etc. is used throughout to indicate this water

TABLE 2

Resin (A). 30°

a_w	W_H	W_{Cu}	W_K	W_{Li}	$\frac{W_H}{W_{Cu}}$	$\frac{W_H}{W_K}$	$\frac{W_H}{W_{Li}}$	$\frac{W_{Cu}}{W_{Li}}$	$\frac{W_{Li}}{W_K}$	$\frac{W_{Cu}}{W_K}$
0·05	0·66	0·58	0·35	0·81	1·14	1·88	0·815	0·72	2·32	1·56
0·10	1·31	1·12	0·66	1·16	1·17	1·98	1·13	0·97	1·76	1·70
0·175	2·07	1·69	1·05	1·60	1·22	1·97	1·29	1·05	1·52	1·61
0·30	3·24	2·59	1·70	2·25	1·25	1·91	1·44	1·15	1·32	1·52
0·40	4·02	3·16	2·07	2·72	1·27	1·94	1·48	1·16	1·31	1·53
0·50	4·49	3·57	2·38	3·07	1·26	1·89	1·46	1·16	1·29	1·50
0·62	5·20	4·00	2·84	3·64	1·30	1·83	1·43	1·10	1·28	1·41
0·73	6·28	4·94	3·54	4·47	1·28	1·72	1·41	1·11	1·26	1·39
0·81	7·57	5·94	4·37	5·50	1·28	1·73	1·38	1·08	1·26	1·36
0·90	9·50	7·42	5·65	7·05	1·28	1·67	1·35	1·05	1·24	1·31
1·00	12·21	9·50	7·58	8·67	1·29	1·61	1·41	1·10	1·14	1·25

TABLE 3

Resin (B). 30°

a_w	W_H	W_{Cu}	$\frac{W_H}{W_{Cu}}$
0·05	0·90	0·70	1·29
0·10	1·47	1·21	1·21
0·16	2·04	1·64	1·24
0·30	3·10	2·46	1·26
0·40	3·67	2·84	1·29
0·53	4·50	3·46	1·30
0·65	5·47	4·18	1·31
0·75	7·02	5·38	1·30
0·81	8·61	6·53	1·32
0·90	12·64	9·74	1·30
0·97	16·95	13·03	1·30
1·00	22·93	17·21	1·33

TABLE 4

Resin (G). 30°

a_w	W_H	W_{Cu}	$\frac{W_H}{W_{Cu}}$	a_w	W_H	W_{Cu}	$\frac{W_H}{W_{Cu}}$
0·05	0·79	0·68	1·16	0·65	4·85	4·07	1·19
0·10	1·19	0·92	1·30	0·75	5·81	4·84	1·20
0·19	2·06	1·78	1·16	0·85	7·80	6·35	1·23
0·30	2·79	2·38	1·17	0·93	9·95	8·00	1·24
0·40	3·39	2·86	1·19	1·00	13·05	10·37	1·26
0·55	4·15	3·42	1·21				

TABLE 5

Resin (F). 30°

a_w	W_H	W_{Cu}	$\frac{W_H}{W_{Cu}}$	a_w	W_H	W_{Cu}	$\frac{W_H}{W_{Cu}}$
0·05	0·60	0·63	0·95	0·65	5·39	4·00	1·35
0·10	1·20	1·25	0·96	0·74	7·00	5·15	1·36
0·17	2·06	1·98	1·04	0·85	11·73	8·42	1·40
0·30	2·86	2·37	1·21	0·93	23·03	15·97	1·45
0·40	3·41	2·69	1·27	0·97	37·23	25·92	1·44
0·50	4·07	3·12	1·30	1·00	83·26	55·80	1·49

TABLE 6

Resin (A). 30°. $a_w = 0{\cdot}81$

(a) *Cations present,* Cu^{2+} *and* H^+			(b) *Cations present,* K^+ *and* H^+		
Proportion of sites occupied by Cu^{2+}	Moles water per equivalent	$\frac{7{\cdot}57 - w}{p}$	Proportion of sites occupied by K^+	Moles water per equivalent	$\frac{7{\cdot}57 - w}{p}$
(p)	(w)		(p)	(w)	
0·000	7·57	—	0·000	7·57	—
0·106	7·40	1·61	0·224	6·85	3·24
0·232	7·19	1·64	0·389	6·31	3·22
0·486	6·79	1·61	0·615	5·66	3·11
0·615	6·56	1·64	0·891	4·70	3·22
0·802	6·26	1·63	1·000	4·37	3·20
1·000	5·94	1·63			

TABLE 7

Resin (F). 30°. $a_w = 1{\cdot}00$

Cations present, Cu^{2+} *and* H^+

Proportion of sites occupied by Cu^{2+} (p)	Moles water per equivalent (w)	$\frac{83{\cdot}26 - w}{p}$	Proportion of sites occupied by Cu^{2+} (p)	Moles water per equivalent (w)	$\frac{83{\cdot}26 - w}{p}$
0·000	83·26	—	0·824	60·61	27·4
0·287	75·40	27·8	1·000	55·80	27·5
0·563	67·86	27·5			

content for the particular cation form of the resin, and the ionic charges are those indicated in Table 9. The remaining columns in Tables 2—5 give the ratios, at each water activity used, of the water contents of the resin in the different cation forms tested.

Tables 6 and 7 give results for the water content of two resins when the counter-ions present in the resin consist of a mixture of two different cations. The constancy of the values shown in the third column in the three cases illustrated shows that, at constant temperature and water activity, the water content for a particular resin is a linear function of the proportion of sites occupied by either ion of the two present.

Table 8 gives results found by Glueckauf and Kitt (*loc. cit.*); these were taken by micrometer measurement from the curves in their Figure 10 (p. 340), and expressed as moles per equivalent as in Tables 2—5.

It has been suggested that water in a cation-exchange resin functions in four ways: (i) by forming water of hydration attached to discrete cations, *i.e.*, by contributing to the building of hydration shells around the cation (ion–dipole attraction), (ii) by solvating ion-pairs (if present) formed between the cations and anionic sites (dipole–dipole attraction) (iii) by hydrating the anionic sites, *i.e.*, by forming an attachment to a negative charge, anchored to the resin framework (ion–dipole attraction), and (iv) by contributing to the swelling of the resin through a pressure rise as the result of osmosis; this water is considered as combining with zero free-energy change. If symbols a_{ion}, b_{ion}, c, and d represent the water per equivalent falling under the headings (i)—(iv) above, respectively, then it follows from the conclusions reached from the study of Tables 6 and 7 that

TABLE 8

(Gluekauf and Kitt [1])

a_w	W_H	W_{Na}	W_{Ag}	W_{Mg}	W_{Sr}	$\frac{W_H}{W_{Na}}$	$\frac{W_H}{W_{Ag}}$	$\frac{W_H}{W_{Mg}}$	$\frac{W_H}{W_{Sr}}$	$\frac{W_{Na}}{W_{Ag}}$	$\frac{W_{Na}}{W_{Sr}}$	$\frac{W_{Mg}}{W_{Sr}}$	$\frac{W_{Mg}}{W_{Na}}$	$\frac{W_{Mg}}{W_{Ag}}$
0·05	1·76	1·19	0·89	1·90	1·335	1·48	1·98	0·93	1·32	1·34	0·89	1·42	1·60	2·12
0·10	2·35	1·58	1·14	2·275	1·695	1·49	2·06	1·03	1·39	1·39	0·93	1·34	1·44	1·99
0·20	3·02	2·14	1·51	2·79	2·16	1·41	2·00	1·08	1·40	1·42	0·99	1·29	1·30	1·85
0·30	3·59	2·52	1·81	3·235	2·51	1·42	1·98	1·11	1·43	1·39	1·00	1·29	1·28	1·79
0·40	4·23	2·98	2·09	3·78	2·835	1·42	2·02	1·12	1·49	1·43	1·05	1·33	1·27	1·81
0·50	4·86	3·46	2·38	4·35	3·25	1·40	2·04	1·11	1·49	1·45	1·06	1·34	1·26	1·83
0·60	5·63	4·00	2·75	5·10	3·82	1·41	2·05	1·10	1·47	1·45	1·05	1·33	1·27	1·85
0·70	6·66	4·84	3·29	5·99	4·55	1·38	2·02	1·11	1·46	1·47	1·06	1·32	1·24	1·82
0·80	8·38	6·15	4·22	—	5·47	1·36	1·98	—	1·53	1·46	1·12	—	—	—
0·90	11·58	10·51	6·26	—	—	1·10	1·85	—	—	1·68	—	—	—	—

$$W = (a_{\text{ion }1} + b_{\text{ion }1} - a_{\text{ion }2} - b_{\text{ion }2})p + a_{\text{ion }2} + b_{\text{ion }2} + c + d \qquad (1)$$

where p is the proportion of sites (fraction of unity) occupied by ion 1. When the latter is in sole occupancy,

$$W_{\text{ion }1} = a_{\text{ion }1} + b_{\text{ion }1} + c + d \qquad (2)$$

and for ion 2 alone,

$$W_{\text{ion }2} = a_{\text{ion }2} + b_{\text{ion }2} + c + d \qquad (3)$$

From both electrostatic considerations and entropy factors, it is to be expected that the liberation of solvent molecules will occur if ion-pairs form, hence an increase in the proportion of cations involved in ion-pair formation must be expected to result in a decrease of total water content; it follows from equation (1) that the respective a, b, c, and d factors probably do not vary with changing proportions of the two cations concerned, if the temperature and water activity remain constant. Although this does not mean that the c and d factors must be the same for all pairs of cations, one might expect this to be so.

When values of $W_{\text{ion }1}/W_{\text{ion }2}$ at different water activities are studied (Tables 2—5 and 8), it is observed that (*a*) between $a_w = 0$ and $a_w = 0{\cdot}3$ marked increases or decreases in the value of the ratio and may occur, and (*b*) between $a_w = 0{\cdot}3$ and $a_w = 1{\cdot}0$ (or to as high an a_w value as a series extends) generally no further marked changes occur in the ratio.

Free-swelling Water.—This can be expected to manifest itself (if at all) at high water activity, when the coulombic forces are weakened by the accumulation of water molecules around the charged centres. Whether swelling water appears suddenly or not with increased water intake, the effect should be to increase d relative to all the other factors at high a_w values; this should result in $W_{\text{ion }1}/W_{\text{ion }2}$ approaching unity at high a_w values in all cases. This is certainly not so, even for the resin (F) of lowest cross-linking, which absorbed about 80 moles water in its H-form. It must be concluded from this that the factor d is negligible.

Redinha and Kitchener (*loc. cit.*) conclude that the first four moles or so of water are significantly different from the remaining water absorbed, because there is no marked change in the thermodynamic functions ΔH, ΔG, and $T\Delta S$ after the intake of about four moles of water. The remaining water, according to these authors, " swells the resin network until contractile tension balances osmotic swelling." The attraction drawing this water into the resin then, is the tendency to dilute the solution within the resin, and electrostatic forces are not involved. This mechanism, involving colligative properties only, is not in accord with the failure of $W_{\text{ion }1}/W_{\text{ion }2}$ to approach unity at high a_{w} values. It must be concluded that water enters, and is retained in, a resin by an electrostatic mechanism.

Ion-pairing.—If $W_{\text{ion }1}/W_{\text{ion }2}$ reduces to $(a_{\text{ion }1} + b_{\text{ion }1} + c)/(a_{\text{ion }2} + b_{\text{ion }2} + c)$ then, when this ratio is observed to be constant with changing water activity, the terms in the numerator and denominator are changing in such a way as to maintain a constant ratio. From the above, this is only possible if (i) ion-pairing is non-existent or (ii) the proportion of cations involved in ion-pairing remains substantially constant with changing water activity. This, taken in conjunction with the study of the ratios at different water activities, leads to the conclusion that in most cases marked ion-pairing changes are complete between $a_{\text{w}} = 0$ and $a_{\text{w}} = 0{\cdot}3$.

The Factor c.—Comparison of the values of $W_{\text{H}}/W_{\text{Cu}}$ in Tables 2—5, which give figures for four different resins at the same temperature shows that, while this ratio is constant for a particular resin, different values are found for different resins. Obviously, if the a and b factors are not affected by the nature of the resin, then c is; this is not unexpected.

Evaluation of Factors a *and* c.—An attempt has been made to evaluate a and c as follows: Table 9, column 2, gives the results for the water content of resin (A) at 30° and constant water activity of 0·81 for a number of ions together with the heat of hydration [5] (column 3) for these ions. The ions were chosen from a larger list tested, most of which—particularly M(III) and M(IV) ions—were rejected because analysis showed that the metals were complexed in whole or in part with ligands other than water. With iron(III), for example, the resin form prepared from the chloride contained 0·219 moles of iron per 100 g. of dry resin ion; no chloride was present. Obviously the species $[\text{Fe}(\text{H}_2\text{O})_Z]^{3+}$ could not occupy all the sites, but others such as $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_{Z-1}]^{2+}$, $[\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_{Z-2}]^{+}$, etc., could do so in admixture with one another or with hydrogen ions. In all such cases where the possibility of complexing with charged ligands exists, together with the possible partial replacement of hydrogen ion when the metallic form of the resin is being prepared, the evidence for complete occupancy of the sites by an ion uncomplexed except by water was (i) the absence of Cl^-, CH_3CO_2^-, etc., in the prepared resins, and (ii) the existence of appropriate reproducible ratios, moles M^{n+}/capacity in equivalents. For the M(II) ions listed in Table 9, this ratio was almost exactly 0·266/0·533; for the M(III) forms, the ratio was 0·178/0·533. The appropriate ratio was not found to hold for any of the M(IV) ions tested, Sn, Th, or Zr.

Glueckauf and Kitt (*loc. cit.*), from a study of the heat of adsorption of water by cation exchange resins, conclude that the mechanism probably involves [for M(I) ions] the attachment of the first water molecule to the site during progressive hydration, and subsequent water molecules to the cation, forming a multi-layer system around the latter. It has been shown [6] that the heat of hydration of an ion should vary directly as the charge (n) and the solvation (S) in terms of an equidistant number of solvent molecules at an equilibrium (minimum energy) distance from the ion greater than about 2 Å. That is, $\Delta H \propto nS$, or, since $S = na$, $\Delta H_1/n_1^2 \propto a_1$; $\Delta H_2/n_2^2 \propto a_2$, etc., if the heavy disproportionation of water in favour of the cation suggested by Glueckauf and Kitt holds, and ion-pairing is small at the water activity of 0·81.

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[5] L. Benjamin and V. Gold, *Trans. Faraday Soc.*, 1954, **50**. 797.

[6] " Physical Chemistry," E. A. Moelwyn-Hughes, Pergamon Press, 1957, p. 859.

This leads to a relationship readily tested, for, if the factor c is constant for a particular resin at fixed temperature, then $-\Delta H/n^2(W_{\text{ion}} - c)$ should be constant.

Table 9, column 5 shows that, with the exception of H^+, Tl^+, and Ag^+, all the other ions listed do indeed give a reasonably constant value for this expression of about 40 when ΔH values are in kcal., and c has a value of 2·6. This value of 2·6 must then (in the absence of free water and ion-pairing) represent the hydration of the anionic site for this resin for the particular conditions chosen; it is a greater value than that expected from the results of Glueckauf and Kitt.

TABLE 9

Resin (A). 30°. $a_w = 0{\cdot}81$

Ion	W_{ion}	$-\Delta H$ (kcal.)	$-\Delta H/n^2$	$\dfrac{-\Delta H}{n^2(W_{\text{ion}} - 2{\cdot}6)}$	S
H^+	7·57	257	257	51·8	4·97
Li^+	5·50	119·33	119·33	41·3	2·90
Na^+	5·02	103·21	103·21	42·6	2·42
K^+	4·37	73·02	73·02	41·3	1·77
Rb^+	4·27	67·10	67·10	40·2	1·67
Cs^+	4·04	59·20	59·20	41·1	1·44
NH_4^+	4·52	72·00	72·00	37·5	1·92
Ag^+	3·24	109·88	109·88	172·0	(0·64)
Tl^+	2·85	74·17	74·17	296·6	(0·25)
Mg^{2+}	5·43	452·0	113·0	39·9	5·66
Ca^{2+}	4·89	373·2	93·3	40·7	4·58
Sr^{2+}	4·78	338·0	84·5	38·8	4·36
Ba^{2+}	4·49	304·2	76·05	40·2	3·78
Co^{2+}	5·84	483·6	120·9	37·3	6·48
Cu^{2+}	5·94	494·55	123·6	37·0	6·68
Y^{3+}	4·92	854·1	94·90	40·9	6·96
La^{3+}	4·84	773·5	85·94	38·4	6·72
Ce^{3+}	4·95	838·0	93·11	40·3	7·05

TABLE 10

Hydration numbers of ions

Ion	Ref. 7	Ref. 1	This Paper	Ion	Ref. 7	Ref. 1	This Paper
Li^+	22 (1·00)	3·3 (1·00)	2·90 (1·00)	Ca^{2+} ...	29 (1·32)	5·2 (1·58)	4·58 (1·58)
Ma^+	13 (0·59)	1·5 (0·46)	2·42 (0·83)	Sr^{2+}	29 (1·32)	4·7 (1·43)	4·36 (1·50)
K^+	7 (0·30)	0·6 (0·18)	1·77 (0·61)	Ba^{2+} ...	28 (1·28)	2·0 (0·61)	3·78 (1·30)
Cs^+	6 (0·27)	0·0 (0·00)	1·44 (0·50)	Cu^{2+} ...	34 (1·54)	—	6·68 (2·29)
Mg^{2+} ...	36 (1·64)	7·0 (2·12)	5·66 (1·93)				

The failure of H^+, Ag^+, and Tl^+ to give constant values is presumably due to the retention of ion-pairing at $a_w = 0{\cdot}81$, while the other ions listed exist as discrete hydrated entities.

The last column in Table 9 is the solvation, S, of the ion in terms of moles of water per mole of ion; this figure is only of interest when relative values are considered—from the foregoing, the concept of a permanent hydration shell is untenable. Table 10 gives a list of some recently determined solvation values; the figures in parentheses represent the corresponding relative values on the basis $S_{Li} = 1$.

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[7] A. J. Rutgers and Y. Hendrikx, *Trans. Faraday Soc.*, 1962, **58**, 2184.