are summarized in Table II and shown in Figs. 3, 4 and 5. They show only the trihydrate of sodium chlorite already known and pure sodium chloride.

SAN ANTONIO, TEXAS

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Anion Exchange Studies. XIII. The Alkaline Earths in Citrate Solutions[1,2]

BY FREDERICK NELSON AND KURT A. KRAUS

RECEIVED JULY 12, 1954

The anion-exchange behavior of the alkaline earths was studied in citrate solutions with a strong base anion-exchange resin. The elements were found to adsorb, and there were sufficient differences in their adsorbabilities to permit their separation from each other. In addition, separation of the alkaline earths from alkali metals, rare earths and a few other elements was demonstrated. The implications of the anion-exchange results on the strength and composition of citrate complexes of the alkaline earths are discussed.

Recent investigations by a number of techniques, including cation exchange, have shown that the alkaline earths form relatively strong citrate complexes in citrate solutions. For most of these elements the formation of a monocitrate complex has been proposed according to the equation

$$\mathrm{M}^{++} + \mathrm{Cit}^{-3} \rightleftarrows \mathrm{MCit}^{-} \qquad (1)$$

where M^{++} = alkaline earth ion and Cit^{-3} = citrate ion. Stability quotients

$$k^{m}_{01} = m_{\mathrm{MCit}}/m_{\mathrm{Cit}}m_{\mathrm{M}} \qquad (2)$$

were estimated to be *ca.* 1700 for Mg[3a,b]; *ca.* 1600 to 1700 for Ca[3a,c,g]; *ca.* 500 to 800 for Sr[3a,c,d,g,h]; *ca.* 200 for Ba[3e]; and *ca.* 100 for Ra.[3f] Strong citrate complexing also has been reported for Be.[4] Although the charge and formula of this complex (or complexes) has not been determined, there is little doubt that it is negatively charged. On the basis of this information on the stability constants of the alkaline earths, one could assume that they exist principally as negatively charged species at moderate citrate concentrations, and hence that they could be adsorbed by anion exchange resins. A systematic study of the anion exchange behavior of the alkaline earths in citrate solutions was carried out over the concentration range *ca.* 5×10^{-3} to *ca.* 1 M $(\mathrm{NH_4})_3\mathrm{Cit}$. The elements were found to be adsorbable, as expected, and a number of separations based on differences in adsorbability were achieved. Confirmation of the existence of the complexes MCit^- was obtained, as well as evidence for the existence of complexes $\mathrm{M(Cit)_2}^{-4}$.

Experimental

Adsorbabilities were measured with the same relatively highly cross-linked "strong base" anion-exchange resin (polystyrene-divinylbenzene quaternary amine resin, Dowex-1, 200–230 mesh) which was used in the earlier work. The resin, initially in the chloride form, was converted to the citrate form[2] by treating a column of the resin with 0.5 M $(\mathrm{NH_4})_3\mathrm{Cit}$ solution of *p*H *ca.* 8 until the effluent gave negligible chloride test with $\mathrm{AgNO_3}$. The column was then washed with water to remove excess $(\mathrm{NH_4})_3\mathrm{Cit}$. The top section, which contained visible adsorbed impurities (principally Fe(III)) was discarded and the remaining resin air-dried. Portions of the resin were analyzed for moisture by drying over Anhydrone at 60° and all-resin weights refer to the Anhydrone-dried material. The citrate content of the resin was determined by eluting[5] the citrate from a weighed amount of resin with a known volume of standardized HCl solution and by washing the resin with water to recover the excess HCl. The combined effluents were analyzed for chloride by titration with standard $\mathrm{AgNO_3}$ and for total acid with standard base. From the differences in the chloride analyses of the original HCl solutions and of the effluents, the amount of chloride retained by the resin was calculated to be 1.49 moles per liter of bed (chloride form), in good agreement with previous values for the capacity of the resin.[6] The citrate content of the effluent was determined from the acid titrations and the chloride titrations and was found to be 0.50 mole of $\mathrm{H_3Cit}$ per l. of bed (chloride form). Thus 0.33 mole of $\mathrm{Cit}^{\equiv}$ was eluted per mole of Cl^- adsorbed, substantiating that the resin originally was essentially in the citrate form and contained only negligible amounts of acid citrates.

The adsorbabilities of Be(II) and Mg(II) were rather high and were most conveniently determined by the equilibrium method,[7] although a few check experiments were also carried out by the column method.[7] The adsorbabilities of the other alkaline earths were relatively low and hence were determined by the column method.

In the equilibrium method, samples of resin and solution were shaken for at least several hours. The Be(II) solutions were analyzed radiometrically (54d Be^7) by counting liquid samples in a re-entrant hole sodium iodide scintillation counter.[8] The Mg(II) analyses were carried out either radiometrically (21b Mg^{28}), spectrographically, or by flame spectrophotometry.[9]

As in earlier work, amounts of resin and solution were chosen so that approximately half of the metal was removed from the solution at equilibrium. Distribution coefficients D (amount per kg. of Anhydrone dry resin/amount per liter

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper: F. Nelson and K. A. Kraus, THIS JOURNAL, **76**, 329 (1954).

[3] (a) A. B. Hastings, F. S. McLean, L. Eichelberger, S. L. Hall and E. DaCosta, *J. Biol. Chem.*, **107**, 351 (1934); (b) R. Nordbo, *Skand. Arch. Physiol.* **80**, 341 (1933); See *C. A.* **33**, 454⁴ (1939); (c) J. Muus and H. Lebel, *Kgl. Danske Vedenskab. Selskab. Math-fys. Medd.* **13**, No. 19 (1936); see *C. A.* **31**, 1722¹ (1937); (d) N. R. Joseph, *J. Biol. Chem.* **164**, 529 (1946); (e) J. Schubert and J. W. Richter, THIS JOURNAL, **70**, 4259 (1948); (f) J. Schubert, E. R. Russell and L. S. Myers, *J. Biol. Chem.*, **185**, 387 (1950); (g) J. Schubert and L. Lindenbaum, THIS JOURNAL, **74**, 3529 (1952); (h) J. Schubert, *J. Phys. Chem.*, **56**, 113 (1952).

[4] See *e.g.* (a) I. Feldman, W. F. Neuman, R. A. Dannley and J. R. Havill, THIS JOURNAL, **73**, 4775 (1951); (b) A. W. Thomas and H. S. Miller, *ibid.*, **58**, 2526 (1936).

[5] F. Nelson and K. A. Kraus, *ibid.*, **76**, 329 (1954).

[6] K. A. Kraus and G. E. Moore, *ibid.*, **75**, 1457 (1953).

[7] K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

[8] C. J. Borkowski, Report ORNL-1153 (1951).

[9] We are indebted to Mr. M. Murray and Mr. W. R. Laing of the ORNL Analytical Division for the spectrographic and flame spectrophotometric analyses.

The Mg^{28} tracer was prepared by a spallation reaction (chlorine) in the 184 inch Berkeley cyclotron (see Lindner, *Phys. Rev.*, **91**, 642 (1953)). The tracer was purified by carrying on $\mathrm{Fe(OH)_3}$, removing Fe(III) by anion exchange in chloride solutions (G. E. Moore and K. A. Kraus, THIS JOURNAL, **72**, 5792 (1950)), followed by cation exchange using 0.5 M HCl as eluent. We are indebted to Dr. R. K. Sheline for γ-ray spectrum analysis of the purified Mg^{28} tracer (purity > 99%).

solution) were calculated from the decrease in metal concentration. The latter were usually sufficiently low so that loadings of the resin of less than 5% of capacity were obtained.

In the column method, adsorbabilities were determined by passing a small portion of the solutions into small columns of the resin previously pretreated with the appropriate citrate solutions. Elution was carried out at flow rates *ca.* 0.1 to 0.5 cm./min. and the volume of effluent at which metal appeared in maximum concentration determined radiometrically or spectrographically. The following tracers were used: 152 d Ca^{45}, 53 d Sr^{89}, 12.8 d Ba^{140} and 1620 y Ra^{226}. Since Ca^{45} and Sr^{89} are β-emitters (without γ-rays), they were counted with a windowless β-proportional counter[10] while the others were γ-counted with the sodium iodide scintillation counter.

Since the Ra^{226} tracer[11] contained decay products (Rn, Po, Pb and Bi) to an appreciable extent, it was purified by anion exchange before use. The tracer in 2 *M* HCl was passed through a small column of the chloride form of the anion exchange resin. Under these conditions Ra passes through the column while Po, Pb and Bi are retained. The purified tracer was analyzed with an α-spectrometer[12] and found to be essentially pure Ra^{226}.

All experiments were carried out in a thermostated room at 25 ± 1°.

Results and Discussion

1. Adsorbabilities of the Alkaline Earths.—The results of both the column and equilibrium experiments are summarized in Fig. 1, a log-log plot of the distribution coefficient *D vs.* molarity of ammonium citrate ($m_{(NH_4)_3Cit}$). For ready comparison of the two types of experiments, the values of *D* given for the column experiments were computed from the observed values of *E*, the elution constant, defined by the equation[13]

$$E = dA/V \qquad (3)$$

where *d* is the length of the column, *A* the cross-sectional area and *V* the volume of effluent at which the metal appears in maximum concentration. A volume distribution coefficient D_v can be computed from E[13] by the relationship

$$E = 1/(i + D_v) \qquad (4)$$

where *i* is the fractional interstitial space. Since $D\rho = D_v$, where ρ is the bed density, *D* can be computed from *E* if *i* and ρ are determined separately. By measuring the volume occupied by a known amount of Anhydrone-dry resin (citrate form) $1/\rho = 2.23$ l. per kg. of dry resin was found. The interstitial volume for which a maximum value $i = 0.42$ had been obtained by a column method (setting $D_v = 0$ for positively charged ions) was determined more accurately by the centrifugation method[14] in which most of the interstitial solution is centrifuged from the resin bed. An additional correction was made for the small amount of liquid adhering to the centrifuged bed after centrifugation (assumed 0.033 l. per l. of bed.[15] In this manner $i = 0.36$ was estimated.

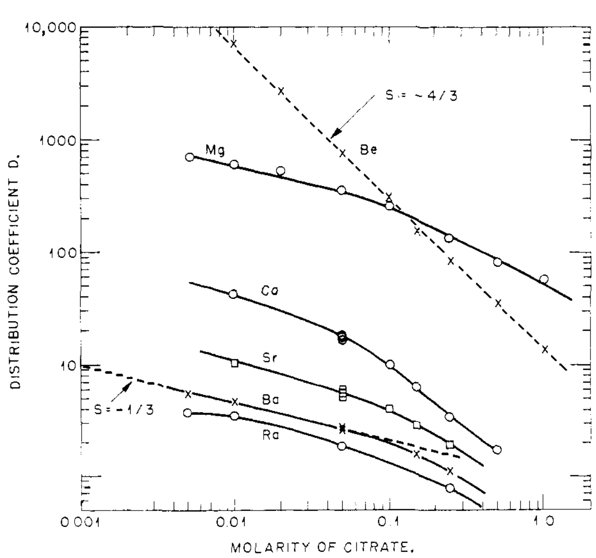

Fig. 1.—Adsorbability of alkaline earths in citrate solution.

As can be seen from Fig. 1, the adsorbabilities of the alkaline earths, except for Be(II) at high citrate concentrations, follow a regular pattern with adsorbabilities increasing from Ra(II) to Be(II). Furthermore, Mg(II) and Be(II) are considerably more strongly adsorbed than the other alkaline earths. All alkaline earths show a decrease in adsorbability with increasing citrate concentration, as one might expect for metals which are predominantly in the form of negatively charged complexes.

2.1. Separation of the Elements Magnesium to Radium.—It may be noticed from Fig. 1 that the differences in adsorbability of the elements Ca, Sr, Ba and Ra are somewhat greater at low m_{Cit} than at high m_{Cit} (as discussed in Section 3, still greater differences are expected at considerably lower m_{Cit}). Advantage was taken of this observation in the separation described in Fig. 2. For this experiment a 2.0-ml. aliquot of a solution containing 0.014 *M* $BaCl_2$ (Ba^{140}), 0.014 *M* $SrCl_2$ (Sr^{89}), 0.014 *M* $CaCl_2$ (Ca^{45}) and 0.03 *M* $MgCl_2$ was added to an 0.27 cm.² × 44-cm. column of the citrate form of the resin which had been pretreated with 0.05 *M* $(NH_4)_3Cit$ at *p*H *ca.* 7.5. Elution was carried out

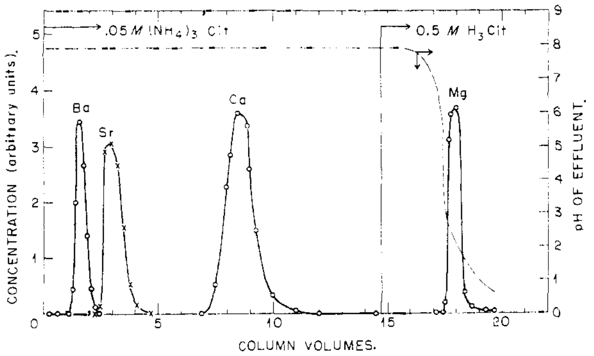

Fig. 2.—Anion-exchange separation of Ba, Sr, Ca and Mg in citrate solution (0.27 cm.² × 44 cm. column, flow rate 0.4 cm./min.).

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[10] C. J. Borkowski, *Anal. Chem.*, **21**, 348 (1949).

[11] We are indebted to Dr. P. S. Rudolph of the ORNL Chemistry Division for the Ra^{226} tracer.

[12] We are indebted to Mrs. Myrlene Davis of the ORNL Instruments Division for the α-spectrometer analyses. Samples were counted immediately after preparation and ignition of the "counting plates" and hence would not reveal any Rn activity. Further, presence of Rn in Ra-solutions is unimportant since it would not be detected by the γ-counters which were used for Ra-analyses.

[13] K. A. Kraus and G. E. Moore, THIS JOURNAL, **73**, 9 (1951).

[14] (a) K. W. Pepper, R. Reichenberg and D. K. Hale, *J. Chem. Soc.*, 3129 (1952); (b) H. P. Gregor, K. M. Held and J. Bellin, *Anal. Chem.*, **23**, 620 (1951); (c) R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **45**, 228 (1953).

[15] K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1457 (1953).

with the same citrate solution and the effluent analyzed radiometrically for Ba, Sr and Ca and spectrographically for Mg.[9] As shown in Fig. 2, the elements eluted in the order Ba, Sr, Ca in this medium. Magnesium remained on the column since it is very strongly adsorbed under these conditions. Its removal was accomplished by treating the column with *ca.* 0.5 *M* H_3Cit. Since the citrate form of the resin acts as a base[5] citric acid is first adsorbed and the appearance of Mg delayed. Magnesium appears in the effluent simultaneously with the citric acid break-through, as also indicated by the *p*H measurements of the effluent (dotted line in Fig. 2).

In a separate experiment, partial separation of Ra and Ba was also demonstrated. Since neither element adsorbs strongly at reasonable citrate concentrations this partial separation is achieved in a very few column volumes of solution. In a typical experiment an 0.1-ml. aliquot of a solution containing Ra^{226} and Ba^{140} tracers was passed into an 0.1 cm.^{2} × 29 cm. column of the citrate form of the resin pretreated with 0.01 *M* $(NH_4)_3Cit$ of *p*H *ca.* 8. Elution was carried out with the same citrate solution. As predicted from Fig. 1, Ra appeared first in the effluent and approximately 50% of the Ra tracer was recovered essentially free of Ba.

2.2. Separation of Magnesium and Beryllium.—As shown in Fig. 1, the relative adsorbabilities of Mg(II) and Be(II) are different at low m_{Cit} and at high m_{Cit}. Since the distribution coefficients are too high at low m_{Cit} to effect satisfactory elution, attempts were made to separate these elements at high m_{Cit} where Be(II) was expected to appear first in the effluent. In a typical experiment (see Fig. 3) an 0.5-ml. aliquot of a solution containing 0.05 *M* $MgCl_2$, 10^{-3} *M* $Be(NO_3)_2$ (Be^7) and 0.5 *M* $(NH_4)_3Cit$ (*p*H *ca.* 7) were added to a 0.114 cm.^{2} × 8-cm. column of the citrate form of the resin pretreated with 1 *M* $(NH_4)_3Cit$. Elution was carried out at a flow rate 0.5 cm./min. with the same citrate solution. The separation was relatively poor since Be(II) under these conditions shows a trailing edge. Thus, when Mg(II) started to appear in the effluent a small amount of Be(II) was still retained by the column. In order to demonstrate this effect clearly, elution of Mg(II) was completed with 1 *M* HCl rather than a citric acid solution (see Section 2.1) since under these conditions both Mg(II) and residual Be(II) are rapidly removed from the column. As shown in Fig. 3 a small peak of Be(II) appeared in the Mg(II) band.

Since separation of these two elements also appeared feasible by elution at lower *p*H, the adsorbability of Be(II) was studied in $(NH_4)_3Cit$–H_3Cit mixtures. An extremely rapid decrease of the adsorbability of Be(II) was found with decreasing *p*H ($D = 310$ in 0.1 *M* $(NH_4)_3Cit$, $D = 60$ in 0.05 *M* H_3Cit–0.05 *M* $(NH_4)_3Cit$, $D < 1$ in 0.1 *M* H_3Cit). Taking advantage of this information, separation was attained under conditions where Be(II) was only slightly adsorbed. In a typical experiment an 0.11-ml. aliquot of a solution containing 0.05 *M* $MgCl_2$, 10^{-3} *M* $Be(NO_3)_2$ (Be^7) and 0.2 *M* $(NH_4)_3Cit$ (*p*H 4.3) was added to an 0.25 cm.^{2} × 8.0-cm. column of the citrate form of the resin pretreated with the same citrate solution. Magnesium under these conditions appeared first in the effluent. Again separation from Be(II) was not quantitative since the Mg(II) band tailed seriously.

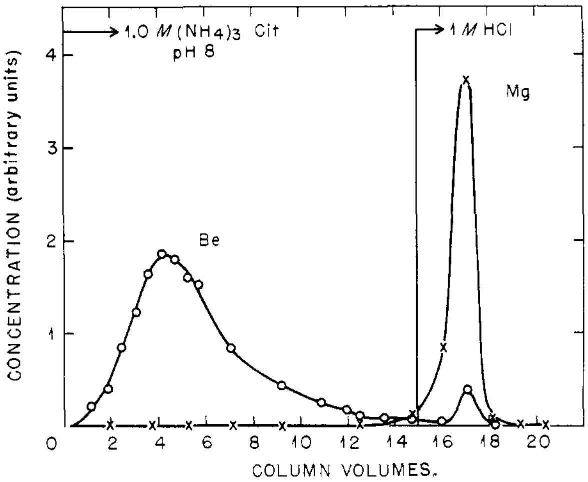

Fig. 3.—Partial separation of Be and Mg by anion exchange in citrate solution (0.114 cm.^{2} × 8.0 cm. column, flow rate *ca.* 0.5 cm./min.).

2.3. Other Separations.—In order to check the general applicability of the separations method in citrate solutions a few other elements were investigated in a cursory manner. It was found that the alkali metals showed essentially no adsorption from ammonium citrate solutions and that they hence could easily be separated as a group from the alkaline earths, in agreement with recent work by Samuelson.[16]

While investigating the adsorbability of Ba, the tracer Ba^{140} was used which also contained its decay product La^{140}. In the course of the investigation it was found that La(III) was strongly adsorbed from ammonium citrate solutions up to 1 *M* $(NH_4)_3Cit$ but that it could be removed readily in 0.5 *M* H_3Cit. In view of this behavior La(III) and presumably the other rare earths can be separated readily from most of the alkaline earths and alkali metals. By proper choice of acidity and concentration of the citrate in the eluent, separation of La(III) from Mg(II) and Be(II), the most strongly adsorbed alkaline earth, could probably also be achieved. Earlier partial separation of two rare earths (Pm(III) and Eu(III)) by anion exchange in citric acid solution has been reported.[17]

In an incidental manner it was found that a very large number of other elements can also be adsorbed from ammonium citrate solutions, again in agreement with the work of Samuelson.[16] Foremost among these is Fe(III) which in all experiments tended to accumulate as an impurity at the top of the columns.

3. Some Considerations Regarding Species in Solution.—Some of the most characteristic features of the adsorption isotherms of the various alkaline earths (Fig. 1) are: (1) for most elements adsorption decreases only slowly with increasing m_{Cit}; (2) Be(II) shows a very much steeper decrease of *D* with m_{Cit} than the other alkaline earths; and

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[16] O. Samuelson, *Z. Elektrochem.*, **57**, 207 (1953).

[17] E. H. Huffman and R. L. Oswalt, THIS JOURNAL, **72**, 3323 (1950).

(3) of a change in slope S of a plot of log D *vs.* log m_{Cit}, particularly for Ca(II) and Sr(II). Although the data are too sketchy to permit quantitative conclusions regarding the stability of the species in solution, it can readily be shown that the small values of S are consistent with the assumption that a monocitrate complex (MCit^-) exists for Ra(II), Ba(II), Sr(II), Ca(II) and Mg(II) at low citrate concentrations, and that Be(II) probably exists as a citrate complex with charge −4.

If we designate the adsorbable complex ion as X^{-x} and the eluting anion as A^{-a} and assume that the species X^{-x} is a predominant species, then the equilibrium expression

$$\frac{K}{G} = \frac{(\text{X}^{-x})_\text{r}^a\,(\text{A}^{-a})^x}{(\text{X}^{-x})^a\,(\text{A}^{-a})_\text{r}^x} \qquad (5)$$

can be written for the ion-exchange equilibrium

$$a\text{X}^{-x} + x(\text{A}^{-a})_\text{r} \rightleftarrows a(\text{X}^{-x})_\text{r} + x\text{A}^{-a} \qquad (6)$$

where K is the exchange constant, G the appropriate activity coefficient ratio and where parentheses indicate concentrations of species. Under the assumption that G is constant and that $(\text{A}^{-a})_\text{r}$ is constant (*i.e.*, that $(\text{X}^{-x})_\text{r}$ is small compared with $(\text{A}^{-a})_\text{r}$) equation 5 can be written in the form

$$\text{Const.} = \frac{K}{G}\,(\text{A}^{-a})_\text{r}^x = D^a\,(\text{A}^{-a})^x \qquad (7)$$

since

$$D = \frac{(\text{X}^{-x})_\text{r}}{(\text{X}^{-x})} \qquad (8)$$

By differentiation of equation 7, the equation

$$\frac{\text{d}\log D}{\text{d}\log(\text{A}^{-a})} = S = -\frac{x}{a} \qquad (9)$$

is obtained, which implies that the slope S of a plot of log D *vs.* log (A^{-a}) yields the ratio of the absolute magnitude of the charge of the complex ion to that of the eluting anion.

The eluting anion in the citrate experiments was essentially $\text{Cit}^{\equiv}$, *i.e.*, $a = 3$, and hence S should be $-{}^1/_3$ for a complex ion of charge minus one and $-{}^4/_3$ for a complex ion of charge −4. The experimental value of S for Be(II) is very close to $-{}^4/_3$, permitting the conclusion that its citrate complex probably carries a charge of −4 although, of course, possible non-constancy of G introduces some doubt. These experiments do not permit a decision if the formula of this complex is Be(Cit)_2^{-4} or a basic complex of Be(II) (probably polymeric) of the same negative charge. Such polymeric basic complexes, though not of this charge, have been suggested earlier.[4b]

For the other alkaline earths a slope of $-{}^1/_3$ seems to be approached at low m_{Cit}, as indicated in Fig. 1, and hence these data are consistent with the earlier observation[3] that they form monocitrate complexes MCit^-. In the general vicinity of 0.1 M $\text{Cit}^{\equiv}$, Ca(II) and Sr(II) in particular show an increase in slope (more negative), which would suggest that they, and possibly Mg(II), Ba(II) and Ra(II) as well, tend to form dicitrate complexes ($M\,(\text{Cit})_2^{-4}$).

From the point of view of separations, it is interesting to note that in the range of m_{Cit} studied here the differences in adsorbability of the alkaline earths (except Be(II)) are primarily due to differences in the selectivity of the complexes MCit^- which follow the order $\text{MgCit}^- > \text{CaCit}^- > \text{SrCit}^- > \text{BaCit}^- > \text{RaCit}^-$. The same order of selectivities appears to exist for the complexes M(Cit)_2^{-4}. At very low m_{Cit}, not reached in the experiments reported here, additional differences in adsorbability are expected when the alkaline earth citrate complexes are only formed to a small extent. Since the stability constants of the complexes MCit^- decrease in the same order as the selectivity of these complexes, the differences in adsorption should become greater at very low citrate concentrations, and hence one might expect improved separations under these conditions.

Acknowledgment.—The authors are greatly indebted to Mrs. L. W. Magnusson, Jr., for valuable technical assistance.

OAK RIDGE, TENNESSEE

NOTES

The Barrier Hindering Internal Rotation in Pentafluorochloroethane[1]

By J. G. ASTON AND T. P. ZOLKI

RECEIVED SEPTEMBER 3, 1954

We have recently computed the entropy of the ideal gas at 1 atm. and the normal boiling point of pentafluorochloroethane from measurements of the heat capacity down to 11°K., heats of transition, fusion, vaporization and vapor pressure. The results are summarized in Table I. The quantities tabulated were determined in our calorimeter C by methods and with accuracy discussed before.[2]

The normal modes of vibration of this compound have been derived completely from Raman and infrared data by Nielsen, Liang, Smith and Smith,[3] who assumed accidental degeneracy of the two modes of lowest frequency. These values have been used directly to calculate the vibrational entropy at the normal boiling point. To compute the rotational entropy values of 1.184×10^{-112} g.^{3} cm.^{6} and 6.989×10^{-39} g. cm.^{2}, respectively,

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[1] Carried out under Contract N6onr-269 T.O. III of the Office of Naval Research. We wish to thank the du Pont Company (Organic Chemicals Dept.) for supplying us with the pure sample and for financial support for the determination of the heat capacities of the liquid.

[2] J. G. Aston, S. V. R. Mastrangelo and G. W. Moessen, THIS JOURNAL, **72**, 5287 (1950).

[3] J. Rud Nielsen, C. Y. Liang, R. M. Smith and D. C. Smith, *J. Chem. Phys.*, **21**, 383 (1953).