

## ANION EXCHANGE STUDIES

XXVI. A COLUMN METHOD FOR MEASUREMENT  
OF ION EXCHANGE EQUILIBRIA AT HIGH TEMPERATURE.  
TEMPERATURE COEFFICIENT OF THE  $\text{Br}^-$ - $\text{Cl}^-$  EXCHANGE REACTION\*

KURT A. KRAUS, RICHARD J. RARIDON\*\* AND DAVID L. HOLCOMB\*\*\*

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. (U.S.A.)*

(Received May 13th, 1959)

Although measurement of ion exchange equilibria as a function of temperature is of considerable importance for an understanding of ion exchange, relatively little work has so far been reported. Further, in spite of currently great interest in ion exchange processes above the boiling point of water, quantitative information in this region seems to be completely lacking. This paucity of information presumably is partly due to the fact that simple equipment for ion exchange measurements at elevated temperatures has not been available. It now appears that an adaptation of the preloaded column technique, used in this laboratory for some time for measurement at room temperature of very large distribution coefficients<sup>3</sup> overcomes this difficulty. It is the purpose of the present paper to describe the technique and newly developed equipment and to illustrate its use with a typical anion exchange reaction, the exchange of tracer bromide ions for chloride ions using a strongly basic anion exchange resin.

In the preloaded column technique a sample of fine-mesh resin, previously uniformly loaded with respect to the ion whose adsorption is to be studied, is placed into a column. Eluent passing through the column, rapidly comes to equilibrium in the upper layers of the bed. With high distribution coefficients  $D$  only relatively small amounts of the adsorbed material need to leave the resin in each column volume of effluent. Hence, at sufficiently slow flow rates, the composition of the bulk of the bed remains essentially unchanged and distribution coefficients may readily be computed from analysis of the effluent solution and the known initial composition of the resin. Equilibration rates within the bed may be made extremely fast. At high values of  $D$  the rate is controlled principally by diffusion through the interstitial space of the bed.

\* This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tenn., operated by Union Carbide Corporation. Previous papers: XXIV and XXV, see ref.<sup>1,2</sup>.

\*\* Based on work submitted by R. J. RARIDON to Vanderbilt University in partial fulfillment for the requirement for a Ph. D. degree. Work carried out at Oak Ridge National Laboratory under sponsorship of the Oak Ridge Institute of Nuclear Studies. Present address, Memphis State University, Department of Physics, Memphis, Tenn.

\*\*\* Engineering and Mechanical Division, Oak Ridge National Laboratory.

The time needed for equilibration varies with the square of the linear diffusion length which may be made extremely small by choice of small mesh particles.

This column method also has the advantage that it readily lends itself to temperature control and even to measurements above the boiling point of water. By utilizing capillary columns, relatively simple pressurized equipment can be developed.

For operation below the boiling point of the solvent the equipment can be extremely simple. As illustrated in Fig. 1, it could consist of a glass column inside a

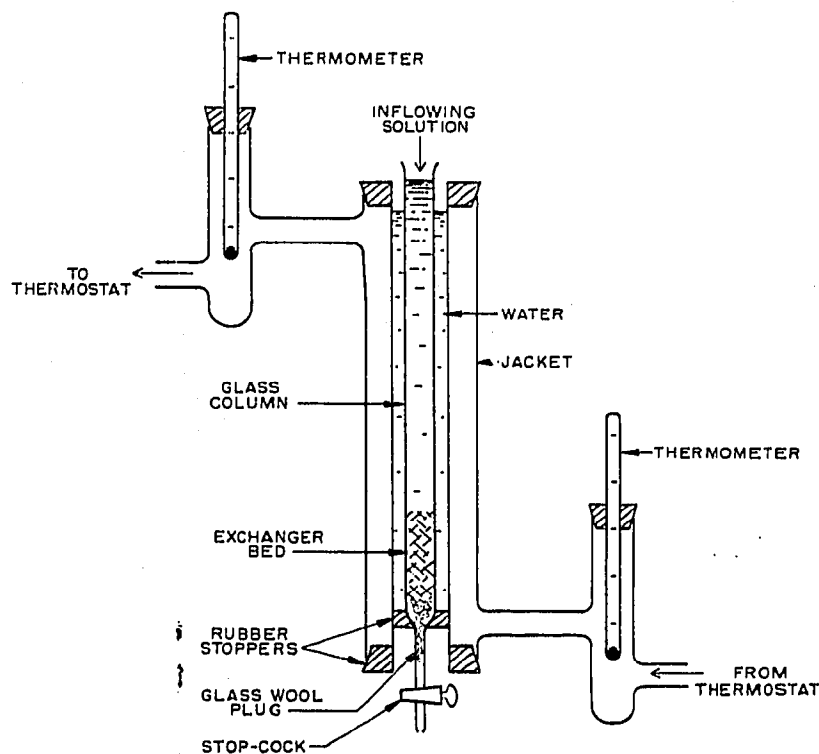


Fig. 1. Jacketed ion exchange column.

jacket through which thermostatic liquid is pumped. In the arrangement, Fig. 1, the column can easily be replaced; it is supported within the jacket by a small rubber ring which also serves as a seal for a small amount of water placed in the annulus between the column and the jacket for better heat conduction.

In the development of equipment suitable for measurements above the boiling point of the solvent the principle of a jacketed column has been retained. The two major design problems involved development of a simple letdown valve which could be used with ease even at slow rates for sampling the effluent under pressure and development of high pressure fittings for connecting the column to a solution reservoir in which the eluent is stored. To simplify design, all valves and fittings are near room temperature and only the bed at high temperature. Thick-walled glass capillaries were chosen for the columns to permit direct observation of the bed even under relatively high pressure. Based on these principles equipment was first built with stainless steel valves and a stainless steel solution reservoir. Another apparatus was then constructed where only glass or plastic tubings were exposed to the solutions.

It was used in the bromide-chloride exchange experiments which will be described below as well as in other experiments with solutions corrosive to stainless steel. We shall describe the principal features of the "stainless steel column" and then describe the alterations used in the all glass-plastic design.

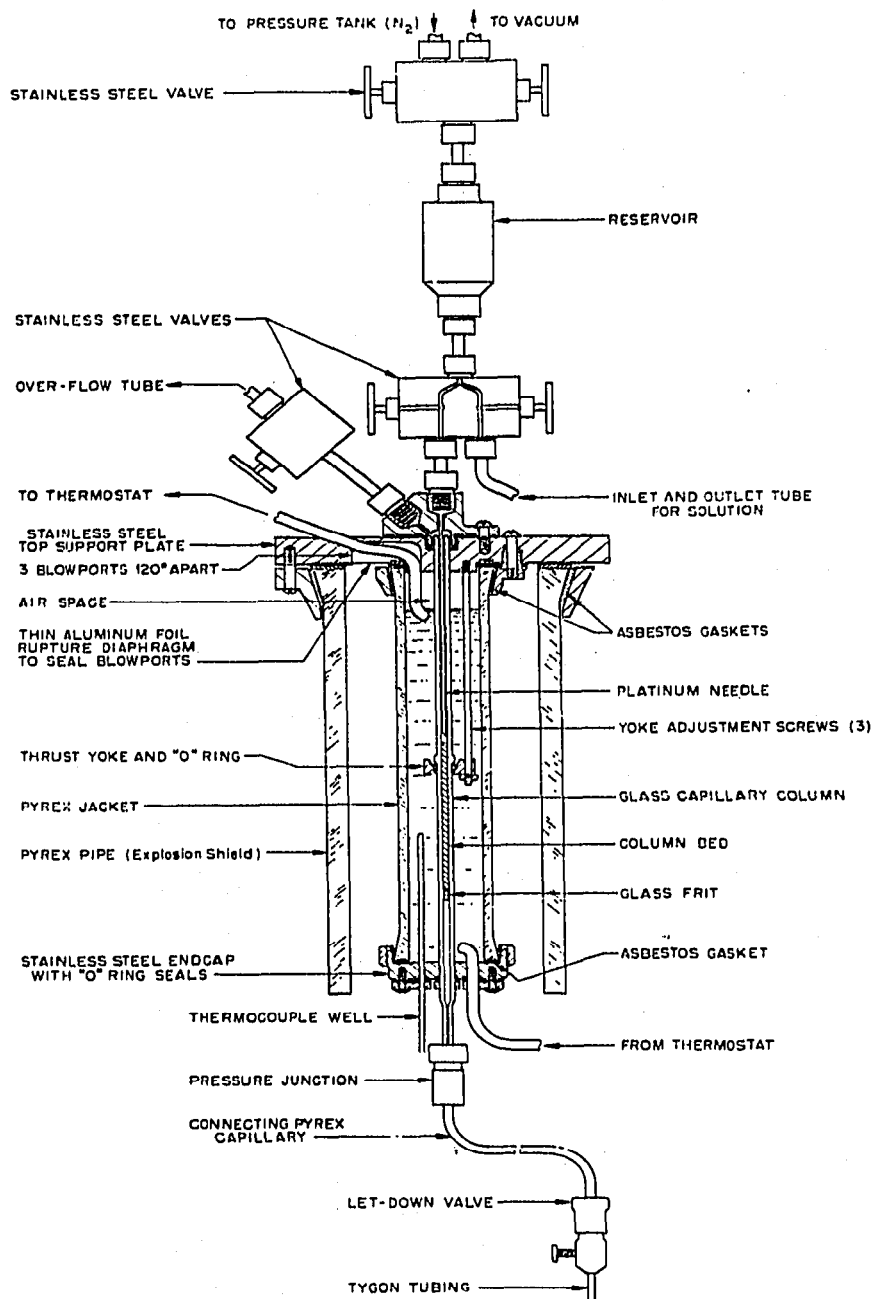


Fig. 2. High temperature pressurized ion exchange column.

### I. High temperature pressurized ion exchange column

The "stainless steel" equipment is illustrated in the diagram, Fig. 2, and the photograph, Fig. 3. This equipment has been used up to 200° and under 250 lb./in.<sup>2</sup> pressure.

The column proper is a thick-walled glass capillary with 2.5 mm I.D. and 9.0 mm O.D. The resin bed is supported by a glass frit sealed inside the capillary. A pressure seal is formed at the top of the column with a compressed "O" ring which fits snugly

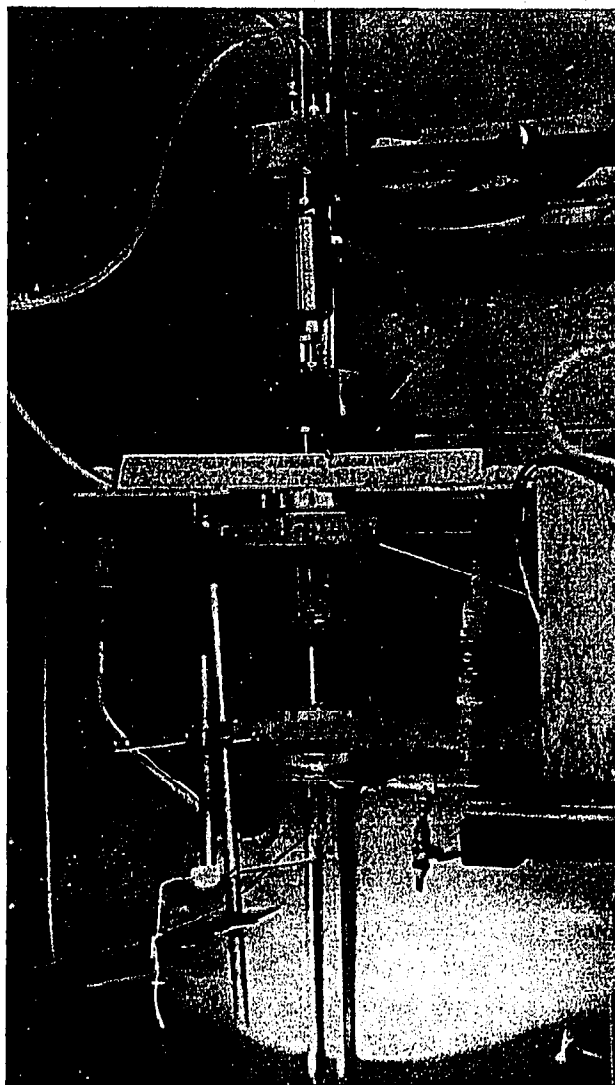


Fig. 3. High temperature pressurized ion exchange column.

around the column. A yoke with an "O" ring cushion, attached to the top plate, prevents the column from being thrust out under pressure.

The eluting solution is placed in a stainless steel reservoir which is kept near room temperature. The solution in the reservoir can be changed while the column is kept under pressure. The reservoir is isolated from the column with a stainless steel needle valve and solution is discharged under pressure through a side valve; the reservoir is filled through the same valve by applying a mild vacuum. The "old" solution can also be removed from the top portion of the column by opening a flush valve that allows the solution to flow back up the column after it has been forced

down through a platinum needle. By this method trapped air may also be removed.

The bottom of the column, narrowed to a 6 mm O.D. capillary, is coupled by a pressure junction to a glass capillary (6 mm O.D., 0.5 mm I.D.) that leads to a letdown

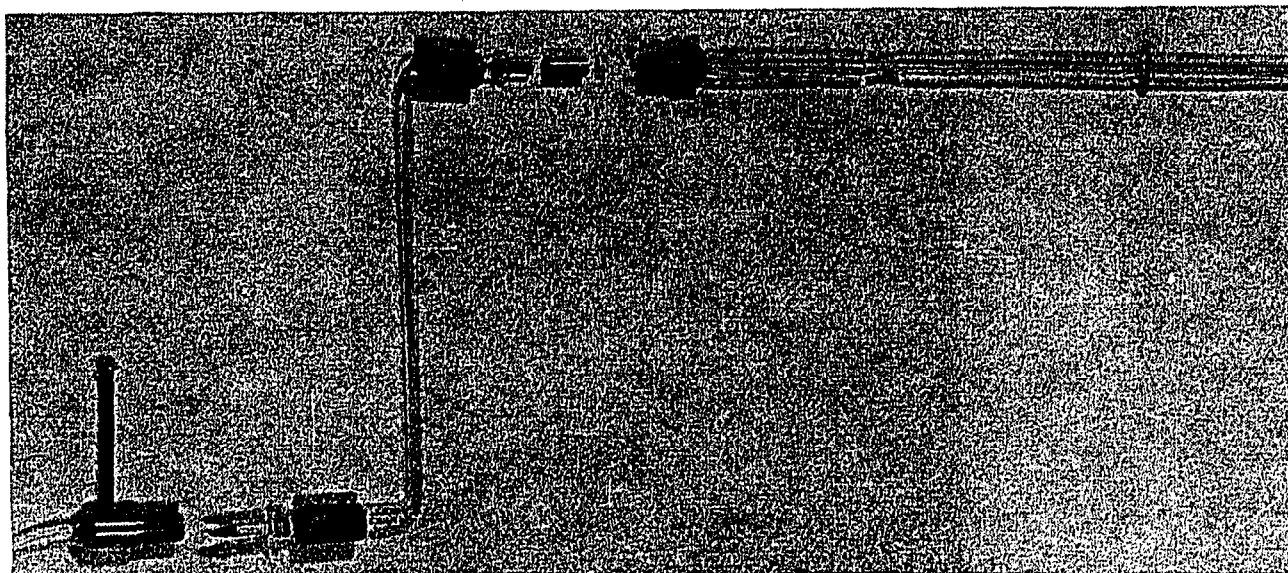


Fig. 4. Column, pressure junction, exit capillary, and letdown valve.

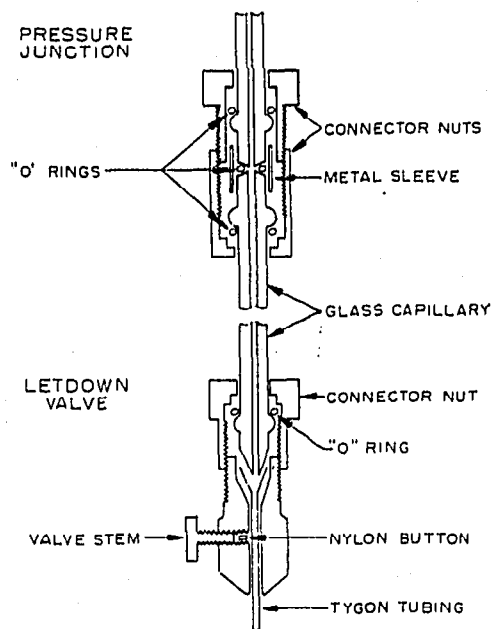


Fig. 5. Details of pressure junction and letdown valve.

(or sampling) valve. Details of the junction and valve are shown in the photograph, Fig. 4, and diagram, Fig. 5. When the connector nuts on the pressure junction are tightened, the "O" ring between the tapered glass ends is compressed, forming a seal. The ring is held in place by a metal sleeve. The other "O" rings serve to cushion the

nuts against the glass. The connector nut on the letdown valve forces the tapered end of the capillary into the flared end of a plastic (*e.g.*, "Tygon") tubing forming a seal. Deformation of the plastic tubing is prevented by a metal sleeve (aluminium) which also serves to hold a screw, the valve stem. When the valve is tightened a nylon button compresses the plastic tubing, thus controlling effluent flow.

The temperature of the column is maintained by circulating silicone oil through a Pyrex pipe surrounding the column. Oil flow is upward through the jacket. It is withdrawn through a tube projecting *ca.* 1 in. below the top plate so that an air gap separates this plate from the hot liquid, leaving the plate at relatively low temperature. The air lock above the oil in the jacket is closed by an aluminum gasket which covers three large ports leading from the jacket to a large diameter Pyrex pipe. If the column should break at high pressure, this gasket would rupture and release the pressure. The oil would then be confined and blow downward in the outer pipe. To further protect the operator, lucite panels were installed in front of the apparatus, which was built into a floor hood. The letdown valve is adjusted through a hole in one panel. The exit Tygon tubing also passes through a small hole so that samples can be collected in front of the shield.

A thermocouple well is inserted into the jacket through the bottom plate and sealed with a compressed "O" ring. Temperature is recorded continuously on a "Brown" recorder which also serves as a regulator by means of a built-in mercury switch in line with one of three heaters immersed in the oil bath. Lag in the temperature response from the bath to the column was sufficiently small to prevent fluctuations of more than  $\pm 0.1^\circ$ .

Presence of stainless steel limits use of the column to nitrate and other non-corrosive solutions. For work with chloride solutions and other solutions corrosive to stainless steel an adaptation of the equipment, employing only glass, plastic and silicone rubber in contact with solution was built. In this equipment (see diagram, Fig. 6) the column and sampling sections were essentially unchanged. The reservoir was made of thick-walled Pyrex glass. All control valves were similar to the letdown valves previously described, *i.e.*, they involved plastic tubings in metal retaining sleeves which also hold the valve stem. The valves were sized somewhat larger than the letdown valve since they connect larger diameter (9 mm O.D.) capillaries. Details of the connections (A, B, C and D of Fig. 6) are shown in Fig. 7. Tygon tubing, flared at both ends, extends through C and D, connecting the column and the lower end of the reservoir. Connections B and D also serve as valves. As in the letdown valve, a nylon button is pushed by a screw against the Tygon tubing. However, to prevent extensive deformation of the plastic tubing, the valve also contains a set screw which provides a flat seat, located approximately in the middle of the opening, against which the valve operates. Since it is desirable to attach the valves to the glass tubings after the glass blowing is complete, the connectors were redesigned. They now involve a split nut which is placed over the wide portion of the glass tubing and which is held in place by a retaining nut with a hole sufficiently large to accommodate the widest part of the glass tubing.

The valve stems extend through a lucite shield which covers all but the back of the equipment. Here a glass wool filter is installed. In case of breakage it prevents dangerous pressure buildup while trapping solution and particles. This feature is especially desirable if substantial amounts of radioactive tracers are used.

With the sleeved plastic tubing as connectors it was unnecessary to install a special thrust cradle for the column. This permitted insertion of the column through the top plate and filling of the column from the top, but necessitated a redesign of the end plates. The top and bottom plates were provided with oversized holes for admission

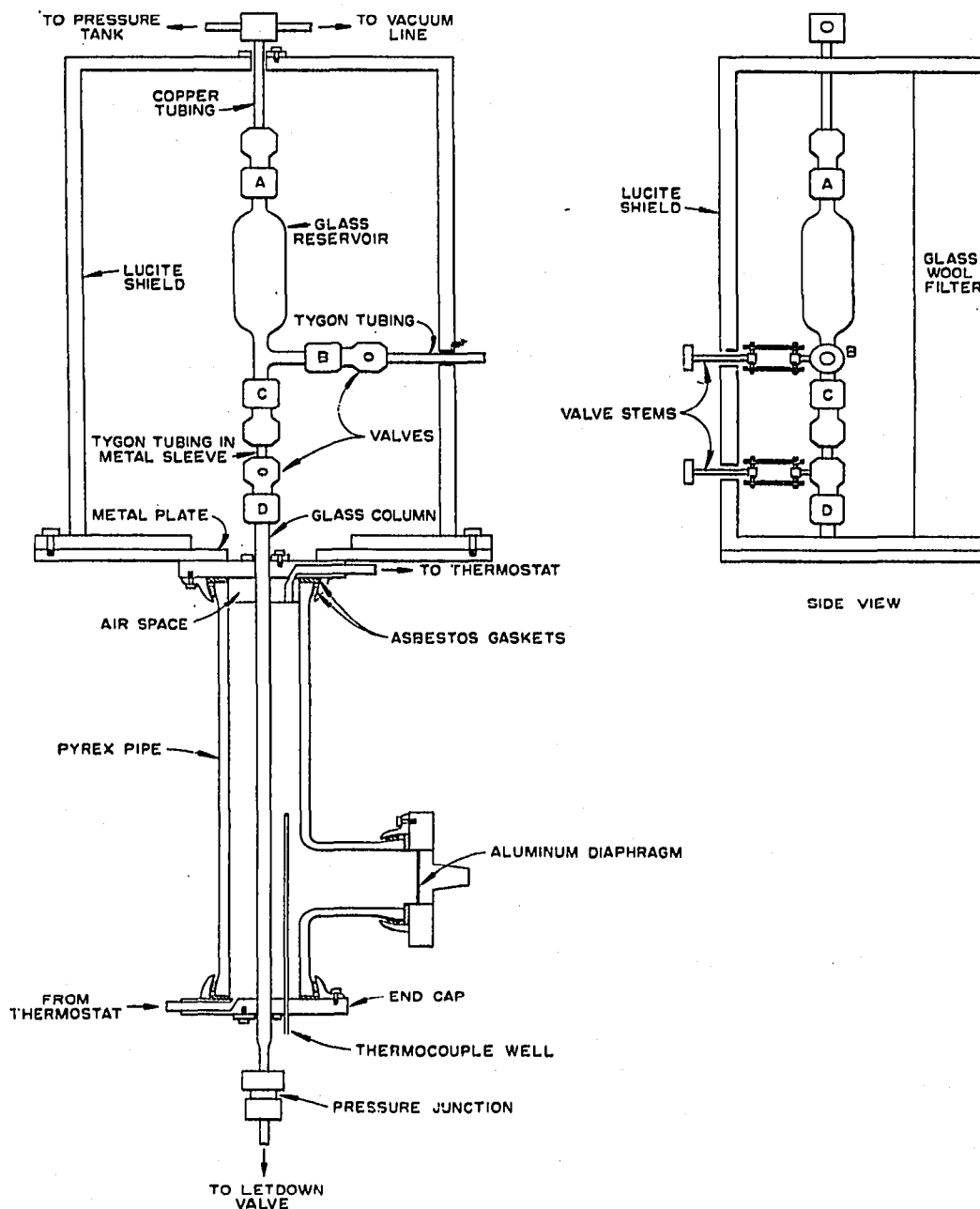


Fig. 6. High temperature ion exchange column (glass-plastic design).

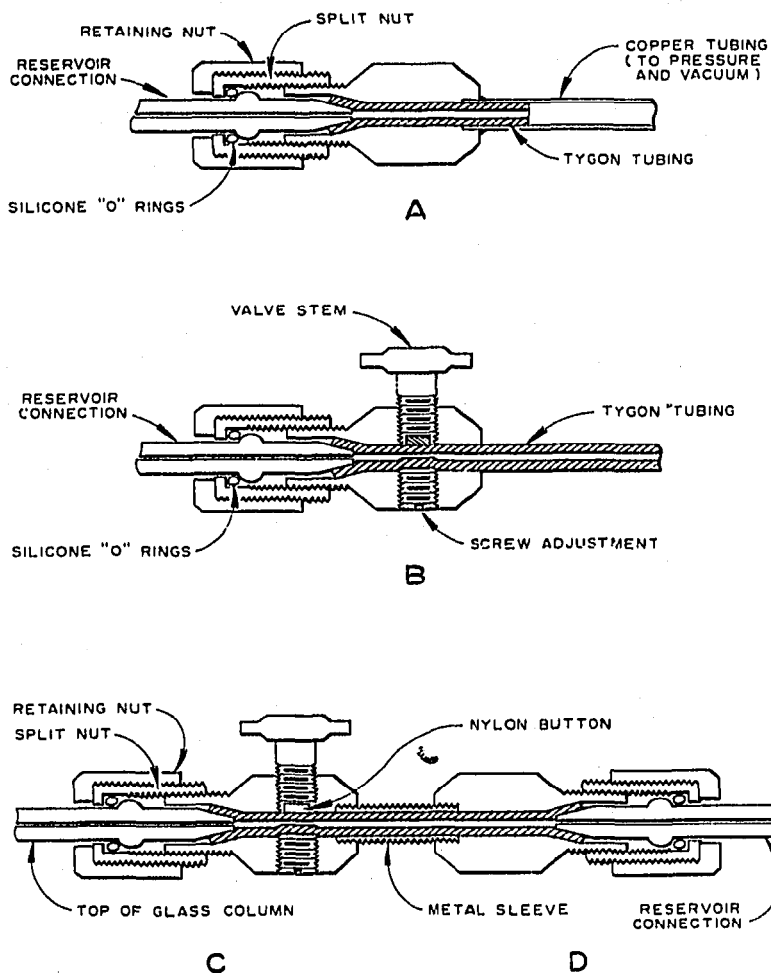


Fig. 7. Details of connections and valves.

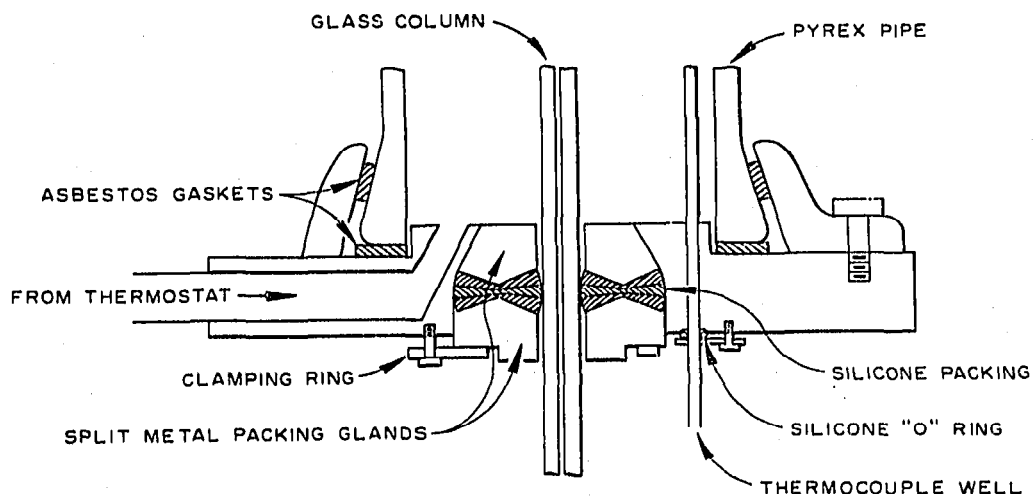


Fig. 8. End cap detail.



of the column. These were closed by insertion of a split metal ring followed by three silicone rubber compression gaskets, a second split ring and a plate which could be tightened with 3 screws (see Fig. 8). This type of closure proved satisfactory since the jacket in general is not under high pressure.

## 2. Bromide-chloride exchange

The adsorption of tracer bromide was studied in the temperature range 5 to 150° with the strongly basic anion exchanger Dowex-1-X10 in the chloride form (mesh size 170-230). The tracer (*ca.* 0.5 millicurie  $^{82}\text{Br}$ ,  $T_{1/2}$  36 h) was adsorbed on the resin from 0.5 *M* HCl. Resin and tracer were agitated for 2 days, which appeared sufficient for uniform loading of the sample. The tracer was of sufficiently high specific activity so that resin loading with respect to bromide was less than 1% of exchange capacity.

The loaded resin was placed into the column and washed with 0.01 *M* HCl. Concentration of bromide in the resin was computed from the known initial concentration of tracer in the sample (corrected for decay) and from analysis of the wash solution. To conform with our usual units, resin concentrations are expressed in terms of kilograms of dried resin. The dry-resin weight was computed from the known weight of the air-dried resin and the separately determined weight ratio of air-dried resin and resin dried (to constant weight) in a vacuum desiccator over the dehydrating agent "Anhydron" at 60°.

Distribution coefficients  $D$  (amount per kg resin/amount per kg of water) were determined by elution of the column with 0.01 *M* HCl. Flow rate was usually 3 cm/min (c.c./cm<sup>2</sup>/min) which was easily in the range where the effluent activity was independent of flow-rate. Samples of the effluent (*ca.* 1 ml) were collected in weighed glass tubes until the tracer concentration in successive samples was essentially constant. The sample size was ascertained by weighing and the bromide concentration by counting the tubes in a well-type scintillation counter (NaI-Tl). Measurements were carried out with increasing and decreasing temperature and the values, which usually agreed to better than  $\pm 1\%$ , and in all cases to better than 2%, were averaged. The observed (average) distribution coefficients as a function of temperature are listed in Table I.

TABLE I  
COEFFICIENTS FOR  $\text{Br}^-$ - $\text{Cl}^-$  EXCHANGE REACTION

$t$ (°C)	$D$	$K'$	$K'_{calc}$
5	1350	3.70	3.71
25	1120	3.07	3.06
50	923	2.52	2.52
75	789	2.16	2.17
100	704	1.92	1.93
125	645	1.76	1.75
140	623	1.70	1.68
150	590	1.61	1.63

The mass action expression for the ion exchange equilibrium may be written as

$$K \equiv 1 = \frac{m_{\text{Br}(r)} m_{\text{Cl}} \gamma_{\text{Br}(r)} \gamma_{\text{Cl}}}{m_{\text{Br}} m_{\text{Cl}(r)} \gamma_{\text{Br}} \gamma_{\text{Cl}(r)}} = K' \Gamma_{(r)} \quad (1)$$

where:

$m$  = concentrations

$\gamma$  = activity coefficients of ions

$K' = \frac{m_{\text{Br}(r)} m_{\text{Cl}} \gamma_{\text{Cl}}}{m_{\text{Br}} m_{\text{Cl}(r)} \gamma_{\text{Br}}} =$  the selectivity coefficient corrected for the activity coefficients in the aqueous phase

$\Gamma_{(r)} = \frac{\gamma_{\text{Br}(r)}}{\gamma_{\text{Cl}(r)}} =$  the activity coefficient ratio of the ions in the resin phase.

As is customary in this laboratory, we have taken the same standard states for the ions in the resin and aqueous phases and hence have set  $K \equiv 1$  at all temperatures.

Since the electrolyte solutions used were very dilute we have assumed  $\gamma_{\text{Cl}}/\gamma_{\text{Br}} = 1$  and hence computed  $K'$  from the observed distribution coefficients ( $D = m_{\text{Br}(r)}/m_{\text{Br}}$ ) and the chloride concentration of the solutions ( $m_{\text{Cl}}$ ). The chloride concentration in the resin ( $m_{\text{Cl}(r)}$ ) was taken to be equal to the capacity of the resin (3.66 equivalents per kg) since in these dilute solutions resin invasion by the electrolyte is negligible.

As shown in Table I,  $K'$  decreases only moderately with temperature from 3.70 at 5° C to 1.61 at 150° C. No measurements at higher temperatures have been recorded since the results tended to be erratic, probably a result of slow decomposition of the resin.

A plot of  $\log K'$  vs.  $1/T$  (Fig. 9) (where  $T$  is the absolute temperature) shows slight curvature, implying that the heat of adsorption  $\Delta H'$  of bromide tracer on the chloride form of the resin is not constant. We have fitted the observed data to the empirical equation

$$\log K' = \log K'_t + \alpha \log (T/T_t) + \beta [1 - (T_t/T)] \quad (2)$$

where  $\alpha$  and  $\beta$  are constants and subscript "t" refers to a reference temperature, here taken as 75° C. This equation is derived from the assumption that the heat capacity

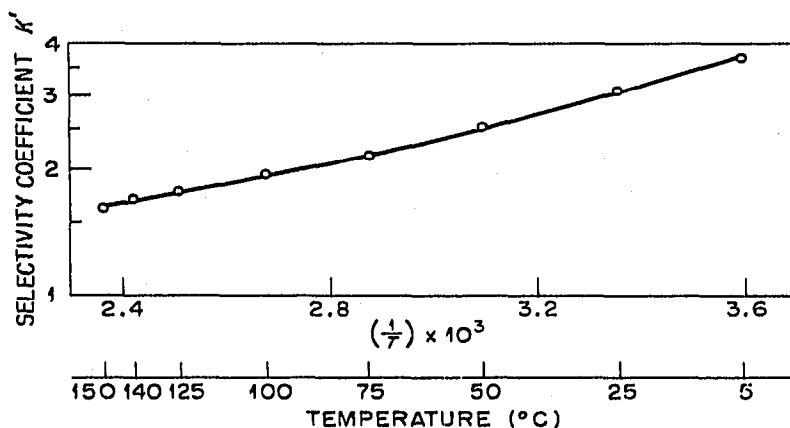


Fig. 9. Temperature dependence of anion exchange equilibria (bromide tracer on Dowex-1-X10, Cl<sup>-</sup> form).

change on adsorption,  $\Delta\bar{C}'_p$ , is constant. Analysis of the data gave  $\alpha = 2.500$ ,  $\beta = -1.893$ , and  $\log K'_t = 0.336$ . The solid curve in Fig. 9 is computed with these parameters and more detailed comparison between calculated and observed values of  $K'$  is included in Table I. The small scatter of observed values of  $K'$  and those calculated by eqn. (2) is noteworthy, since it further demonstrates the high inherent precision of the method.

Through differentiation of eqn. (2) we obtain

$$\Delta\bar{H}' = -R \, d \ln K' / d(1/T) = aRT + 2.303 \beta RT_t \quad (3)$$

$$\Delta\bar{C}'_p = d(\Delta\bar{H}')/dT = aR \quad (4)$$

and

$$\begin{aligned} \Delta\bar{S}' &= (\Delta\bar{H}' - \Delta\bar{F}')/T \\ &= aR + 2.303 \beta RT_t/T + R \ln K' \\ &= aR + 4.576 \beta + R \ln K'_t + aR \ln (T/T_t) \end{aligned} \quad (5)$$

through which the partial molal enthalpy, heat capacity and entropy changes for the adsorption reaction may be computed from the parameters  $\alpha$ ,  $\beta$  and  $K'_t$ . Values of  $\Delta\bar{H}'$ ,  $\Delta\bar{S}'$  and of  $(-RT \ln K')$  computed at round temperatures and extrapolated to 200° C are given in Table II. The heat capacity change  $\Delta\bar{C}'_p$  for the reaction was calculated to be 5.0 cal/°C and  $T_{\min}$ , where the fitting function has a minimum, is 607° K.

TABLE II  
PARTIAL MOLAL ENTHALPY AND ENTROPY CHANGES FOR Br<sup>-</sup>-Cl<sup>-</sup> EXCHANGE REACTION

$t$ (°C)	$-RT \ln K'$ (kcal)	$\Delta\bar{H}'$ (kcal)	$\Delta\bar{S}'$ (e.u.)
0	-0.74	-1.66	-3.4
25	-0.66	-1.53	-2.9
50	-0.59	-1.41	-2.5
75	-0.54	-1.29	-2.2
100	-0.49	-1.16	-1.8
125	-0.44	-1.04	-1.5
150	-0.41	-0.91	-1.2
175	-0.39	-0.79	-0.9
200	-0.37	-0.67	-0.6

#### ACKNOWLEDGEMENT

We are greatly indebted to Mr. W. L. VAN HOOZIER of the Oak Ridge National Laboratory Chemistry Division Shop for the construction of the high temperature columns.

#### SUMMARY

A packed column method for the precision measurement of temperature coefficients of ion exchange equilibria has been developed and equipment suitable for operation up

to 200° is described. Use of the equipment is illustrated with the bromide (tracer)-chloride anion exchange system in the range 0° to 150° for which the enthalpy change was found to be a linear function of temperature.

## REFERENCES

- <sup>1</sup> K. A. KRAUS AND F. NELSON, in *Proceedings of the Spring 1957 Symposium of the Electrochemical Society on Structure of Electrolytes*, (W. HAMER Editor), John Wiley & Sons, Inc., New York, 1959.
- <sup>2</sup> Y. MARCUS AND F. NELSON, *J. Phys. Chem.*, 63 (1959) 77.
- <sup>3</sup> K. A. KRAUS AND F. NELSON, *Symposium on Ion Exchange and Chromatography in Analytical Chemistry*, Am. Soc. Testing Materials, Special Publication, No. 195 (1958).

*J. Chromatog.*, 3 (1960) 178-189