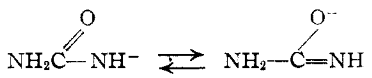
40–50% of the urea in 8 *M* urea solutions existed in an activated form as the anion



$$NH_2C(=O){-}NH^- \rightleftarrows NH_2{-}C(O^-){=}NH$$

and that this reacts rapidly with the formaldehyde *not* in the methylene glycol form. The subsequent slow bimolecular reaction (Stage 2) then takes place as indicated previously[1] with the additional concept of dehydration of the remaining methylene glycol as after Crowe and Lynch.[2]

HOBART, TASMANIA, AUSTRALIA RECEIVED OCTOBER 4, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Thermodynamics of Fluorine–Chlorine Exchange Reactions. The Systems NaF–NaCl, BaF_2–$BaCl_2$, NiF_2–$NiCl_2$ and PbClF–$PbCl_2$[1]

BY GEORGE C. HOOD AND MARK M. WOYSKI

This investigation was undertaken to study the thermodynamics of reactions of the type: $HF(g) + MCl(s) \rightleftarrows HCl(g) + MF(s)$. The information was desired in order to evaluate the thermodynamic fluorinating ability of several metal fluorides and to obtain data which may give reliable values for the free energies of formation of these metal fluorides.

The thermodynamic fluorinating abilities of NaF, BaF_2, NiF_2 and PbClF were determined by a dynamic equilibrium method. These data along with information available in the literature were employed to set up a thermochemical scale of reactivity for certain halogen exchange reactions. It was determined that the fluorination of lead chloride by anhydrous hydrogen fluoride yields lead chlorofluoride as a product rather than lead fluoride. An approximate value for the heat of formation of lead chlorofluoride was obtained.

Experimental

Equilibria in reactions $HF(g) + MCl(s) = HCl(g) + MF(s)$ were determined by a dynamic method. Anhydrous hydrogen fluoride diluted with nitrogen was passed over the solid metal chloride kept at a constant temperature and the composition of the effluent gas mixture determined. The equilibria were approached from the other direction by passing anhydrous hydrogen chloride over the metal fluorides. X-Ray procedures were employed to determine whether solid solutions formed and to check on the crystalline state of the solid substances.

Preparation and Purity of the Materials. Hydrogen Fluoride.—Harshaw Chemical Co., anhydrous, hydrogen fluoride was used without special purification. Part of the contents of a six pound cylinder were allowed to escape in order to reduce the concentration of volatile impurities.

Hydrogen Chloride.—Harshaw Chemical Co. anhydrous hydrogen chloride was used without special purification except for the removal of condensable material in a trap cooled in a Dry Ice–acetone-bath.

Nitrogen.—Commercial nitrogen was used directly from the cylinder. The condensable impurities were removed by passage through a trap cooled by liquid air.

Sodium Chloride.—Mallinckrodt analytical reagent sodium chloride was recrystallized once from water in a porcelain dish and then dried at 600° for six hours. A gravimetric analysis for chloride ion by the precipitation of silver chloride gave 60.69 ± 0.04% chloride (theoretical 60.66%).

Barium Chloride.—Anhydrous barium chloride was prepared for use by recrystallizing Merck reagent grade material twice from water in a porcelain dish and drying at 600° for eight hours in a stream of anhydrous hydrogen chloride. Analysis for chloride ion showed 34.06 ± 0.04% chloride (theoretical 34.09%).

Nickel Chloride.—Merck reagent grade nickel chloride was recrystallized from a mixture of hydrochloric acid and water. It was dried at 300° in an atmosphere of anhydrous hydrogen chloride. The salt was then sublimed in a Vycor tube in a stream of anhydrous hydrogen chloride. Analysis for chloride ion showed 54.38 ± 0.04% chloride (theoretical 54.72%).

Lead Chloride.—Mallinckrodt analytical reagent material was recrystallized from a mixture of hydrochloric acid and water in a porcelain dish. It was dried at 400° for six hours. Analysis for chloride ion gave 25.62 ± 0.04% chloride (theoretical 25.49%).

Sodium Fluoride.—Two different samples of sodium fluoride were prepared in different ways in order to determine whether or not the previous history of the sample had any appreciable effect on the measurable equilibrium constant.

Sample A was prepared by recrystallizing Merck reagent grade sodium fluoride twice from water in a platinum dish. The sample was dried at 550° for 12 hours.

Sample B was prepared by decomposing solvated sodium fluoride ($NaF \cdot xHF$) which was produced from Sample A.

Analyses for the fluoride ion by the precipitation of lead chlorofluoride showed for sample A 45.20 ± 0.2% fluoride, and for sample B 45.21 ± 0.2% fluoride (theoretical 45.24%).

Barium Fluoride.—Two different samples of barium fluoride were also prepared. Sample A was prepared by the action of aqueous hydrofluoric acid on barium chloride in a platinum dish. The sample was dried at 600° for six hours. Sample B was prepared by treating anhydrous barium chloride with anhydrous hydrogen fluoride at various temperatures over 250° in a silver tube. Analyses for fluoride ion showed for sample A 21.70 ± 0.2% fluoride and for sample B 21.75 ± 0.2% fluoride (theoretical 21.67%).

Nickel Fluoride.—This material was prepared by the action of anhydrous hydrogen fluoride on anhydrous nickel chloride prepared as previously indicated. The reaction was carried out at various temperatures between 100 and 500° in a fine silver tube. The reaction was not complete and there was some nickel chloride in the sample.

Lead Fluoride.—This salt was prepared by treating Mallinckrodt N.F. VII lead monoxide with aqueous hydrofluoric acid in a platinum dish. The lead fluoride was dried at 550° for six hours. Analysis for fluoride ion showed 15.09 ± 0.2% fluoride (theoretical 15.49%).

Lead Chlorofluoride.—The compound was prepared according to the procedure of Starck.[2] It was dried at 350° for five hours. Gravimetric analysis for chloride ion yielded 13.61 ± 0.04% chloride (theoretical 13.55%).

Apparatus.—The apparatus consisted of two main systems, one for passing hydrogen fluoride through metal chlorides and the other for passing hydrogen chloride through metal fluorides.

To control the rate of flow of hydrogen fluoride a steady stream of nitrogen was saturated with hydrogen fluoride vapor at 0°. The rate of flow of nitrogen was varied by adjusting the pressure across a capillary tube, by means of a bubbler attached at the input side of the flow meter. The retaining fluid was dibutyl phthalate. The nitrogen was dried by passage through a glass wool filter immersed in liquid air and was then bubbled through liquid hydrogen

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[1] From the Ph.D. Dissertation of George C. Hood.

[2] G. Starck, *Z. anorg. allgem. chem.*, **70**, 173 (1911); *C. A.* **5**, 2049 (1911).

fluoride in a copper tank. The hydrogen fluoride container was immersed in an ice-bath to maintain a constant temperature and vapor pressure.

The gases were then conducted into the reaction chamber inside a thermostat. The effluent gases were bubbled through a solution of 3% sodium hydroxide to absorb the hydrogen fluoride and hydrogen chloride. The entire system operated at atmospheric pressure.

A similar design was employed for the handling of hydrogen chloride. The gas direct from a cylinder was led through a bubbler, Dry Ice–acetone trap, and a capillary. It was then diluted with nitrogen flowing at a constant rate and run into the reaction chamber. The nitrogen was added to prevent the solution in the absorber from being sucked into the system due to the great solubility of hydrogen chloride and fluoride.

That portion of the apparatus which came in contact with hydrogen fluoride was constructed chiefly of one-quarter inch copper tubing. All joints were made using flare fittings. The valves in contact with hydrogen fluoride were brass Hoke bellows valves. Corrosion in the system was not serious. A McLeod gage was connected into the system and employed to detect leaks.

Reaction and Thermostat.—The reaction tube was constructed of fine silver throughout. It was twelve inches in length, 1.25″ in o.d. and was reduced at each end to 0.25″ connecting tubes. The sample was placed in the tube for a given series of runs and the tube was welded shut.

The tube was contained in a thermostat consisting of a massive cylindrical copper block 16″ in length and 3.25″ in o.d. The block was bored to receive the silver reactor, two 500-watt cartridge heaters and a thermocouple. Heavy copper end blocks with holes for necessary connecting tubes and leads were bolted to the main block so that the reaction tube was entirely surrounded by the thermostat. The entire assembly was contained in a nichrome wound vertical tube furnace, well insulated with magnesia. The furnace was maintained at a temperature slightly below the control temperature.

Temperature Control.—Temperature control was maintained by a Brown electronic recorder-controller Model 153X10V-W5-20FI working with a single junction chromel-alumel thermocouple. The thermocouple was calibrated at several points over the temperature range 100–800° using pure compounds and metals as standards. The Brown instrument was checked against a Rubicon High Precision Type B Potentiometer. It was possible to maintain temperatures as high as 800° with deviations of less than ±1°. The largest gradient found in the block was 1° at a furnace temperature of 500°.

Sampling.—The effluent gases were bubbled into a bulb containing 3% sodium hydroxide solution which absorbed most of the hydrogen fluoride and chloride. The remaining gases were passed through a second bulb filled with glass beads kept moist with sodium hydroxide solution dripping from a reservoir at a constant rate. A sample was usually collected for a period of one hour, placed in a 250-ml. volumetric flask and diluted with water. Aliquots of this solution were then taken to give sufficient amounts of chloride and fluoride ions for analysis.

Analysis.—Fluorine was determined by precipitation and weighing as lead chlorofluoride according to the modified procedure of Starck.[2] The precipitates were collected and weighed on sintered glass crucibles. This analytical procedure when checked against carefully purified sodium fluoride gave results with an accuracy of ±0.2% fluoride.

Chlorine was determined by precipitation and weighing as silver chloride with the usual accuracy for that procedure.

X-Ray Analysis.—Upon the completion of a series of runs a sample of the solid material from the reaction tube was subjected to X-ray examination. Powder patterns showed in all cases the existence of crystalline fluorides and chlorides. Thus the absence of solid solutions was proved and the presence of macrocrystalline phases established. The patterns also established the course of the reaction.

Calculation of Results.—The ratio HCl/HF was determined for several rates of flow of the gaseous reactant (HF or HCl). The equilibrium ratio HCl/HF was then determined by plotting the observed ratios against rate of flow and extrapolating to zero rate of flow. Somewhat unexpectedly it was found that at the rates of flow employed the value of $N(\mathrm{HCl})/N(\mathrm{HF})$ remained constant for each system within experimental error at each temperature investigated. Therefore, the extrapolation was unnecessary and the equilibrium constant readily determined. Regardless of the direction in which the reaction was run the ratio of $N(\mathrm{HCl})/N(\mathrm{HF})$ was used in the calculations with appropriate sign changes.

The standard free energy change of a particular reaction was computed utilizing the relation $\Delta F° = -RT \ln K$ along with the average value of K obtained at each isotherm.

The standard change in the heat content for a reaction was computed using the relation $\ln K_p = -(\Delta H°/RT) + c$. A plot of $\ln K_p$ *versus* $1/T$ was made and the slope of the curve determined.

The standard entropy change was calculated from the average value of the standard free energy changes and the value of the standard heat content change by use of the relation $\Delta S° = (\Delta H° - \Delta F°)/T$.

Discussion and Results

Sodium System.—At room temperature anhydrous hydrogen fluoride reacted with sodium chloride to form solvated sodium fluoride. At 200° there was no reaction. These results are in accord with the work of I. V. Tananaev.[3] The reaction $\mathrm{HF(g)} + \mathrm{NaCl(s)} \rightleftarrows \mathrm{HCl(g)} + \mathrm{NaF(s)}$ was investigated in the temperature interval 500–650°. As shown by the data in Table I the sodium fluoride prepared in two different ways had no noticeable effect on the equilibrium. Curve A on Fig. 1 shows a plot of log K *versus* $1/T$.

For this particular system an extended series of calculations was made in an attempt to correlate the data with known thermochemical values. The thermochemical changes were calculated at 298°K. using standard free energies of formation, standard heats of formation and standard entropies. The data for HCl, NaCl and NaF was taken from the National Bureau of Standards[4] and the data for HF from the work of Murphy and Vance.[5]

TABLE I

THERMOCHEMICAL DATA FOR THE REACTION:

$$\mathrm{HF(g)} + \mathrm{NaCl(s)} \underset{\mathrm{b}}{\overset{\mathrm{a}}{\rightleftarrows}} \mathrm{HCl(g)} + \mathrm{NaF(s)}$$

T, °K.	Direction of reaction	K	$\Delta F°$ (cal.)
796	bx	0.0290	5600
799	a	.0292	5610
823	by	.0325	5580
834	a	.0342	5570
862	by	.0372	5620
868	a	.0386	5620
942	a	.0500	5610

x = NaF from reaction $\mathrm{NaF}\cdot x\mathrm{HF} \longrightarrow \mathrm{NaF} + x\mathrm{HF}$
y = NaF recrystallized
$\Delta F° = +5600$ cal.
$\Delta H° = +5555$ cal. Mean values 870°K.
$\Delta S° = -0.05$ e.u.
Probable error in $\Delta F° = \pm 50$ cal.

In order to evaluate the data at 796°K. heat capacity data were necessary for the components of the reaction. The following equations applicable in the temperature range 298–1000°K. were calculated by us from information in the literature.

$$C_p(\mathrm{HF}) = 6.9343 - 1.84\cdot10^{-4}T + 4.65\cdot10^{-7}T^2 \quad [5]$$

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[3] I. V. Tananaev, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 267 (1941); *C. A.*, **35**, 6179 (1941).

[4] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1947.

[5] G. M. Murphy and J. E. Vance, *J. Chem. Phys.*, **7**, 806 (1939).

$C_p(\mathrm{HCl}) = 6.7319 + 4.33 \cdot 10^{-4}T + 3.70 \cdot 10^{-7}T^2$ [6]
$C_p(\mathrm{NaCl}) = 10.3350 + 5.39 \cdot 10^{-3}T - 2.19 \cdot 10^{-6}T^2$ [7]
$C_p(\mathrm{NaF}) = 9.9173 + 2.82 \cdot 10^{-3}T + 5.45 \cdot 10^{-6}T^2$ [8]

The equation for NaF was calculated from rather meager data and is probably not accurate. Thus we obtain the following comparison at 870°K., the mean experimental temperature.

Calculated values, 870°.	Observed values, 870°K.
$\Delta F° = +4880$ cal.	$\Delta F° = +5600$
$\Delta H° = +5020$ cal.	$\Delta H° = +5555$
$\Delta S° = +0.24$ e.u.	$\Delta S° = -0.05$

Barium System.—This system was investigated in the temperature range from 477 to 1033°K. Again, the use of barium fluoride prepared in different ways had no noticeable effect on the equilibrium constant. The thermochemical results are listed in Table II. Curve B on Fig. 1 shows a plot of log *K versus* 1/*T*.

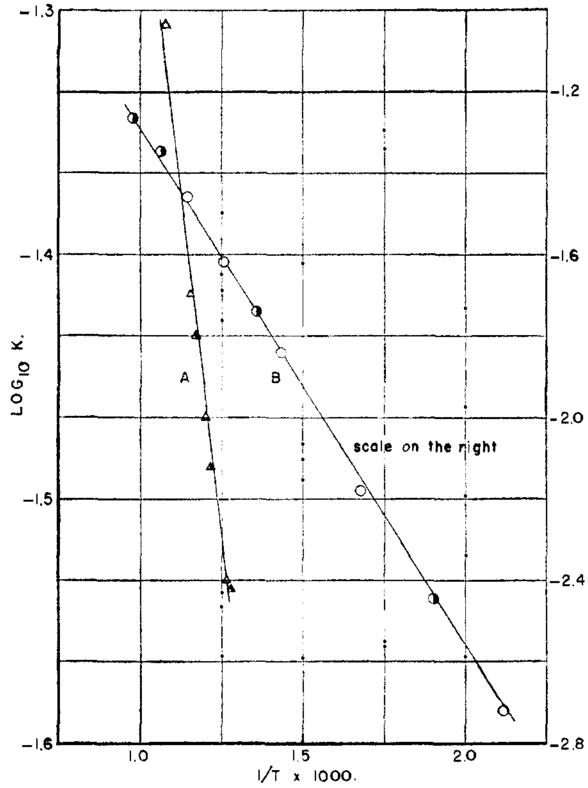

Fig. 1.—△, HF + NaCl; ▲, HCl + NaF; ○, HF + BaCl₂; ◑, HCl + BaF₂.

Nickel System.—The reaction $\mathrm{HF(g)} + {}^1/_2\mathrm{NiCl_2(s)} \rightleftarrows {}^1/_2\mathrm{NiF_2(s)} + \mathrm{HCl(g)}$ was studied in the temperature interval 477 to 833°K. The thermochemical constants were calculated and appear in Table III. A plot of log *K versus* 1/*T* is shown as Curve A on Fig. 2.

TABLE II

THERMOCHEMICAL DATA FOR THE REACTION:

$$\mathrm{HF(g)} + {}^1/_2\mathrm{BaCl_2(s)} \underset{b}{\overset{a}{\rightleftarrows}} \mathrm{HCl(g)} + {}^1/_2\mathrm{BaF_2(s)}$$

T, °K.	Direction of reaction	K	ΔF° (cal.)
477	a	0.00193	5920
531	bx	.00365	5920
598	a	.00673	5940
701	a	.0145	5900
744	by	.0186	5890
809	a	.0247	5950
888	a	.0359	5870
969	bx	.0455	5950
1033	by	.0546	5970

x = BaF₂ from reaction $\mathrm{HF(g)} + {}^1/_2\mathrm{BaCl_2(s)} \rightleftarrows {}^1/_2\mathrm{BaF_2(s)} + \mathrm{HCl(g)}$
y = BaF₂ from reaction $\mathrm{HF(aq)} + {}^1/_2\mathrm{BaCl_2(s)} \longrightarrow {}^1/_2\mathrm{BaF_2(s)} + \mathrm{HCl(aq)}$

$\Delta F° = +5920$ cal.
$\Delta H° = +5910$ cal. Mean values at 755°K.
$\Delta S° = -0.02$ e.v.
Probable error in $\Delta F° = \pm 60$ calories.

TABLE III

THERMOCHEMICAL DATA FOR THE REACTION:

$$\mathrm{HF(g)} + {}^1/_2\mathrm{NiCl_2(s)} \underset{b}{\overset{a}{\rightleftarrows}} {}^1/_2\mathrm{NiF_2(s)} + \mathrm{HCl(g)}$$

T, °K.	Direction of reaction	K	ΔF° (cal.)
477	a	0.2262	1410
520	b	.2633	1380
589	a	.3055	1390
623	b	.3197	1410
684	a	.3620	1380
735	b	.3755	1430
801	a	.4093	1420
833	b	.4288	1400

$\Delta F° = +1400$ cal.
$\Delta H° = +1390$ cal. Mean values at 680°K.
$\Delta S° = -0.02$ e.u.
Probable error in $\Delta F° = \pm 56$ calories

Lead System.—It was determined that hydrogen fluoride reacts with lead chloride with the formation of lead chlorofluoride. Further reaction with lead chlorofluoride with formation of lead fluoride does not take place in the temperature range of this investigation (553 to 668°K.). Lead chlorofluoride was identified by its X-ray diffraction pattern which was identical with that of a sample prepared by the procedure of Starck[2] and annealed at 300°. The pattern of these samples was not the same as that of the mineral PbClF as given in the Hanawalt card file.

TABLE IV

THERMOCHEMICAL DATA FOR THE REACTION:

$$\mathrm{HF(g)} + \mathrm{PbCl_2(s)} \underset{b}{\overset{a}{\rightleftarrows}} \mathrm{PbClF(s)} + \mathrm{HCl(g)}$$

T, °K.	Direction of reaction	K	ΔF° (cal.)
553	b	0.2125	1700
568	a	.2254	1680
593	b	.2385	1690
621	a	.2455	1730
649	b	.2460	1810
668	a	.2682	1750

$\Delta F° = +1710$ cal.
$\Delta H° = +1440$ cal. Mean values at 680°K.
$\Delta S° = -0.45$ e.u.
Probable error in $\Delta F° = \pm 83$ calories.

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(6) H. M. Spencer and J. L. Justice, THIS JOURNAL, **56**, 2311 (1934).

(7) W. A. Roth and W. Bertram, *Z. Elektrochem.*, **35**, 297 (1929).

(8) A. N. Krestovnikov and G. A. Karetnikov, *Legkie Metal.*, **3**, No. 4 29-31 (1934); *C. A.*, **29**, 32 (1935).

The thermochemical constants for the system are given in Table IV. A plot of log *k* *vs.* $1/T$ is shown as curve B on Fig. 2.

Approximate values of the free energies of formation of lead chlorofluoride from the elements and from lead chloride and lead fluoride were calculated from the data of this section and the standard free energies of formation of HF(g), HCl(g), $PbCl_2(s)$[4] and $PbF_2(s)$[4] at 298°K.

$$Pb(s) + {}^1/_2Cl_2(g) + {}^1/_2F_2(g) \longrightarrow PbClF(s) \quad \Delta F^\circ_{298} = -115{,}000 \text{ cal.}$$

$$ {}^1/_2PbCl_2(s) + {}^1/_2PbF_2(s) \longrightarrow PbClF(s) \quad \Delta F^\circ_{298} = -7.900 \text{ cal.}$$

Scale of Reactivity.—A very convenient form for tabulating the thermodynamic fluorinating ability of metal fluorides is to set up a series of couples similar in form to oxidation–reduction potentials.[9] The experimentally determined thermochemical data are expressed in Table V as differences of free energy of formation of chlorides and fluorides. The free energy change of a particular exchange reaction can be determined by taking the algebraic difference of the respective couplets. As a consequence we have a table giving the thermodynamic fluorinating ability of several metal fluorides in decreasing order.

TABLE V

THERMODYNAMIC FLUORINATION SCALE

(Results extrapolated to 298°K.)

Couple	$\Delta F^\circ_{Cl} - \Delta F^\circ_F$ (cal.)
${}^1/_2BaF_2(s)$—${}^1/_2BaCl_2(s)$	36,200
NaF(s)—NaCl(s)	36,900
PbClF(s)—$PbCl_2(s)$	40,600
${}^1/_2NiF_2(s)$—${}^1/_2NiCl_2(s)$	40,800
HF(g)—HCl(g)	42,200

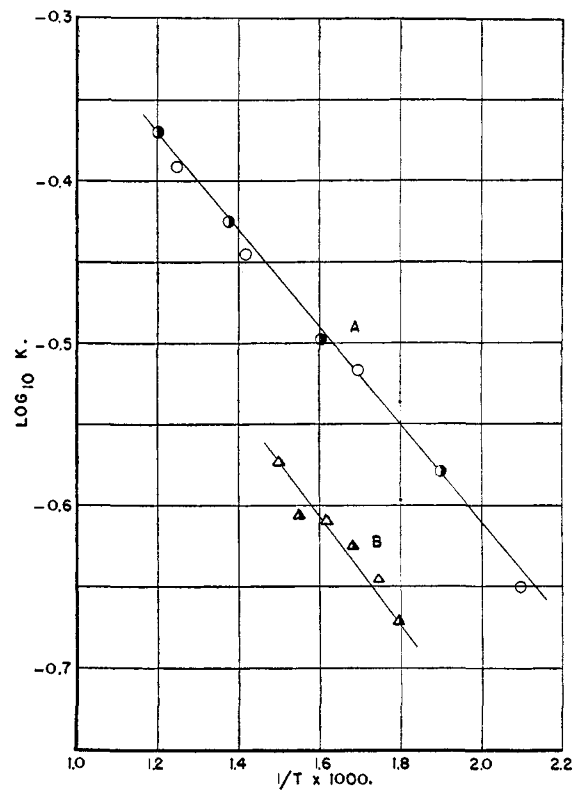

Fig. 2.—△, HF + $PbCl_2$; ▲, HCl + PbClF; ○, HF + $NiCl_2$; ◐, HCl + NiF_2.

MADISON, WIS. RECEIVED DECEMBER 16, 1950

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[9] M. M. Woyski, THIS JOURNAL, **72**, 919 (1950).

[CONTRIBUTION FROM THE KELLEX CORPORATION LABORATORIES]

Reactions of Cesium in Trace Amounts with Ion-exchange Resins

BY HOKE S. MILLER AND G. E. KLINE

Phenolsulfonic and sulfonic types of ion-exchange resins are effective for the adsorption of cesium in trace amounts. The phenolsulfonic type exhibits two *p*H ranges of strong adsorption, corresponding to the two species of exchange groups present. Cesium is selectively adsorbed by phenolic groups in the presence of high concentrations of sodium salts in alkaline solutions.

Introduction

The reactions of metal salts with ion-exchange resins have been studied for the most part in solutions containing appreciable amounts of the metal salts under investigation.[1] This investigation, however, is concerned with the reactions of cesium salts with resins in essentially infinitely dilute solutions, the concentrations involved being as low as 10^{-8} part/million of active cesium. Accordingly, radioactive tracer techniques were employed to permit accurate analysis.

Adsorption isotherms and the effect of added acid or alkali on the adsorptive capacity of the resins were determined by static equilibrium methods. Some of the more significant results obtained in this manner were confirmed in dynamic tests.

Experimental

Procedure for Static Equilibrium Measurements.—The analytical technique used in this investigation is similar to that employed by Ketelle and Boyd,[2] Spedding, *et al.*,[3] and Tompkins, *et al.*,[4] in the study of the separation of radioactive rare earths in which the concentrations encountered could not be analyzed by ordinary chemical methods.

The source of the active cesium was carrier-free $Cs^{137}Cl$ solution as obtained from the Oak Ridge National Laboratory. This solution, containing about 2 millicuries of Cs^{137} per ml., was reported to contain spectrographic traces of other materials, principally calcium and magnesium. A small amount of active Cs was added to 250 ml. of

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[1] F. C. Nachod, "Ion Exchange," Academic Press, Inc., New York, N. Y., 1949.

[2] B. E. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

[3] F. H. Spedding, *et al.*, *ibid.*, **69**, 2777 (1947).

[4] E. R. Tompkins, J. X. Khym and W. E. Cohn, *ibid.*, **69**, 2769 (1947).