[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

The Heats of Reaction of the Dichlorides of Samarium and Ytterbium with Hydrochloric Acid. A Microcalorimeter[1]

BY G. R. MACHLAN, C. T. STUBBLEFIELD AND L. EYRING

RECEIVED NOVEMBER 6, 1954

The heats of reaction at 25° of $SmCl_2$ and $YbCl_2$ with hydrogen-saturated 6.00 *M* HCl were found to be -42.2 ± 0.2 and -41.2 ± 0.2 kcal./mole, respectively. These values were combined with other thermochemical data to obtain the corresponding heats of formation of the dichlorides of -195.6 ± 1.0 and -184.5 ± 1.7 kcal/mole, respectively. The heats of reaction were measured in an adiabatic microcalorimeter which was constructed for that purpose. The description and characteristics of the instrument are given.

Introduction

Three members of the rare earth group, samarium, ytterbium and europium are known to exhibit the dipositive oxidation state. In order to study the stability of the compounds of that state thermochemical data are useful. Such information on the divalent compounds of samarium, ytterbium and europium was found to be practically non-existent; therefore, it was necessary to investigate their thermochemical properties.

The dichlorides appeared to be most suitable for this study because: (1) they are very soluble in water and acids, (2) the heats of solution of the corresponding trichlorides are known, and (3) methods of their preparation on the milligram scale have been perfected.

The reaction of the dichloride of samarium or ytterbium with HCl solutions results in rapid oxidation of the cations to the trivalent state with the evolution of hydrogen

$$M^{++} + H^{+} \longrightarrow M^{+++} + {}^{1}/{}_{2}H_2$$

The reaction of europium dichloride with HCl solution is not so simple. In the absence of oxygen, the reaction proceeds with oxidation by hydrogen ions, but the rate is so slow that it is unsuitable for calorimetric measurements in the apparatus described. If the acid contains dissolved oxygen, oxidation proceeds more rapidly according to the equation

$$Eu^{++} + {}^{1}/{}_{4}O_2 + H^{+} \longrightarrow Eu^{+++} + {}^{1}/{}_{2}H_2O$$

Since the extent to which the latter reaction occurred was not reproducible, it was necessary to limit this investigation to the determination of the heats of reaction of samarium and ytterbium dichlorides with 6.00 *M* HCl.

The Microcalorimeter

Construction.—A diagram of the adiabatic microcalorimeter is shown in Fig. 1. Westrum and Eyring[2] described an isothermal microcalorimeter of comparable size which had some of the features of this instrument.

The chemical reactions proceeded in the tantalum vessel (U) which had walls 0.025–0.038 cm. thick. About 9 ml. of acid solution was stirred with a platinum propeller (V) which was sealed with "Apiezon W" wax to the 1 mm. glass shaft (J). The brass housing into which the shaft was fitted rotated in the ball bearing (C), power being furnished through a flexible cable by a synchronous motor geared to 75 r.p.m. Sealed below the propeller with "Apiezon W" wax was the sample bulb (I) which could be broken on the anvil (W) by depressing the stirring shaft against the action of the spring (B). The sample bulb has been described previously.[2]

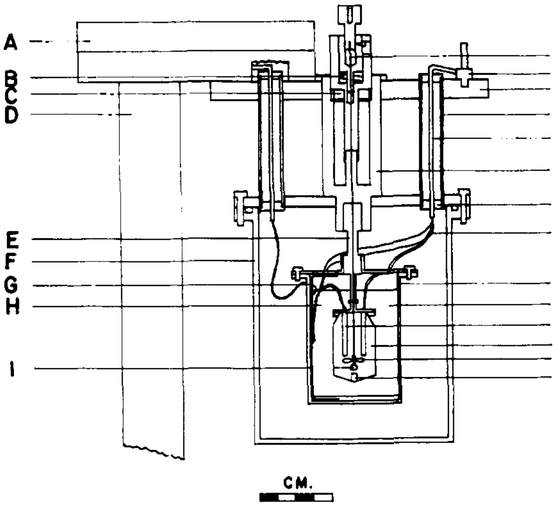

Fig. 1.—Microcalorimeter.

The reaction vessel was held with screws against its tantalum top, a "Teflon" gasket being used to make a high vacuum seal. Shrunk-fitted into the top were two tantalum wells (T), respectively, containing one end of the main thermal and the heat-input element, each sunk in "Apiezon W" wax.

Enclosing the reaction vessel was the adiabatic shield (R) which was made of 1.59 mm. thick copper. The temperatures of the body, top and bottom of the adiabatic shield were kept equal to the temperature of the reaction vessel by three B. and S. 30 manganin heaters wound bifilarly on their outsides, the currents through these heaters having been controlled by auto-transformers. Three multijunction thermels were used as indicating devices.

The main thermel (H) indicated the temperature difference between the reaction vessel and the side of the adiabatic shield. It was a thirty-junction, B. and S. 40, chromel P-constantan thermopile, the output voltage of which was amplified by a Liston-Folb, Model 10, d.c. Breaker-Type Amplifier and then by the Leeds and Northrup recording potentiometer (Speedomax). Temperature changes less than 10^{-5} degree were observed by this system. Two ten-junction, B. and S. 30 copper–constantan thermels indicated when the temperatures of the top and bottom of the adiabatic shield were equal to that of the body. Each of these output voltages was observed on a high sensitivity (0.05 microvolt per mm.) Leeds and Northrup suspension galvanometer.

The temperature of the adiabatic shield was measured by means of the copper resistance thermometer (S), the measuring circuit for which was described by Westrum and Robinson.[3]

Surrounding the adiabatic shield was the isothermal

---

[1] The data reported here were included in dissertations submitted by G. R. Machlan and C. T. Stubblefield to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] E. F. Westrum, Jr., and L. Eyring, THIS JOURNAL, **74**, 2045 (1952).

[3] E. F. Westrum, Jr., and H. P. Robinson, "Natl. Nuclear Energy Ser.," Div. IV, 14B, Transuranium Elements, Pts. II, 889–907 (1949).

shield (F) which was a machined brass can with walls and flange 3.18 mm. thick. The flange had a groove machined in it for an "O" ring seal. This shield was supported in the isothermal bath by the stirring mechanism housing and four 1.27 cm. tubes (M) all of which were attached to a 9.5 mm. thick bakelite disc (L) in the cover of the isothermal bath. One of these tubes contained fourteen B. and S. 14 copper lead-in wires (N) for the three thermopiles and the input heater. They were spaced by "Lucite" plugs (P) and vacuum sealed with "Apiezon W" wax. The second tube was similarly arranged to supply the a.c. currents for heating the adiabatic shield. The third tube contained the two thermometer leads (B. and S. 10 copper wires) terminating in the Wheatstone bridge tube (D). The last tube was open to high vacuum.

The "Lucite" hanger (E) was screwed against an "O" ring into the top of the isothermal shield. It supported the adiabatic shield and the reaction vessel. A hole through the center allowed the stirring shaft to pass.

The isothermal shield and bridge tube were lowered into an isothermal water-bath which was thyratron-regulated to 23.000 ± 0.003°. Heating and cooling of the bath were accomplished with a 250-watt knife heater and a cold finger. The bath-water was circulated at the rate of 380 liters per minute by a "Cenco" centrifugal pump.

The electrical energy input circuit was similar to that described by Westrum and Robinson.[3]

Calibration.—The temperature increases caused by accurately measured quantities of heat delivered by the energy-input circuit were used to calibrate the instrument over its entire 1.4° range. An appropriate graph of a convenient function of temperature rise *versus* a heat-input function was constructed. This graph was used to determine the heat which must have been evolved in the reaction of the sample to create the observed temperature rise of the calorimeter.

A chemical calibration was made by determining the heat of solution of pure magnesium in hydrogen-saturated 1.00 *M* HCl. The magnesium samples were weighed on a very sensitive (0.1239 microgram per division) quartz-fiber microbalance. The values obtained were in satisfactory agreement with those of Shomate and Huffman.[4]

The temperature scale was established by reference to a platinum resistance thermometer calibrated by the National Bureau of Standards. Results were calculated using the value of one calorie = 4.1840 absolute joules. The atomic weights of the elements used were: H, 1.0080; Cl, 35.457; Sm, 150.43; Eu, 152.0; and Yb, 173.04.

Some characteristics of the calorimeter are: (1) a thermal leakage modulus of 5×10^{-3} min.$^{-1}$ under the high vacuum obtained with the DPI-GF20A oil diffusion pump, 7×10^{-3} min.$^{-1}$ using only the Cenco-Megavac, and 2×10^{-2} min.$^{-1}$ at atmospheric pressure; (2) a temperature sensitivity of 2×10^{-5}° over a 1.4° range; and (3) a heat capacity of about 10 cal./deg.

Experimental Methods

Preparation and Properties of the Dichlorides.—The preferred method of preparing samarium and ytterbium dichlorides was hydrogen reduction of the corresponding anhydrous trichlorides.

The anhydrous trichlorides were prepared by passing thionyl chloride vapor over the sesquioxide at 450° for 24 hours

$$M_2O_3 + 3SOCl_2 \longrightarrow 2MCl_3 + 3SO_2$$

The yields were 100% as indicated by the complete solubility of the products in water.

A special apparatus was designed for the chlorination. The all-Pyrex system was constructed by sealing a 50-ml. round-bottom flask to a 22 × 1.5 cm. reaction tube, the top of the tube being fitted with a ground glass stopper. The upper end of a 20-cm. condenser was connected by means of a 6 cm. length of one cm. tubing to the reaction tube just below the stopper; and its lower end, which was fashioned in the form of a jet, was connected through 6 mm. tubing to the bottom of the flask. The jet was placed at the level of the lower end of the reaction tube. Just above the jet, a side-arm extended to a soda-lime trap.

The flask and the reaction tube were wrapped with heaters consisting of B. and S. 30 and B. and S. 26 "Nichrome" wires, respectively. Both heaters were insulated with asbestos tapes and controlled by auto-transformers.

The flask was half-filled with thionyl chloride, and a Pyrex bulb containing 150 mg. of the sesquioxide was suspended in the middle of the reaction tube by means of a 1.5 mm. glass rod sealed to the stopper. The sesquioxides of samarium and ytterbium were 99.9% pure, and were obtained from Dr. F. H. Spedding. Ames Laboratory of Iowa State College. The temperature of the reaction tube was raised to 450° while the temperature of the flask was adjusted for minimum cycling of the chlorinating agent.

The soda-lime trap prevented the escape of corrosive gases into the room and the entrance of water.

After 24 hours, the bulb containing the trichloride was quickly removed from the chlorinating apparatus and transferred in a small desiccator containing "Drierite" to the "dry-box," where it was loaded into a molybdenum boat and placed in a reduction apparatus of quartz. The stopcocks of the reduction apparatus were closed off before removing it from the "dry-box."

Reduction to the dichlorides in a stream of pure hydrogen at 650° was accomplished within 6 hours. The temperature of the tubular furnace was carefully controlled.

After the reduction the hydrogenation apparatus was closed off and moved into the "dry-box." There the sample was removed in the dry, oxygen-free atmosphere, and ground to a fine powder in a "Mullite" mortar.

The calorimeter bulbs which were to be filled with 10- to 20-mg. samples had previously been thoroughly cleaned, dried and accurately weighed. After making sure that none of the sample remained in the neck of the bulb, it was sealed with the glass bead and the "Apiezon W" wax by means of a "hot wire" electric heater. The bulbs were taken from the "dry-box," reweighed and stored in a desiccator until used.

All the weighings were made on an Ainsworth FDJ, optical lever type, microbalance (sensitivity: 2.5 micrograms per division).

X-Ray diffraction patterns showed the reddish-brown samarium dichloride to have the lead dichloride structure while grayish-white ytterbium dichloride had a rhombohedral structure. These observations agree with those of Klemm and Döll.[5]

Analysis.—Gravimetric analysis for chloride content of the dichlorides showed the samarium samples to be only 69.4% reduced and the ytterbium samples to be completely reduced.

Calorimetric Measurements.—Two processes occurred upon reaction of these dichlorides with hydrochloric acid: solution and oxidation. The heat of reaction observed by the calorimeter was the total heat evolved in those two processes. Since the calorimeter could not resolve the observed heat into the heat of solution and the heat of oxidation, the heat of reaction was combined with other thermochemical data to effect a resolution. Fortunately, all the thermochemical data necessary for the resolution had either been measured or could be estimated.

The reaction which occurred in the acid solution was approximately given by the equation

$$MCl_2(c) + 6.00\ M\ HCl \longrightarrow MCl_3 \cdot 6.00\ M\ HCl + {}^1/_2H_2(g)$$

The acid was saturated with hydrogen in order to eliminate the error due to heat evolved in the solution of hydrogen released by the sample. Also, the displacement of air dissolved in the acid was accomplished.

The heats evolved in the reactions of samarium and ytterbium dichlorides in 6.00 *M* HCl are given in Tables I and II, respectively. The correction has not been made here for the presence of trichloride in the samarium samples.

Results and Discussion

Heat of Reaction.—The heat of reaction (in kcal./mole) of ytterbium dichloride was equal to the product of the molecular weight and the value of Q/W which was the heat evolved in kilocalories per gram.

Since the samarium samples contained some tri-

---

(4) C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1625 (1943).

(5) W. Klemm and W. Döll, *Z. anorg. allgem. Chem.*, **241**, 233 (1939).

TABLE I

HEAT EVOLVED IN THE REACTION OF $SmCl_2$ WITH 6.00 *M* HCl AT 25°

Preparation[a]	*W* (mg.)	*Q* (cal.)	*Q/W*
1	17.782	2.960	0.1664
	14.889	2.485	.1669
	9.167	1.531	.1670
2	12.630	2.106	.1667
	12.069	2.010	.1673
		Av.	0.1669 ± 0.0003

[a] The samples of preparation 1 were run in hydrogen-saturated acid, and the samples of preparation 2 were run in air-saturated acid.

TABLE II

HEAT EVOLVED IN THE REACTION OF $YbCl_2$ WITH 6.00 *M* HCl AT 25°

Preparation[a]	*W* (mg.)	*Q* (cal.)	*Q/W*
1	22.782	3.829	0.1680
	14.300	2.414	.1688
	16.561	2.773	.1674
2	11.879	2.009	.1691
	15.739	2.645	.1680
		Av.	0.1683 ± 0.0006

[a] All runs were made in hydrogen-saturated acid.

chloride, the following formula was used to obtain the heat of reaction

$$\Delta H_i = -\frac{M_i}{f_i}\left[\frac{Q}{W} + \frac{(1 - f_i)\Delta H_j}{M_j}\right]$$

Here ΔH is the heat of reaction in kcal./mole of the pure component in 6 *M* HCl; *M* is the molecular weight of that component; *f* is the fraction by weight of that component as determined by chloride analysis; and *Q*/*W* is the observed value of the heat evolved per gram when the samarium dichloride–trichloride mixture reacted with acid solution. The subscripts i and j refer to the di- and trichloride, respectively. The value of ΔH_j was −29.5 ± 0.2 kcal./mole, which was determined calorimetrically as described below, and f_i was 0.694.

The heats of reaction of the dichlorides in 6.00 *M* HCl are given in Table III.

TABLE III

HEATS OF REACTION OF $SmCl_2$ AND $YbCl_2$ WITH 6.00 *M* HCl

Dichloride	Mol. wt.	ΔH (kcal./mole)[a]
$SmCl_2$	221.34	−42.2 ± 0.2
$YbCl_2$	243.95	−41.2 ± 0.2

[a] Includes a correction of 0.15 kcal. per mole for vaporization of water into the 1/2 mole of evolved hydrogen.

Heats of Solution and Heats of Formation.—These enthalpy changes were calculated from the following set of thermochemical equations

$$MCl_2(c) + xHCl\cdot yH_2O = MCl_3\cdot(x - 1)HCl\cdot yH_2O + {}^1/_2H_2(g) \quad (1)$$

$$MCl_2\cdot HCl\cdot\infty H_2O = MCl_3\cdot\infty H_2O + {}^1/_2H_2(g) \quad (2)$$

$$MCl_3(c) + \infty H_2O(l) = MCl_3\cdot\infty H_2O \quad (3)$$

$$MCl_3(c) + xHCl\cdot yH_2O = MCl_3\cdot xHCl\cdot yH_2O \quad (4)$$

$$MCl_3\cdot(x - 1)HCl\cdot yH_2O + HCl(g) = MCl_3\cdot xHCl\cdot yH_2O \quad (5)$$

$$MCl_2\cdot\infty H_2O + HCl(g) = MCl_2\cdot HCl\cdot\infty H_2O \quad (6)$$

$$M(c) + 3/2Cl_2(g) + \infty H_2O(l) = MCl_3\cdot\infty H_2O \quad (7)$$

$${}^1/_2H_2(g) + {}^1/_2Cl_2(g) = HCl(g) \quad (8)$$

ΔH_1 is the heat of reaction measured in these experiments. ΔH_2 is the ΔH°_{298} of the oxidation–reduction reaction . It was calculated from the formal oxidation–reduction potential of samarous–samaric salts observed by Timnick and Glockler,[6] (E^0 = 1.55 v.), or of ytterbium by Laitinen[7] (E^0 = 1.15 v.). The entropy estimation was made by the method used by Brewer[8] in which the available entropies were plotted against the ionic radii for divalent and trivalent ions, respectively. Nearly straight lines were obtained; thus, it was possible to estimate the entropies of all the rare earth ions for which the ionic radii were given, ($\Delta S_{Sm(II)-Sm(III)}$ = −20.8 cal. deg.$^{-1}$mole^{-1}, $\Delta S_{YB(II)-Yb(III)}$ = −28.4 cal. deg.$^{-1}$ mole^{-1}).

ΔH_3 is the heat of solution of the trichloride at infinite dilution. This value was taken from the data of Spedding and Flynn.[9]

ΔH_4 is the heat of solution of the trichloride in 6.00 *M* HCl. Its value was established by direct calorimetric measurement. The results when plotted together with data on the heat of solution in water[10] gave curves consistent with the results on other trichlorides discussed by Klemm.[11] The calorimetric determinations of the heat of solution at 25° of the trichlorides are as follows: $SmCl_3$ (in 6.00 *M* HCl), −29.5 ± 0.2 kcal./mole; $EuCl_3$ (in 6.00 *M* HCl), −30.9 ± 0.2 kcal./mole; $EuCl_3$ (in 0.015 *M* HCl), −40.2 ± 0.3 kcal./mole; and $YbCl_3$ (in 6.00 *M* HCl), −39.6 ± 0.3 kcal./mole.

ΔH_5 is evaluated as the differential heat of solution of HCl(g) in 6.84 molal HCl (6*M* HCl). The necessary relative partial molal quantities are available in the literature.[12,13] The heat of this reaction is considered not to be influenced by the presence of small concentrations of MCl_3.

ΔH_6 is the heat of solution of hydrogen chloride at infinite dilution.[13] The presence of MCl_2 was assumed to have no effect.

ΔH_7 is the heat of formation of the trichloride at infinite dilution calculated from the data of Spedding and Flynn.[14]

ΔH_8 is the heat of formation of hydrogen chloride gas.[13]

The values of ΔH_i for $SmCl_2$ and $YbCl_2$ are tabulated in Table IV.

TABLE IV

Salt	ΔH_1	ΔH_2	ΔH_3	ΔH_4
$SmCl_2$	−42.2	−42	−39.93	−29.5
$YbCl_2$	−41.2	−35	−51.64	−39.6
Salt	ΔH_5	ΔH_6	ΔH_7	ΔH_8
$SmCl_2$	−14.78	−17.96	−285.1	−22.06
$YbCl_2$	−14.78	−17.96	−274.6	−22.06

---

(6) A. Timnick and G. Glockler, THIS JOURNAL, **70**, 1347 (1948).

(7) H. Laitinen, *ibid.*, **64**, 1133 (1942).

(8) L. Brewer, *et al.*, "Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics," National Nuclear Energy Series IV-19B, Paper 6.

(9) F. H. Spedding and J. P. Flynn, THIS JOURNAL, **76**, 1477 (1954).

(10) H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 373 (1941).

(11) W. Klemm, *ibid.*, **249**, 23 (1942).

(12) F. D. Rossini, *J. Research Natl. Bur. Standards*, Paper 499, Vol. 9, November 1932.

(13) Selected Values of Chemical Thermodynamic Properties, Circular 500 of the National Bureau of Standards.

(14) F. H. Spedding and J. P. Flynn, THIS JOURNAL, **76**, 1474 (1954).

The heat of solution of the dichlorides at infinite dilution corresponds to the heat absorbed in the reaction

$$\mathrm{MCl_2(c)} + \infty \mathrm{H_2O} = \mathrm{MCl_2} \cdot \infty \mathrm{H_2O}$$

$$\Delta H_{\text{soln.}} = \Delta H_1 - \Delta H_2 + \Delta H_3 - \Delta H_4 + \Delta H_5 - \Delta H_6$$

The standard heat of formation is the enthalpy change for the reaction

$$\mathrm{M(c)} + \mathrm{Cl_2\,(g)} = \mathrm{MCl_2(c)}$$

when all the substances are in their standard states.

$$\Delta H^0{}_{f_{298.16}} = -\Delta H_1 - \Delta H_3 + \Delta H_4 - \Delta H_5 + \Delta H_7 - \Delta H_8$$

Table V lists the heats of solution and the heats of formation of the dichlorides.

TABLE V

HEATS OF SOLUTION AND HEATS OF FORMATION OF THE DICHLORIDES AT 298.16°K.

Substance	$\Delta H_{\text{soln.}_{298.16}}$	$\Delta H^{\circ}{}_{f_{298.16}}$
$SmCl_2$	$-\ 7 \pm 6^a$	-195.6 ± 1.0
$YbCl_2$	-15 ± 5^a	-184.5 ± 1.7

[a] The greatest uncertainty lies in the entropy estimation in the calculation of ΔH_2.

That the oxidation of samarium(II) to samarium(III) by oxygen did not occur to any significant extent was evidenced by the data of Table I. There was no discernible difference between the results obtained in hydrogen-saturated acid and those obtained in air-saturated acid. The small value of the standard deviation obtained for the heat of reaction of ytterbium dichloride (Table II) also indicated that oxidation by oxygen did not take place to an appreciable extent.

Acknowledgment.—The authors wish to express their gratitude to Dr. F. H. Spedding for supplying pure rare earth oxides; to Mr. Harry Eick for help in obtaining some of the calorimetric data; and to the U. S. Atomic Energy Commission for their financial support of the project.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Factors Influencing Ion-exchange Equilibria in Concentrated Solutions: Behavior of the Alkaline Earth and Alkali Ions[1]

BY R. M. DIAMOND[2]

RECEIVED DECEMBER 16, 1954

A study has been made of the elution behavior of beryllium(II), calcium(II), strontium(II), barium(II), radium(II), sodium(I), rubidium(I) and cesium(I), from a Dowex-50 (10–12% DVB) cation-exchange resin column, and of radium(II), strontium(II), cesium(I) and sodium(I) from nominal 2 and 16% DVB sulfonic acid resins with 2.6, 5.5, 8.7 and 12.2 *M* HCl solutions. The results cannot be explained by simple mass-action considerations, but postulation of ion dehydration, resin shrinkage, and non-exchange electrolyte absorption effects makes possible a reasonable interpretation.

The ion-exchange elution behavior of tracer quantities of rare earths from the sulfonic acid resin, Dowex-50, with hydrochloric acid of varying concentration as the eluant shows an interesting pattern.[3] As the hydrochloric acid concentration is raised above 1 *M*, the elution peak position, or volume of eluant at which the tracer ion concentration is a maximum, occurs at a smaller and smaller volume. Around 7 *M* HCl it is at a minimum, and with higher hydrochloric acid concentrations the elution peak volume increases. This behavior was attributed to the simultaneous operation in varying degree of some of the following factors influencing the exchange process, namely: 1, the mass-action effect of hydrogen ion; 2, complex ion formation of the metal ion with chloride; 3, disruption of the hydration shell of the metal ion; 4, shrinkage of the resin; 5, entrance of non-exchange electrolyte into the resin.

Since the interplay between so many factors makes interpretation difficult, it was felt that in studying families of ions of lower charge, such as the alkaline earth and alkali metal ions, where certain of the factors would be expected to be less important, confirmation might be obtained for the effects of the last three factors and simplifications introduced in estimating their relative importance.

Experimental

Resins.—The resins used were commercial Dowex-50 (*ca.* 10–12% DVB), 250–500 mesh, and two sulfonic acid exchangers of nominal 2 and 16% divinylbenzene content and of 50-100 mesh.[4] The exchange capacities of these resins are 5.1, 5.3 and 4.8 meq./g. of dry hydrogen-form resin, respectively, as determined by titration of the acid displaced from the hydrogen form resin with a large excess of sodium chloride solution. Before use the resins were washed thoroughly with concentrated hydrochloric acid and with water.

Tracers.—Na^{22}, Ca^{45} and Rb^{86} were obtained through the courtesy of Prof. J. Irvine, Jr., of the Massachusetts Institute of Technology. Cs^{137}, Sr-Y^{90} and Ba^{140} were purchased from Oak Ridge National Laboratory; Ra^{226} was kindly furnished by Prof. G. T. Seaborg, University of California; Be^{7} was made using the Harvard synchrocyclotron.

Procedure.—The technique employed was to study the variation in elution behavior of the tracer cations from resin columns when using 2.6, 5.5, 8.7 and 12.2 *M* HCl as eluting agents. The column of Dowex-50 resin contained 0.095 g. of dry resin and was 10 cm. long by 1.5 mm. in diameter; 0.418 g. of dry 2% DVB sulfonic acid resin was used in a column 10 cm. long (when in contact with 3 *M* HCl) and 4 mm. in diameter, and 0.184 g. of dry 16% DVB resin was used in a column 10 cm. long by 2 mm. in diameter. Before an elution the resin column was rinsed overnight with the

---

[1] This work was supported by the U. S. Atomic Energy Commission.

[2] Baker Laboratory of Chemistry, Cornell University, Ithaca, New York.

[3] R. M. Diamond, K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **76**, 1461 (1954).

[4] These two sulfonic acid resins of nominal 2 and 16% DVB content were kindly furnished by Dr. K. S. Spiegler, Gulf Res. and Dev. Co.