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

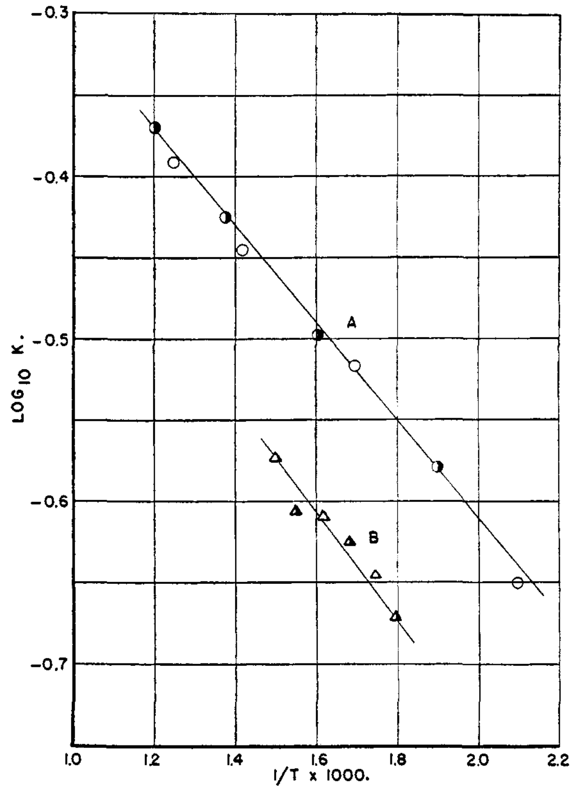

Fig. 2.—△, HF + $PbCl_2$; ▲, HCl + PbClF; ○, HF + $NiCl_2$; ◑, HCl + NiF_2.

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).

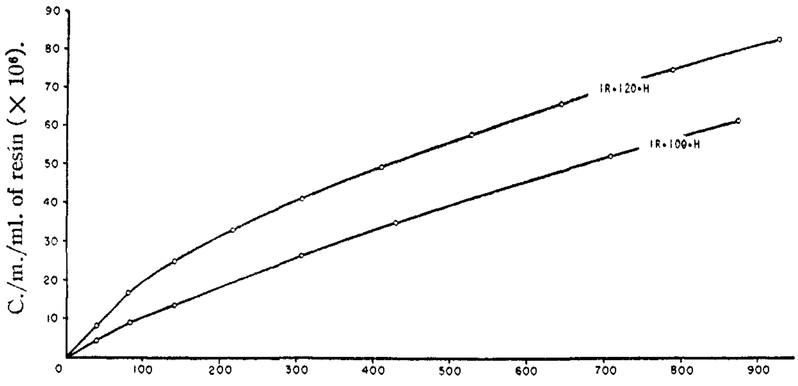


Fig. 1.—Adsorption of Cs by resins IR-120-H and IR-100-H: 0.5 ml. of resin per 250 ml. of solution of active cesium in water.

distilled water previously treated with cation exchange resin in the hydrogen form. The initial concentration of cesium was determined by evaporating a small portion of the solution on a shallow stainless steel planchet $1^{1}/_{4}''$ in diameter and then counting the activity on the planchet with a mica end window Geiger counter at a geometry of about 30%. A measured amount of ion-exchange resin then was added to the solution with mechanical agitation. Preliminary tests showed that equilibrium was established in less than one hour, hence after one hour agitation, a portion of the equilibrium solution was evaporated and counted to determine the residual cesium in the solution.

In the development of this procedure, it was found that erratic results were obtained when ordinary Pyrex glassware was used in handling the radioactive solutions, due to the adsorption of the cesium by the glass surfaces. This difficulty was eliminated by coating with paraffin or beeswax all glassware coming into contact with the solutions, or by using equipment made of polystyrene.

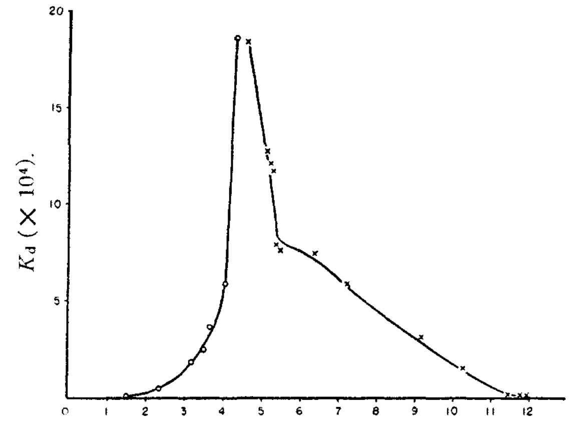
Adsorption of Cesium from Water.—The ion exchange resins used were Amberlites IR-100 and IR-120 manufactured by Rohm & Haas, Philadelphia, Pa. The former is of the phenosulfonic type which has both phenolic and sulfonic groups available for exchange reactions. The latter is a nuclear sulfonic type resin having only sulfonic groups available for exchange reactions. A measured amount of the resin was added to water containing a relatively low amount of active cesium. After equilibrium was established more active cesium was added and the equilibrium concentration measured again. In this manner the concentration of the equilibrium solution was increased in steps until a final activity of about 900 c./m./ml. was obtained.

The results obtained with these resins are given in Fig. 1. It is seen that under the conditions of these tests, at the normal *p*H of the hydrogen form of the resins in the absence of salts the adsorptive capacity of IR-120 for cesium is substantially greater than that of IR-100.

Adsorption of Cesium from Water Containing Added Acid or Alkali.—For this study a solution was prepared by the addition of active cesium to 250 ml. of water to give about 16,000 c./m./ml. After the addition of a measured volume of IR-120 resin equilibrium was established at *p*H 4.4. Then 1 molar nitric acid was added in steps, until a *p*H of 1.5 was reached, the residual activity of the equilibrium solution being measured after each addition. In a similar manner the effect of the addition of alkali to water containing active cesium was determined in the *p*H range 4.4 to 11.8. The results are given in Fig. 2 in which the distribution coefficient, K_d, the ratio of c./m./ml. of resin to the c./m./ml. of solution is plotted against the *p*H of the equilibrium solution. It is noted that very strong adsorption of cesium is obtained at about *p*H 4.4 with a notable decrease on the addition of either acid or alkali.

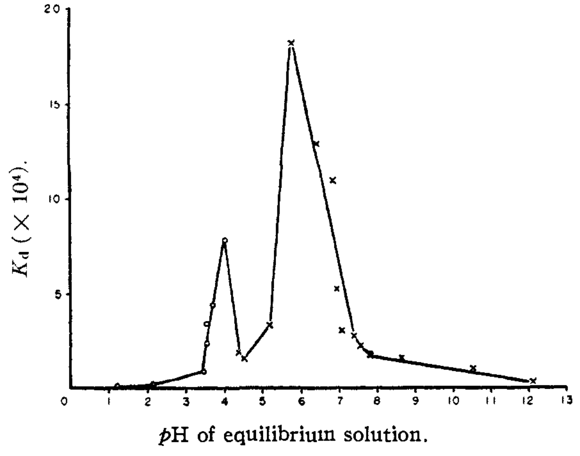
A similar experiment was performed using IR-100. The results are given in Fig. 3. Strong adsorption is obtained at *p*H 4.0, with rapid decrease on the addition of acid. A marked decrease in adsorption also is obtained on the addition of alkali until *p*H 4.5 is reached. However, the addition of further alkali results in another region of strong adsorption at about *p*H 6.0. At still higher *p*H the adsorption of cesium again decreases to a relatively low value.

Since a peak in the curve for each resin is obtained at about *p*H 4.0, this peak may be attributed to the action of the sulfonic group which is common to both resins. The peak occurring at *p*H 6.0 in the case of IR-100 must be attributed to the action of the phenolic group which is present in this resin, but not in IR-120.



*p*H of equilibrium solution.

Fig. 2.—Effect of adding acid or alkali on adsorption of Cs by resin IR-120: O, starting with water, HNO_3 added; X, starting with water, NaOH added.



*p*H of equilibrium solution.

Fig. 3.—Effect of adding acid or alkali on adsorption of Cs by resin IR-100: O, starting with water, HNO_3 added; X, starting with water, NaOH added.

Adsorption of Cesium from Alkaline Salt Solutions.—Active cesium was added to a solution containing about 20% by weight of mixed sodium nitrate, sulfate, phosphate and carbonate at about *p*H 13, to give an activity of about 1800 c./m./ml. At equilibrium 0.7 ml. of IR-120 adsorbed about 30% of the original activity, whereas 0.7 ml. of IR-100 adsorbed 97% of the activity.

These experiments were repeated using the sodium form of both resins. Closely comparable results were obtained, IR-120–Na adsorbing 23% and IR-100–Na adsorbing 98% of the original activity.

It is evident that in the strongly alkaline solutions IR-100 has much greater selective adsorptive capacity for cesium ions than IR-120.

This was confirmed in dynamic tests in which an alkaline solution containing 0.4 p.p.m. of inactive cesium to which was added about 7,000 c./m./ml. of active cesium was passed over IR-100 in a column. Cesium was removed quantitatively from the solution until 112 volumes of solution per volume of resin were passed. Under comparable conditions resin IR-120 gave immediate breakthrough.

Tabulation of Results

The performance of resins IR-100 and IR-120 in the adsorption of cesium in trace amounts may be compared as

	IR-100	IR-120
Maximum K_d at *p*H 4 to 4.4	7.8×10^4	18.7×10^4
K_d at *p*H 5.8	18.3×10^4	7.7×10^4
Cs adsorbed from alkaline Na-salt solutions in batch tests	98%	23%
Volume of alkaline Na-salt solution passed per volume resin before breakthrough in dynamic tests	112	0

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Ammonia Decomposition and Related Phenomena on Rhenium Catalysts[1]

BY JAMES PETER MCGEER[2] AND HUGH S. TAYLOR

The kinetics of decomposition of ammonia over metallic rhenium between 380 and 440° at one atmosphere total pressure has been studied with and without added helium, nitrogen and hydrogen. The kinetics conform to those obtained with iron synthetic ammonia catalysts, proportional to $[NH_3]^{0.53}$ and $[H_2]^{-0.89}$ with nitrogen inert and with an observed activation energy of 32 ± 3 kcal. Chemisorption and decomposition of small amounts of ammonia occur on rhenium surfaces at low pressure and temperatures below that at which continuous macro-decomposition occurs. The data indicate strong nitrogen adsorption, weak hydrogen adsorption and surface heterogeneity. Hydrogen adsorption is measurable between −196 and 330°, and parallels similar measurements with iron surfaces. A low temperature interaction between rhenium and nitrogen is indicated by comparison with the behavior of argon on rhenium. Activated adsorption of nitrogen on rhenium has been measured above 250°. Isotopic exchanges occur on rhenium catalysts between ammonia and deuterium, hydrogen and deuterium, and water and deuterium at temperatures between 0 and 100°. Nitrogen isotopes exchange rapidly on rhenium only at 500° and above. Addition of hydrogen accelerates this last exchange. It has been shown that the nitrogen isotope exchange reaction is very sensitive to reduction techniques in catalyst preparation both with iron and rhenium catalysts. The nitrogen exchange increases in rate at a given temperature with increasing thoroughness of reduction. Traces of water vapor are strong poisons for the nitrogen exchange with both iron and rhenium.

The catalytic properties of rhenium have been extensively investigated in relation to dehydrogenation of alcohols. The work was published in a series the last paper of which is given here as a reference.[3] Hydrogenation with rhenium was investigated by Tropsch and Kassler.[4] The catalytic synthesis of ammonia using various forms of rhenium was demonstrated by Greek workers.[5]

The literature on problems related to ammonia decomposition and synthesis has been frequently reviewed. In this country the bulk of the work has been done by Emmett and his collaborators, while other contributions have been made by the Russian school. The latter workers employ the theory of Temkin and Pyzhev[6] to explain all cases of catalytic synthesis and decomposition of ammonia. There are, however, certain well documented cases[7] where the results cannot be fitted to this theory. This investigation was undertaken to determine the course of the ammonia decomposition on a catalyst previously untested in this regard and to relate the results obtained to the other known facts concerning this catalytic reaction.

A. Kinetics of Ammonia Decomposition

Experimental.—The apparatus and technique used were essentially those of Love and Emmett.[7] du Pont anhydrous synthetic ammonia was used, while tank nitrogen, helium and hydrogen were purified using standard procedures.

Two portions of a 25-g. lot of commercial rhenium metal powder were used. These were in the form of a fine, unsupported powder. Catalyst 1 weighed 4.8 g. It was reduced in hydrogen at 490 to 520°. There was no interrup-

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[1] This paper represents a portion of a thesis submitted by J. P. McGeer to the Faculty of Princeton University in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1949.

[2] Ethyl Corporation Fellow 1947–1948; American Cyanamid Company Fellow 1948–1949; now Aluminum Laboratories Limited, Arvida, Quebec, Canada.

[3] M. S. Platanov, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 683 (1941); *C. A.*, **36**, 397 (1942).

[4] H. Tropsch and R. Kassler, *Ber.*, **63B**, 2149 (1930).

[5] C. Zenghelis and C. Stathis, *Compt. rend.*, **209**, 797 (1939).

[6] M. Temkin and V. Pyzhev, *Acta Physicochim.* (*U. R. S. S.*), **12**, 327 (1940).

[7] K. S. Love and P. H. Emmett, THIS JOURNAL, **63**, 3297 (1941).