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On Ion Exchange Equilibria

I. The Silver-Hydrogen Equilibrium on Wofatit KS and Dowex 50

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Way [1] in 1850 observed the phenomenon of ion exchange and Eichhorn [2] showed that the ion exchange process is reversible. Since then many quantitative investigations have been performed on ion exchange equilibria, and a number of experimental methods have been developed.

In earlier investigations empirical equations were often used to represent the experimental data. One equation that has frequently been applied is that of Rothmund and Kornfeld [3]. Bacon [4] and Møller [5] indicated that the mass action law was applicable to ion exchange equilibria. Recent investigations show that it is sometimes approximately obeyed within small concentration ranges: cf Samuelson [6], Boyd, Schubert and Adamson [7], Marinsky [8], Kressman and Kitchener [9], and Duncan and Lister [10, 11]. Some of these authors, however, point out that the mass action "constant" is really a variable [6, 8, 10, 11].

Samuelson [6] measured the equilibria: $Na^+ - H^+$, $NH_4^+ - H^+$ and $Li^+ - H^+$ on a commercial sulfonic acid exchanger. He found that the equilibrium quotient (which would be $\varkappa_{Me,H}$ with the notation in eq. (3) below) increased with decreasing mole fraction (β_{MeR}) of Na^+ and NH_4^+ in the exchanger (Me = Na^+, NH_4^+, R^- = negative group of the exchanger) within the concentration interval $0.2 \leqq \beta_{MeR} \leqq 0.8$. For the exchange $Li^+ - H^+$, $\varkappa_{Li,H}$ increased in the same manner but to a lesser degree.

Boyd, Schubert and Adamson[7] studied a number of exchange equilibria on Amberlite IR-1. Data were given for the exchange $Na^+ - H^+$ within the interval $0.26 \leqq \beta_{NaR} \leqq 0.93$. Just as in Samuelson's work, $\varkappa_{Na,H}$ showed a small but marked tendency to increase with decreasing β_{NaR}. However, these authors preferred to regard it as a constant.

Marinsky [8] studied the exchange reactions $Na^+ - H^+$, $Ca^{2+} - H^+$, $Ba^{2+} - H^+$ and $Ce^{3+} - H^+$ on especially treated Dowex 50. The exchange $Na^+ - H^+$ was studied within the range $6.10^{-4} \leqq \beta_{NaR} \leqq 0.95$, and $\varkappa_{Na,H}$ was found to increase with increasing β_{NaR}. The other exchange reactions also gave equilibrium quotients that varied considerably within the concentration ranges studied. Marinsky demonstrated by careful analyses that the assumption of equivalent exchange was valid within the limits of experimental error.

Kressman and Kitchener [9] studied a number of exchange reactions on a resin synthesized by themselves. For the exchange between NH_4^+ on one side, and Li^+, H^+, Na^+, K^+, Rb^+, Cs^+, Ag^+ or Tl^+ on the other, they obtained nearly straight lines when plotting $\left(\frac{\beta_{NH_4R}}{\beta_{MeR}}\right)_{resin}$ against $\left(\frac{[NH_4^+]}{[Me^+]}\right)_{aq}$ within the interval $0.3 \leqq \beta_{MeR} \leqq 0.7$ This means that $\varkappa$ is almost constant.

Actually, although this was not stressed by these authors, there is generally a steady increase of $\varkappa_{Me,NH_4}$ with decreasing β_{MeR}. The approximate constancy probably depends on the small β range covered. Kressman and Kitchener also studied the reaction at different T and found that $\varkappa$ is little affected by temperature changes.

Duncan and Lister [10] have studied the exchange $Na^+ - H^+$ on Amberlite IR — 100 H and Dowex 50. For Amberlite IR — 100 H, $\varkappa_{Na,H}$ varied from 1.4 to 1.2 when β_{NaR} varied from 0.03 to 0.8. For Dowex 50, a maximum in $\varkappa$ was obtained for $\beta_{NaR} \approx 0.1$. The equilibrium on Dowex 50 was also studied at 87° C. The maximum was found to be flatter at this temperature. The differences between their results and Marinsky's are probably due to the pretreatment of Marinsky's resin with 6 C NaOH for 48 h at 95° C.

The aim of the present work was to make a thorough investigation of the exchange equilibrium between Ag^+ and H^+ on two ion exchangers at various ratios $Ag^+ : H^+$ and at different ionic strengths.

The combination $Ag^+ - H^+$ was chosen because in this case a very wide concentration range could be covered by use of chemical and emf methods.

Two different ion exchangers were used: Wofatit KS, the same as used in the filtration experiments,[12, 13] and Dowex 50. Both exchangers contain nuclear sulfonic acid groups. Dowex 50 is considered to be more homogeneous; it has a higher capacity and reacts more slowly.

The temperature was kept constant at 25° C, although variations of a few degrees seem to be of little influence on ion exchange processes [9]. The experiments were carried out at two different ionic strengths: 100 mC and 20 mC. Since the equilibrium quotient (3) proved to be independent of ionic strength

within the limits of experimental error, experiments with lower ionic strengths did not seem necessary.

The experiments were carried out by shaking weighed-out resin samples and 100 ml of a solution of $AgNO_3$ and HNO_3 in a thermostat and analysing them as described below.

Symbols: The reaction studied can be written as (R^- = anion framework of resin):

	Ag^+	+	HR	$\rightleftharpoons$	H^+	+	AgR (1)
concentration	αa_0		$s_0\ (1-\beta)$		$(1-\alpha)a_0$		βs_0
number of moles in batch	n_{Ag^+}		n_{HR}		n_{H^+}		n_{AgR}

a_0 is the ionic strength, s_0 is the sorption capacity of the exchanger and α and β are the mole fractions of silver in the solution and the resin.

$$\alpha = \frac{n_{Ag^+}}{n_{Ag^+} + n_{H^+}} \text{ and } \beta = \frac{n_{AgR}}{n_{AgR} + n_{HR}} \tag{2}$$

We shall define the equilibrium quotient $\varkappa$, or more exactly $\varkappa_{Ag,H}$ by:

$$\varkappa_{Ag,H} = \varkappa = \frac{(1-\alpha)\ \beta}{\alpha\ (1-\beta)} = \frac{n_{H^+} \cdot n_{AgR}}{n_{Ag^+} \cdot n_{HR}} = \frac{[H^+]\ n_{AgR}}{[Ag^+]\ n_{HR}} \tag{3}$$

The last equality is approximately valid, since the activity factors of H^+ and Ag^+ almost cancel out.

EXPERIMENTS

Ion exchangers. 1. Wofatit KS with a grain size of 0.5 — 1.0 mm diameter was purified and saturated with H^+ as described in ref. [12]. After purification, part of it was dried in air and kept in a glass-stoppered bottle. 2. Dowex 50 of the same grain size was saturated with H^+ in the same manner as Wofatit KS. Then it was washed with dist. water until methyl red gave neutral reaction. The sorbent was placed in a glass filter funnel and dried by sucking a filtered air stream through it for 10—20 hours.

Silver saturated sorbent (AgR) was prepared from the H^+ form (HR) by running an excess of 1 C $AgNO_3$ through it (*cf.* Fig. 2 c in ref. [12]). It was washed with dist. water until the wash liquid was free from Ag^+, and then dried in a filtered air stream for about 5 hours.

Chemicals and standard solutions. 100.0 mC (millimoles per liter) HNO_3 was prepared from conc. nitric acid (Baker's analysed, sp. gr. 1.42) and dist. water. It was standardized against weighed HgO and KI [14]. 100.0 mC $AgNO_3$

was prepared from high grade pure $AgNO_3$ and dist. water. It was standardized according to Volhard against 0.1 C *KSCN* which was prepared from pure (Baker's analysed) KSCN and dist. water and standardized against weighed silver wire. 0.1 C *NaOH* was prepared from a solution of about 50 % NaOH and CO_2-free dist. water, and standardized against the 100.0 mC HNO_3 with methyl red as indicator.

Batches. Solutions of accurately known concentrations of Ag^+ and H^+, and of the ionic strength desired, were prepared from the standard solutions of $AgNO_3$, and HNO_3. With $a_0 = 100.0$ mC about 30, and with $a_0 = 20.0$ mC about 10 different solutions were prepared.

A batch was made by weighing out 1.000 g of HR or 1.500 g of AgR in 150 ml glass bottles, pipetting 100.00 ± 0.05 ml $Ag^+ - H^+$ solution to the sample, and then sealing the bottles. The bottles were shaken to equilibrium in the thermostat at $25.0 \pm 0.1°$ C. The period of shaking was never less than 24 hours. It was found to be important that the batches with AgR were mixed immediately after the AgR had been dried, because when left standing, silver ions are easily reduced in the dry sorbent. In our first experiments a number of batches were prepared in 150 ml bottles with rubber stoppers. Since the rubber might reduce the Ag^+ and hence give rise to errors, the batches were later on prepared in 150 ml pyrex glass bottles with constricted necks, which were then sealed.

Analysis. After shaking, the equilibrium solution was sucked off through a glass filter funnel and the sorbent was washed with about 100 ml dist. water.

For small silver concentrations in the *equilibrium solution* the wash water was discarded, the Ag^+ content determined by measuring the emf of a concentration cell, and the H^+ content determined by pipetting 20.00 ml of the solution and titrating with 0.1 C NaOH and methyl red as indicator.

For higher silver concentrations in the solution, the wash liquid was mixed with the equilibrium solution, and the total amounts of H^+ and Ag^+ (n_{H^+} and n_{Ag^+}) were determined by titration with NaOH and KSCN. These titrations were performed in tall 2 l beakers. After the titration with NaOH, 25—50 ml nitrobenzene and a few ml of conc. HNO_3 were added. The beaker was shaken until all methyl red had been transferred to the nitrobenzene phase. Iron (III) alum was added, and the silver titrated with 0.1 C KSCN.

After the *sorbent* had been separated from the solution, 0.5—1 l 2 C KNO_3 was run through it to expel Ag^+ and H^+. The arrangement was the same as shown in Fig. 2 c ref. [12]. Then the total amounts of AgR and HR (n_{AgR} and n_{HR}) were determined as described above. For small AgR contents, the most accurate way of obtaining n_{AgR} was to subtract n_{Ag^+} (which was determined by emf measurements) from the total amount of Ag in the batch.

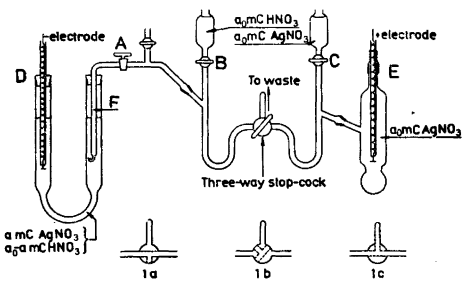


Fig. 1. Side view of emf apparatus for measuring $[Ag^+]$. *The stop-cock A is opened only when measuring emf. The stop-cocks B and C are opened when rinsing the three-way stop-cock. D and E are the electrode vessels. The narrow part of the U-tube D prevents* a_0 *mC* HNO_3 *from F to diffuse to the negative electrode. The tube F is filled with* a_0 *mC* HNO_3. *The three-way stop-cock 1 a) set for measuring emf, 1 b) closed and 1 c) set for rinsing.*

In order to test whether all Ag^+ was expelled by the KNO_3 solution, the AgR forms of Wofatit KS and Dowex 50 were treated with KNO_3 in the same manner as described above. The resins were then ignited in porcelain crucibles. After ignition HNO_3 was added to dissolve the silver. The presence of silver was tested with HCl. With Wofatit KS a very faint turbidity was obtained, and with Dowex 50 no turbidity at all. This test also shows that the reduction of silver during the exchange process is negligible.

EMF MEASUREMENTS

The apparatus used for the emf measurements was of the type designed by Forsling and Sillén (to be published). It was immersed in a paraffin oil thermostat with the temperature 25.0 $\pm$ 0.1° C in a thermostat room of 23.5° C.

The emf was measured by means of a Jensen potentiometer, with a Multiflex galvanometer MG2 as zero instrument.

The electrodes were Ag, AgI electrodes of the same kind as used in refs. 12 and 13. The cell can be described schematically by:

$$-\text{Ag/unknown } [Ag^+]/a_0 \text{ mC } HNO_3/a_0 \text{ mC } AgNO_3/\text{Ag} + \qquad (4)$$

Fig. 1 gives a picture of the apparatus.

In the following way a fresh diffusion layer was always obtained. Previous to each measurement the three-way stop-cock was rinsed with a_0 mC HNO_3 and a_0 mC $AgNO_3$. Stop-cocks B and C were opened simultaneously for a moment, and the three-way stop-cock was kept in the position shown in Fig. 1 c. Then the three-way stop-cock was turned to the position shown in Fig. 1 a. The stop-cock A was opened and the emf of the cell measured.

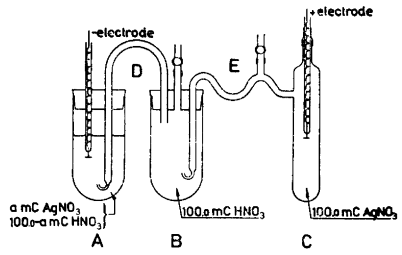


Fig. 2. Side view of first emf apparatus for measuring $[Ag^+]$. *A and C are the electrode vessels. Tube B with 100.0 mC* HNO_3 *prevents silver ions from C from diffusing to the electrode vessel A. D and E are bridges. D containing 100.0 mC* HNO_3 *and E 100.0 mC* $AgNO_3$.

THE DIFFUSION POTENTIAL

Before the apparatus in Fig 1 was used, measurements were made in a simpler apparatus (Fig. 2). The minus electrode at A is connected to the tube B containing 100.0 mC HNO_3 with the bridge D, also containing 100.0 mC HNO_3. Tube B is connected to the positive electrode at C with the bridge E containing 100.0 mC $AgNO_3$. The solutions in A and C are a mC $AgNO_3$ + + (100.0-a) mC HNO_3 and 100.0 mC $AgNO_3$. The cell was thus of the same type (4) as described above, though the diffusion layer could not be so easily renewed. The diffusion layer was developed in tube B between bridge E and the solution in B. The diffusion potential between the test solution in A and the HNO_3 solution in D could be expected to vary but slightly in the concentration interval studied. Moreover it is small in comparison to the diffusion potential in B. The variation should depend only upon the diffusion layer between B and E. The various electrodes used were compared with each other in the same silver solution; no potential difference was detected between them.

Some attempts were made to get a defined diffusion layer. When the layer was developed in sand (Bjerrum [15]), the resistance of the cell became too high for accurate measurements with our potentiometer. When the diffusion layer was placed in a cotton plug, the diffusion potential was constant for a few hours, but then began to decrease; simultaneously the cotton was coloured black by reduction of silver ions to silver. When finally the diffusion layer was placed in the three-way stop-cock, the diffusion potential decreased by 1 mV in 24 hours.

When the Forsling-Sillén apparatus was used as described above, the emf was reproducible within $\pm$ 0.1 mV. The emf changed by less than 0.1 mV during the first minutes after the three-way stop-cock was rinsed and opened for measurement. Then it rose fast to a maximum value, and finally decreased slowly to values even lower than the initial one. The maximum value was not reproducible.

If Henderson's equation is applicable, the emf of our cell should be the same as that of a cell without the insertion of pure HNO_3. This latter cell can be described by:

$$-Ag/[Ag^+]=\alpha a_0;\ [H^+]=a_0\,(1-\alpha);\ [NO_3^-]=a_0/[Ag^+]=a_0;\ [NO_3^-]=a_0/Ag+ \quad (5)$$

$$E = E_{corr} + E_d \quad (6)$$

where E = the measured emf, E_d = the diffusion potential, and E_{corr} = the corrected emf:

$$E_{corr} = \frac{RT}{F} \ln \frac{1}{\alpha} = 59.16^1 \log \frac{1}{\alpha} \text{ mV at } 25.0^\circ \text{ C} \quad (7)$$

At both ionic strengths, E was measured for a number of solutions with known silver concentration (αa_0) and ionic strength (a_0). E_{corr} was calculated from (7), after which E_d could be calculated from (6). It was found that equation (13b) in [12] satisfied the measurements if the values $d = 2.26$ for $a_0 = 100.0$ mC and $d = 2.15$ for $a_0 = 20.00$ mC were used:

$$(13b)\ [12] \qquad E_d = 59.16 \log (1 + d\ (1 - \alpha)) \quad (8)$$

Table 1 gives the values of E_d from (6) and (7) for $a_0 = 100.0$ mC and the value of d calculated from these E_d and (8). The last column gives the value for E_d calculated from (8) with the average value $d = 2.26$.

Table 2 gives the values of E_d for $a_0 = 20.00$ mC and the d values calculated from these E_d values and (8). The last column gives the values of E_d from (8) with the average value $d = 2.15$.

Table 1. Emf and diffusion potential in cells (5) with $a_0 = 100.0$ mC.

$\alpha \cdot a_0$ mC	E mV	E_{corr} from (7) mV	E_d from (6) mV	d from (8)	E_d from (8) mV $d = 2.26$
0.0100	266.9	236.6	30.3	2.25	30.4
0.1000	207.8	177.5	30.3	2.25	30.3
1.000	148.6	118.3	30.3	2.27	30.2
5.000	106.6	77.0	29.6	2.27	29.5
10.00	87.8	59.2	28.6	2.27	28.5

Table 2. The diffusion potential at a_0 = 20.00 mC.

$a \cdot a_0$ mC	E mV	E_{corr} from (7) mV	E_d from (6) mV	d from (8)	E_d from (8) mV d = 2.15
0.0500	183.2	153.9	29.3	2.13	29.4
0.2500	142.1	112.6	29.5	2.18	29.3
0.5000	123.8	94.8	29.0	2.15	29.0
1.000	105.6	77.0	28.6	2.15	28.6
5.000	60.2	35.6	24.6	2.14	24.7
10.00	36.4	17.8	18.6	2.13	18.8

The agreement is seen to be good. It can be noted that the average d value 2.15 in Table 2 is in close agreement with the value d = 2.16 obtained by Sillén and Ekedahl [12] for a_0 = 20.2 mC.

THE TIME FOR ATTAINMENT OF EQUILIBRIUM

A few experiments were made to study whether equilibrium was reached within one day. Dowex 50 was chosen because it is known to react more slowly than most other organic ion exchangers.

Four batches containing the HR form of the sorbent and one common standard solution were prepared. They were taken from the thermostat and analysed after 1, 2, 3, or 7 days. n_{Ag+} and thus a was determined by emf measurements. n_{AgR} and thus β was calculated from $n_{Ag+\,tot} - n_{Ag+}$ and n_{H+} and n_{HR} were determined by titration with 0.1 C NaOH as described above. Table 3 gives the values of the equilibrium quotient ($\varkappa$) and the time of shaking.

Table 3. The influence of the time of shaking a_0 = 100.0 mC. Sealed pyrex bottles.

Time of shaking Days	$a \cdot 10^4$	$\beta \cdot 10^3$	$\varkappa$ from (3)
1	21.3	20.6	9.9
2	19.8	20.7	10.7
3	21.0	20.6	10.0
7	20.3	20.9	10.5

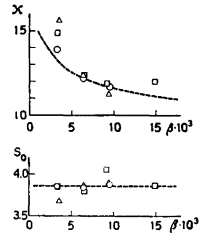


Fig. 3. Comparison of a) the equilibrium quotient $\varkappa$ and b) the exchange capacity s_0 for Dowex 50 of different particle sizes.
β = silver fraction in ion exchanger.
○ particle size 0.5 — 1.0 mm
△ » » 0.13 »
□ » » 0.04 »
The dotted line in Fig. 3 a is a smooth curve based on all determinations in Tables 8 a and c.
The dotted line in Fig. 3 b is the mean of the s_0 values in Table 4.

From Table 3 is seen that within the limits of experimental error the equilibrium is attained within one or two days; probably it is attained within even shorter time than one day. Nachod and Wood [16] have shown that for a number of different ion exchangers equilibrium is practically attained within 30 minutes. These results have been corroborated by the later findings of Holm and Westermark.[21] Marinsky [8] found that for Dowex 50 3.3 hours was enough for attaining equilibrium.

THE INFLUENCE OF THE PARTICLE SIZE

To study whether $\varkappa$ and s_0 depend upon the particle size, dry Dowex 50 in the HR form was ground in a mortar. In that process particles of all sizes between colloidal and unbroken grains were obtained. Two different times of grinding, and thus different mean particle sizes were used. The diameters of 100 particles from each sample were measured in a microscope with

Table 4. The influence of the particle size.
a_0 = 100.0 mC, sealed pyrex bottles. HR form of Dowex 50.

Mean particle size	$n_{Ag^+ tot}$ mmol	n_{Ag^+} 10^3 mmol	n_{H^+} mmol	n_{HR} mmol	s_0 mmol	$\alpha \cdot 10^4$	$\beta \cdot 10^3$	$\varkappa$ from (3)
0.5—1.0	0.01500	2.367	10.04	3.856	3.868	2.367	3.265	13.9
— » —	0.03000	5.278	9.90	3.815	3.840	5.278	6.438	12.2
— » —	0.04500	8.193	10.01	3.837	3.874	8.193	9.502	11.7
0.13	0.01500	2.227	—	3.671	3.684	2.227	3.466	15.6
— » —	0.03000	5.237	—	3.852	3.877	5.237	6.386	12.3
— » —	0.04500	8.387	—	3.859	3.896	8.387	9.397	11.3
0.04	0.01500	2.227	—	3.849	3.862	2.227	3.367	14.9
— » —	0.03000	5.278	—	3.764	3.789	5.278	6.524	12.4
— » —	0.04500	7.789	—	4.023	4.060	7.789	9.165	11.9
— » —	0.0700	12.57	—	3.790	3.847	12.57	14.93	12.0

a calibrated ocular micrometer. The mean diameters were found to be 0.13 and 0.04 mm. Batches with both samples were prepared, and after shaking in thermostat they were analysed as described above with the exception that the equilibrium solution was centrifuged from the sorbent at 1 500 r. p. m. for 0.5 — 1 h instead of filtrated. Table 4 and Fig. 3 give the results of the analyses compared with those for unground particles.

In Table 4 $n_{Ag^+\ tot}$ = the silver amount in mmol per 100 ml of the Ag^+ — H^+ solution. Only directly determined n-values are listed; n_{AgR} was determined indirectly from $(n_{Ag^+\ tot} - n_{Ag^+})$. The titrated n_{H^+}-values for the ground samples were too high and are not listed. This is due to the fact that even after centrifuging a certain quantity of resin particles containing H^+ remained in the equilibrium solution. Thus it was preferred to calculate n_{H^+} from $(0.1\ a_0 - n_{Ag^+})$. The total capacity s_0 is defined by:

$$s_0 = n_{HR} + n_{AgR} \tag{9}$$

Fig. 3 indicates that both $\varkappa$ and s_0 seem to be independent of the particle size within the limits of experimental error.

VARIOUS WAYS OF CALCULATING $\varkappa$

Since both solution and sorbent were analysed, the equilibrium quotient $\varkappa$ could be calculated in a number of different ways by excluding one or two determinations and calculating $\varkappa$ from the rest of the data. Table 5 gives the different methods possible.

Table 5. Possible combinations of experimental data to calculate the equilibrium quotient $\varkappa$.

Method of evaluatn.	n_{H^+}	n_{Ag^+}	n_{HR}	n_{AgR}	$0.1\ a_0$	$n_{H^+\ tot}$	$n_{Ag^+\ tot}$	$n_{H^+\ tot}$ known	$n_{Ag^+\ tot}$ known
1	+	+	+	+	—	—	—	x	x
2	+	—	+	+	+	—	—	x	(x)
3	—	+	+	+	+	—	—	(x)	x
4	+	+	+	—	—	—	+		x
5	+	—	+	+	—	—	+		(x)
6	+	—	+	—	+	—	+		(x)
7	—	+	+	—	+	—	+		x
8	—	—	+	+	+	—	+		(x)
9	+	+	—	+	—	+	—	x	
10	—	+	+	+	—	+	—	(x)	
11	+	—	—	+	+	+	—	x	
12	—	+	—	+	+	+	—	(x)	
13	—	—	+	+	+	+	—	(x)	

Between the quantities in Table 5 the following relations are valid:

$$0.1\ a_0 = n_{H^+} + n_{Ag^+} \quad (10); \qquad n_{Ag^+\,tot} = n_{Ag^+} + n_{AgR} \quad (11)$$

$$n_{H^+\,tot} = n_{HR} + n_{H^+} \quad (12)$$

Of the relations (11) and (12), only one can be applied to a certain experiment since only $n_{Ag^+\,tot}$ is known when starting from the HR form of the resin and only $n_{H^+\,tot}$ when starting from the AgR form. + means the data used and — the data excluded.

The last two columns show which method can be used when n_{H^+tot} ($n_{Ag^+\,tot}$) is known. "x" means that the method is applicable and "(x)" that it is inaccurate if the known quantity $n_{H^+\,tot}$ (or $n_{Ag^+\,tot}$) is small.

Tables 6 a and b give the values of $\varkappa$ calculated by different methods for four batches of Wofatit KS, two starting from the HR form and two from the AgR form.

Table 6 a. Comparison of $\varkappa$ values calculated by methods 1—8 (Table 5). a_0 = 100.0 mC. Bottles with rubber stoppers. HR form of Wofatit KS.

Method of evaluatn.	$n_{Ag^+\,tot}$ mmol	n_{Ag^+} mmol	n_{H^+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	0.1 a_0 mmol	$\beta \cdot 10^3$	$\varkappa$ from (3)
1	3.500	2.439	7.533	1.038	0.638	1.676	10.00	619.3	5.02
2	— » —	(2.467)	7.533	1.038	0.638	1.676	—»—	619.3	4.97
3	— » —	2.439	(7.561)	1.038	0.638	1.676	—»—	619.3	5.04
4	— » —	2.439	7.533	(1.061)	0.638	1.699	—»—	624.5	5.14
5	— » —	(2.462)	7.533	1.038	0.638	1.676	—»—	619.3	4.98
6	— » —	(2.467)	7.533	(1.033)	0.638	1.671	—»—	618.2	4.94
7	— » —	2.439	(7.561)	(1.061)	0.638	1.699	—»—	624.5	5.16
8	— » —	(2.462)	(7.538)	1.038	0.638	1.676	—»—	619.3	4.98
								Mean:	5.03 ± 0.13
1	2.700	1.776	8.214	0.898	0.782	1.680	—»—	534.5	5.31
2	— » —	(1.786)	8.214	0.898	0.782	1.680	—»—	534.5	5.28
3	— » —	1.776	(8.224)	0.898	0.782	1.680	—»—	534.5	5.32
4	— » —	1.776	8.214	(0.924)	0.782	1.706	—»—	541.6	5.46
5	— » —	(1.802)	8.214	0.898	0.782	1.680	—»—	534.5	5.23
6	— » —	(1.786)	8.214	(0.914)	0.782	1.696	—»—	538.9	5.38
7	— » —	1.776	(8.224)	(0.924)	0.782	1.706	—»—	541.6	5.47
8	— » —	(1.802)	(8.198)	0.898	0.782	1.680	—»—	534.5	5.22
								Mean:	5.33 ± 0.14

The values in parenthesis are those calculated from the other data.

Table 6 b. Comparison of $\varkappa$ values calculated by methods 1—3 and 9—13 (Table 5). a_0 = 100.0 mC. Pyrex bottles. AgR form of Wofatit KS.

Method of evaluatn.	n_{H+tot} mmol	n_{Ag+} mmol	n_{H+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	0.1 a_0 mmol	$\beta \cdot 10^3$	$\varkappa$ from (3)
1	9.000	2.092	7.939	1.314	1.051	2.365	10.00	555.6	4.74
2	— » —	(2.061)	7.939	1.314	1.051	2.365	—»—	555.6	4.82
3	— » —	2.092	(7.908)	1.314	1.051	2.365	—»—	555.6	4.73
9	— » —	2.092	7.939	1.314	(1.061)	2.375	—»—	553.2	4.70
10	— » —	2.092	(7.949)	1.314	1.051	2.365	—»—	555.6	4.75
11	— » —	(2.061)	7.939	1.314	(1.061)	2.375	—»—	553.2	4.77
12	— » —	2.092	(7.908)	1.314	(1.092)	2.406	—»—	546.1	[4.55]
13	— » —	(2.051)	(7.949)	1.314	1.051	2.365	—»—	555.6	4.85
								Mean:	4.77 ± 0.08
1	8.000	2.899	7.160	1.522	0.827	2.349	—»—	647.9	4.55
2	— » —	(2.840)	7.160	1.522	0.827	2.349	—»—	647.9	4.64
3	— » —	2.899	(7.101)	1.522	0.827	2.349	—»—	647.9	4.51
9	— » —	2.899	7.160	1.522	(0.840)	2.362	—»—	644.4	4.48
10	— » —	2.899	(7.173)	1.522	0.827	2.349	—»—	647.9	4.55
11	— » —	(2.840)	7.160	1.522	(0.840)	2.362	—»—	644.4	4.57
12	— » —	2.899	(7.101)	1.522	(0.899)	2.421	—»—	628.7	[4.15]
13	— » —	(2.827)	(7.173)	1.522	0.827	2.349	—»—	647.9	4.67
								Mean:	4·57 ± 0.10

The n values in parenthesis are those calculated from the other data. From Table 6 is seen that the method of evaluation does not affect the $\varkappa$ values in any significant manner. The $\varkappa$ values calculated by the especially inaccurate method 12 are given in brackets in the last column and have been omitted in the calculation of the mean $\varkappa$. All other values are within the limits ± 3 %.

In the Tables 7 and 8, $\varkappa$ has as far as possible been calculated with method 1. Only directly determined n values are listed. If it was not possible to use 1, one of the methods 4 and 7 were used.

The authors have preferred to plot $\varkappa$ as a function of β instead of β as a function of α, which is commonly used, since the former mode of representation is more sensitive to small variations in $\varkappa$ with β. In Figs. 4 and 5, $\varkappa$ is plotted against β for Wofatit KS and Dowex 50. Obviously $\varkappa$ is far from being constant and the points fall on a smooth curve. If it had been constant, the isotherm would have been of the Langmuir type. From Figs. 4 b and 5 b it is seen that the error in $\varkappa$ is about ± 5 %. It is also seen that, within the limits of experimental error, $\varkappa$ is independent of ionic strength. As is seen in the

Table 7 a. $a_0 = 100.0$ *mC. Bottles with rubber stopper. * denotes pyrex bottles. HR form of Wofatit KS.*

$n_{Ag^+ tot}$ mmol	$n_{Ag^+} \cdot 10^3$ mmol	n_{H^+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	$a \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
0.00500	0.8023	10.00	—	1.724	1.728	0.8023	2.429	4	30.4
*0.00500	0.9980	10.06	—	1.810	1.814	0.9980	2.206	4	22.3
0.01000	1.788	10.01	—	1.729	1.737	1.788	4.728	4	26.6
0.01500	3.097	—	—	1.720	1.732	3.097	6.871	7	22.3
*0.01500	2.831	10.00	—	1.764	1.776	2.831	6.852	4	24.4
0.02000	3.942	10.01	—	1.721	1.737	3.942	9.246	4	23.7
0.02500	5.116	10.00	—	1.720	1.740	5.116	11.43	4	22.6
0.03000	6.718	10.00	—	1.720	1.743	6.718	13.36	4	20.1
*0.03000	6.931	10.00	—	1.754	1.777	6.931	12.98	4	19.0
0.03500	8.098	—	—	1.716	1.743	8.098	15.43	7	19.3
0.04500	11.06	—	—	1.710	1.744	11.06	19.46	7	17.9
0.05000	12.24	9.95	—	1.708	1.746	12.24	21.63	4	18.0
*0.07000	18.63	10.04	—	1.777	1.828	18.63	28.10	4	15.6
0.1000	28.36	9.94	—	1.663	1.735	28.36	41.29	4	15.1
*0.1500	46.49	10.00	—	1.712	1.816	46.49	56.99	4	13.0
0.2000	68.88	9.91	—	1.598	1.729	68.88	75.82	4	11.8
0.3000	116.5	9.89	—	1.553	1.737	116.5	105.6	4	10.0
0.4000	165.0	9.82	0.218	1.435	1.653	165.0	131.9	1	9.0
0.4150	168.6	9.81	—	1.491	1.737	168.6	141.9	4	9.6
0.5600	236.5	9.74	—	1.426	1.750	236.5	184.9	4	9.3
0.6800	319.2	9.67	—	1.378	1.739	319.2	207.5	4	7.9
0.8000	374.4	9.60	—	1.333	1.759	374.4	242.0	4	8.2
0.9000	468.0	9.53	0.412	1.226	1.638	468.0	251.5	1	6.8
0.9200	451.3	9.55	—	1.304	1.773	451.3	264.4	4	7.6
1.040	537.7	9.45	—	1.236	1.738	537.7	289.0	4	7.1
1.180	616.2	9.36	—	1.192	1.756	616.2	321.1	4	7.2
1.400	800.0	9.208	0.587	1.072	1.659	800.0	353.8	1	6.3
*1.750	1020	9.057	0.730	1.080	1.810	1020	403.3	1	6.0
2.000	1228	8.678	0.731	0.919	1.650	1228	443.0	1	5.6
*2.350	1354	8.691	0.996	0.956	1.952	1354	510.2	1	6.7
2.700	1776	8.214	0.898	0.782	1.680	1776	534.5	1	5.3
3.500	2439	7.533	1.038	0.638	1.676	2439	619.3	1	5.0
*4.350	3119	6.935	1.231	0.564	1.795	3119	685.8	1	4.9
4.600	3389	6.539	1.178	0.484	1.662	3389	708.8	1	4.7
6.000	4638	5.358	1.357	0.354	1.711	4638	793.1	1	4.4
8.300	6766	3.212	1.509	0.201	1.710	6766	882.5	1	3.6
*10.00	8379	1.682	1.621	0.150	1.771	8379	915.3	1	2.2

Table 7 b. $a_0 = 100.0$ *mC. Pyrex bottles. AgR form of Wofatit KS.*

n_{H^+tot} mmol	n_{Ag^+} mmol	n_{H^+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	$a \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
10.00	1.260	8.740	0.943	1.236	2.179	1260	432.8	1	5.3
10.00	1.238	8.762	0.921	1.227	2.148	1238	428.8	1	5.3
10.00	1.239	8.761	0.916	1.234	2.150	1239	426.0	1	5.2
9.000	2.092	7.939	1.314	1.051	2.365	2092	555.6	1	4.7
9.000	2.068	7.933	1.317	1.045	2.362	2068	557.6	1	4.8
8.000	2.899	7.160	1.522	0.827	2.349	2899	647.9	1	4.5
8.000	2.873	7.178	1.485	0.815	2.300	2873	645.7	1	4.6
7.000	3.731	6.329	1.666	0.639	2.323	3731	717.2	1	4.4
7.000	3.736	6.320	1.679	0.657	2.336	3736	718.8	1	4.3
6.000	4.549	5.449	1.659	0.531	2.190	4549	757.5	1	3.7
6.000	4.548	5.449	1.650	0.521	2.171	4548	760.0	1	3.8
4.000	6.347	3.641	1.864	0.337	2.201	6347	846.9	1	3.2
4.000	6.407	3.602	2.121	0.372	2.493	6407	850.8	1	3.2
2.000	8.360	1.766	2.347	0.216	2.563	8360	915.7	1	2.3
2.000	8.353	1.770	2.363	0.213	2.576	8353	917.3	1	2.4
1.000	9.264	0.789	2.642	0.128	2.770	9264	953.8	1	1.8
1.000	9.404	0.831	2.467	0.109	2.576	9404	957.7	1	2.0

Table 7 c. $a_0 = 20.00$ *mC. Pyrex bottles. HR form of Wofatit KS.*

n_{Ag^+tot} mmol	$n_{Ag^+} \cdot 10^3$ mmol	n_{H^+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	$a \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
0.00500	0.2313	2.01	—	1.813	1.818	0.1157	2.623	4	22.9
0.00500	0.2239	2.01	—	1.761	1.766	0.1119	2.704	4	24.3
0.02500	1.318	2.01	—	1.774	1.798	0.6590	13.17	4	20.4
0.02500	1.328	2.01	—	1.850	1.874	0.6640	12.63	4	19.4
0.05000	3.030	2.00	—	1.816	1.863	1.515	25.21	4	17.1
0.05000	3.238	2.01	—	1.816	1.863	1.619	25.10	4	16.0
0.1000	7.594	2.00	—	1.760	1.852	3.797	49.90	4	13.8
0.1000	7.684	1.99	—	1.745	1.837	3.842	50.26	4	13.7
0.5000	7.344	1.93	0.4081	1.433	1.841	3.672	221.7	1	7.5
0.5000	7.316	1.93	0.4133	1.457	1.870	3.658	221.0	1	7.5
1.000	21.1	1.788	0.7755	1.115	1.891	10.6	410.1	1	5.9
1.000	22.0	1.789	0.7755	1.058	1.834	11.0	422.8	1	6.0
1.500	41.0	1.607	1.081	0.765	1.846	20.5	585.6	1	5.5
1.500	40.5	1.595	1.090	0.780	1.870	20.3	582.9	1	5.5
2.000	65.3	1.331	1.322	0.546	1.868	32.7	707.7	1	4.9
2.000	64.5	1.337	1.323	0.557	1.880	32.3	703.7	1	4.9

Table 8 a. $a_0 = 100.0$ *mC. Pyrex bottles. HR form of Dowex 50*

$n_{Ag^+ tot}$ mmol	$n_{Ag^+} \cdot 10^3$ mmol	n_{H^+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	$\alpha \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
0.00500	0.7422	10.01	—	3.886	3.890	0.7422	1.095	4	14.8
0.00500	0.9521	10.11	—	3.848	3.852	0.9521	1.051	4	11.2
0.01000	1.537	10.02	—	3.863	3.871	1.537	2.186	4	14.3
0.01000	1.592	10.11	—	3.868	3.876	1.592	2.169	4	13.8
0.01500	2.367	10.04	—	3.856	3.868	2.367	3.265	4	13.9
0.01500	2.433	10.14	—	3.865	3.878	2.433	3.241	4	13.6
0.02000	3.426	10.01	—	3.856	3.873	3.426	4.278	4	12.6
0.02500	4.344	10.02	—	3.842	3.863	4.344	5.348	4	12.4
0.03000	5.278	9.90	—	3.815	3.840	5.278	6.438	4	12.2
0.03000	5.176	10.10	—	3.856	3.881	5.176	6.395	4	12.6
0.03500	6.264	9.99	—	3.836	3.865	6.264	7.436	4	11.9
0.03500	6.024	9.99	—	3.845	3.874	6.024	7.481	4	12.5
0.04000	7.206	10.01	—	3.845	3.878	7.206	8.455	4	11.8
0.04500	8.193	10.01	—	3.837	3.874	8.193	9.502	4	11.7
0.04500	7.911	10.09	—	3.856	3.893	7.911	9.527	4	12.3
0.05000	9.462	10.00	—	3.808	3.849	9.462	10.53	4	11.3
0.06000	11.32	9.99	—	3.805	3.854	11.32	12.63	4	11.3
0.06000	10.97	10.11	—	3.715	3.764	10.97	13.03	4	12.2
0.08000	15.82	10.01	—	3.827	3.891	15.82	16.49	4	10.6
0.09000	18.20	9.99	—	3.825	3.897	18.20	18.42	4	10.3
0.09000	17.57	10.10	—	3.812	3.884	17.57	18.65	4	10.9
0.1000	20.29	10.01	—	3.792	3.872	20.29	20.59	4	10.4
0.2000	44.20	9.96	—	3.732	3.888	44.20	40.07	4	9.4
0.3000	69.41	9.92	—	3.648	3.879	69.41	59.45	4	9.0
0.4000	95.14	9.83	—	3.528	3.833	95.14	79.55	4	8.9
0.5000	123.5	9.87	—	3.475	3.852	123.5	97.74	4	8.7
0.6000	150.3	9.85	—	3.392	3.842	150.3	117.0	4	8.7
0.7000	180.1	9.82	—	3.323	3.843	180.1	135.3	4	8.5
0.8000	205.6	9.81	—	3.260	3.854	205.6	154.2	4	8.7
0.9000	216.9	9.78	—	3.201	3.884	216.9	175.9	4	9.6
0.9000	228.4	9.69	—	3.135	3.807	228.4	176.4	4	9.1
0.9500	240.3	9.84	—	3.195	3.905	240.3	181.7	4	9.1
0.9500	242.1	9.84	—	3.155	3.863	242.1	183.3	4	9.1
1.000	264.8	9.80	—	3.125	3.860	264.8	190.5	4	8.7
1.500	405.3	9.601	1.065	2.789	3.854	405.3	276.3	1	9.0
1.500	430.1	9.584	1.036	2.528	3.564	430.1	290.7	1	9.1
1.500	437.3	9.582	1.030	2.520	3.550	437.3	290.1	1	9.0
2.000	589.6	9.437	1.412	2.464	3.876	589.6	364.3	1	9.2
2.500	761.0	9.240	1.691	2.150	3.841	761.0	440.2	1	9.5
2.500	756.9	9.248	1.702	2.183	3.885	756.9	438.1	1	9.5
3.000	992.3	9.001	2.015	1.895	3.910	992.3	515.3	1	9.6

Table 8 a (continued).
a_0 = 100.0 mC. Pyrex bottles. HR form of Dowex 50.

n_{Ag^+tot} mmol	$n_{Ag^+} \cdot 10^3$ mmol	n_{H^+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	$a \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
4.000	1599	8.356	2.365	1.218	3.583	1599	660.1	1	10.1
4.000	1607	8.354	2.370	1.209	3.579	1607	662.2	1	10.2
4.000	1471	8.479	2.433	1.367	3.800	1471	640.3	1	10.3
4.000	1471	8.541	2.473	1.400	3.873	1471	638.5	1	10.3
5.000	2130	7.873	2.875	1.013	3.888	2130	739.5	1	10.5
6.000	2804	7.170	3.083	0.653	3.736	2804	825.2	1	12.1
6.000	2774	7.202	3.150	0.726	3.876	2774	812.7	1	11.3
6.000	2977	6.969	2.928	0.616	3.544	2977	826.2	1	11.1
7.000	3885	6.153	3.147	0.445	3.592	3885	876.1	1	11.2
7.000	3888	6.151	3.151	0.445	3.596	3888	876.3	1	11.2
7.000	3665	6.359	3.357	0.536	3.893	3665	862.3	1	10.9
7.000	3660	6.399	3.353	0.505	3.858	3660	869.1	1	11.6
8.000	4496	5.493	3.493	0.372	3.865	4496	903.8	1	11.5
10.00	6378	3.708	3.719	0.173	3.892	6378	955.5	1	12.5

tables, s_0 shows a good constancy with a few exceptions. These are probably due to differences in water content of the dry resin.

The $\varkappa$ (β) curve for Dowex 50 differs much from that of Wofatit KS but both increase for small β. The curve for Dowex 50 has a minimum at $\beta \approx 0.15$.

Table 8 b. a_0 = 100.0 mC. Pyrex bottles. AgR form of Dowex 50.

n_{H^+tot} mmol	n_{Ag^+} mmol	n_{H^+} mmol	n_{AgR} mmol	n_{RH} mmol	s_0 mmol	$a \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
10.00	1.469	8.531	2.589	1.481	4.070	1469	636.1	1	10.2
10.00	1.471	8.529	2.596	1.493	4.089	1471	634.9	1	10.1
10.00	1.476	8.524	2.612	1.469	4.081	1476	640.0	1	10.3
10.00	1.480	8.520	2.595	1.471	4.066	1480	638.2	1	10.2
6.000	4.380	5.611	3.682	0.383	4.065	4380	905.8	1	12.3
6.000	4.384	5.603	3.648	0.390	4.038	4384	903.4	1	12.0
4.000	6.133	3.810	3.899	0.214	4.113	6133	948.0	1	11.3
4.000	6.159	3.795	4.087	0.224	4.311	6159	948.0	1	11.2
2.000	8.111	1.929	4.194	0.075	4.269	8111	982.4	1	13.3
2.000	8.127	1.926	4.105	0.086	4.191	8127	979.5	1	11.3

Table 8 c. $a_0 = 20.00$ *mC. Pyrex bottles. HR form of Dowex 50.*

$n_{Ag+\ tot}$ mmol	$n_{Ag+} \cdot 10^3$ mmol	n_{H+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	$a \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
0.00500	0.2482	2.00	—	3.563	3.568	1.241	1.332	4	10.7
0.00500	0.1875	1.99	—	3.539	3.544	0.938	1.358	4	14.4
0.02500	1.028	2.00	—	3.537	3.561	5.140	6.731	4	13.2
0,02500	1.043	1.99	—	3.534	3.558	5.215	6.734	4	12.9
0.05000	2.344	1.99	—	3.500	3.548	11.72	13.43	4	11.6
0.05000	2.326	1.99	—	3.552	3.600	11.63	13.24	4	11.5
0.1000	4.930	2.00	—	3.407	3.502	24.65	27.14	4	11.3
0.1000	4.969	1.99	—	3.463	3.558	24.85	26.71	4	11.0
0.5000	31.30	1.97	0.4565	3.084	3.541	156.5	128.9	1	9.3
0.5000	31.93	1.97	0.4498	3.081	3.531	159.7	127.4	1	9.0
1.000	70.91	1.93	0.9130	2.636	3.549	354.6	257.3	1	9.4
1.000	71.75	1.93	0.9082	2.630	3.538	358.8	256.7	1	9.3
1.500	120	1.868	1.362	2.218	3.580	599.0	380.4	1	9.6
1.500	117	1.863	1.360	2.210	3.570	585.0	381.0	1	9.8
2.000	185	1.795	1.781	1.792	3.573	922.5	498.5	1	9.6
2.000	184	1.792	1.774	1.778	3.552	917.5	499.4	1	9.7

Table 8 d. $a_0 = 20.00$ *mC. Pyrex bottles. AgR form of Dowex 50.*

$n_{H+\ tot}$ mmol	n_{Ag+} mmol	n_{H+} mmol	n_{AgR} mmol	n_{HR} mmol	s_0 mmol	$a \cdot 10^4$	$\beta \cdot 10^3$	Method of evaluatn.	$\varkappa$ from (3)
1.500	0.877	1.111	3.699	0.383	4.082	438	906.2	1	12.2
1.500	0.881	1.105	3.699	0.374	4.073	440	908.2	1	12.4
0.5000	1.576	0.413	4.010	0.091	4.101	788	977.8	1	11.5
0.5000	1.580	0.410	4.017	0.087	4.104	790	978.8	1	12.0

It is interesting to note that our results are in qualitative agreement with those of Samuelson [6] and Duncan and Lister [10], who have also shown that $\varkappa_{Me,H}$, increases with decreasing β_{MeR}.

In papers to follow, the results in this paper will be compared with those obtained by Ekedahl from leaking curves [17], and it will be shown how data on ion exchange equilibria can be used for calculating the activities of the components in the resin. Some of these latter results have already been published in preliminary communications [18–20].

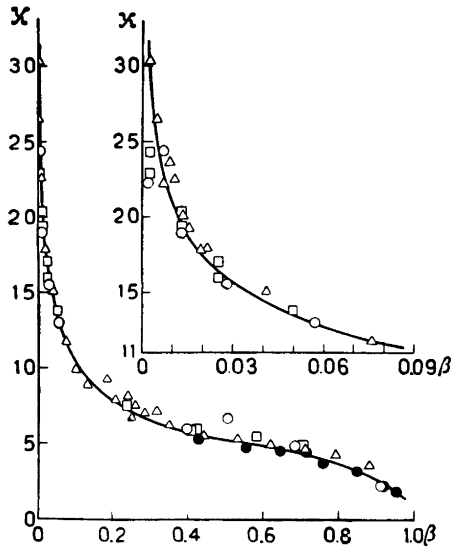


Fig. 4. The equilibrium quotient $\varkappa$ as function of the silver fraction for Wofatit KS. The same data as in Tables 7 a—c. The range $\beta < 0.09$ is also given on a larger scale.

△ *Starting with HR form, $a_0 = 100.0$ mC. Bottles with rubber stoppers.*
○ *Starting with HR form, $a_0 = 100.0$ mC. Pyrex bottles.*
● *Starting with AgR form, $a_0 = 100.0$ mC. Pyrex bottles.*
□ *Starting with HR form, $a_0 = 20.00$ mC. Pyrex bottles.*

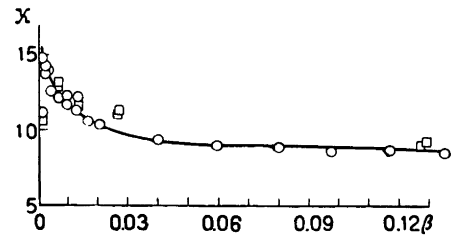
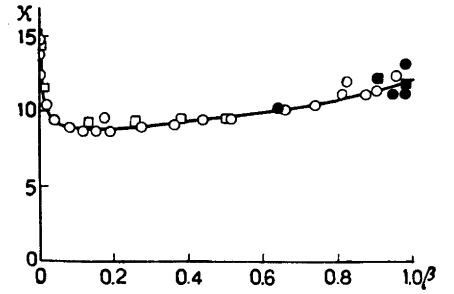


Fig. 5. The equilibrium quotient $\varkappa$ as function of the silver fraction β for Dowex 50. The same data as in Table 8 a-d. The range $\beta < 0.13$ is also given on a larger scale.

○ *Starting with HR form, $a_0 = 100.0$ mC. Pyrex bottles.*
● *Starting with AgR form, $a_0 = 100.0$ mC. Pyrex bottles.*
□ *Starting with HR form, $a_0 = 20.00$ mC. Pyrex bottles.*
■ *Starting with AgR form, $a_0 = 20.00$ mC. Pyrex bottles.*



SUMMARY

The exchange equilibrium $Ag^+ — H^+$ has been studied at two ionic strengths ($I = 0.100$ and 0.020) on Wofatit KS and Dowex 50. A broad concentration range was covered $0.001 \leqq \beta \leqq 0.98$, using emf and chemical methods. The equilibrium was attained from both sides. No corrections for activities were tried.

The authors have preferred to represent their measurements with $\varkappa$ (β) curves Figs. 4 and 5, where $\varkappa$ is the equilibrium quotient, and β the molar fraction of AgR. The $\varkappa$ (β) curves are very different for the two exchangers but both increase for small β. The $\varkappa$ (β) curve for Dowex 50 has a minimum at $\beta \approx 0.15$. The error in $\varkappa$ is about $\pm$ 5 %.

$\varkappa$ is found to be independent of the ionic strength for both exchangers. For Dowex 50, $\varkappa$ and s_0 did not change when the particle size was decreased by grinding. It was also checked that the equilibrium is attained within the shortest time of shaking (24 hours).

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