Table I

Typical Potentials Obtained with the Ag, AgCl and the Hg, Hg_2Cl_2 Electrode System as a Function of Temperature and HCl Concentration

1 *M* HCl		0.5 *M* HCl		0.1 *M* HCl	
Temp., °C.	Pot., mv.	Temp., °C.	Pot., mv.	Temp., °C.	Pot., mv.
25	46	25	46	25	46
50	55	54	56	60	57
87	68	78	65	110	82
110	75	98	73	135	92
154	89	142	88	143	106
166	95	153	92	173	128
200	107	190	104		
235	120	263	143		
247	128				
254	133				

approached as a limit after perhaps several stages of basic salt formation.

The life of the electrode pair was comparatively short at temperatures above 200°. Of the two electrodes the calomel apparently deteriorated the more rapidly. This was due in part to loss of mercury and calomel from the cell compartment.

The electrode pair was also briefly studied in 1 *M* KCl solution and 0.01 *M* HCl. In 1 *M* KCl the electrodes showed the expected potential at 25° but became very erratic at temperatures above 70°. In 0.01 *M* HCl the electrode pair showed very erratic behavior. In two experiments no consistent potentials were obtained, even at 25°, and further work below 0.1 *M* HCl was postponed.

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The Beryllium-Citrate System. II. Ion-exchange Studies[1]

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Ion-exchange studies have been performed on mixtures composed of radiotracer concentrations of beryllium isotope, Be^7, in excess citrate at various *p*H's, 34° and $\mu = 0.15$ The results in the *p*H range 3-4 are explainable on the basis of the existence of three complexes, BeH_2Cit^+, $BeHCit^0$ and $BeCit^-$, the respective instability constants being 4×10^{-2}, 6×10^{-3} and 3×10^{-5}. The results above *p*H 4 suggest that polynuclear complexes begin to form above this *p*H. In slightly alkaline solution there exists a complex having a charge more negative than −1.

In this paper we have applied to the beryllium-citrate system the ion-exchange method originated by Schubert[2] for the study of complex ions and, of necessity, have elaborated upon the scope of the applicability of this technique.

Experimental

Materials.—The beryllium isotope, Be^7, was obtained from the Oak Ridge National Laboratory and was purified by the method of Toribara and Chen.[3]

The cation-exchange resin, Dowex 50, ammonium form, 40-60 mesh, was a preparation previously described.[4] Some of this resin was converted to the hydrogen form by shaking six times (1 to 4 hours each time) with 5 *M* HCl, washing with distilled water, and air-drying. The Dowex 1 resin, chloride form, was prepared by shaking a batch of the hydroxide form six times with 1 *M* HCl, washing with water and air-drying.

All other chemicals were C.P. grade.

Procedure.—Except for the experiments at *p*H 1.0 (see Table I), 28.0 ml. of each solution was prepared by mixing the indicated quantities (see Tables I and II) of beryllium isotope, citric acid and 5 ml. of 0.75 *M* NH_4ClO_4, diluting to *ca.* 25 ml. with water, adjusting to the indicated *p*H with a measured volume of 0.25 *M* NH_4OH, dissolving the amount of solid ammonium perchlorate calculated to give the desired ionic strength, μ, and then diluting to 28.0 ml. with water. A Beckman Model G *p*H meter was employed for the *p*H adjustments. A 20-ml. volume of each solution was added to the indicated amount of resin in a 50-ml. glass-stoppered erlenmeyer flask. The unused portion of each solution was used as a standard in the final counting procedure. Each stopper was sealed with paraffin and then wrapped tightly with parafilm. The flasks were shaken for three hours on a Boerner oscillating platform shaker in a constant-temperature room maintained at 34°. After being shaken, the solutions were decanted from the resin, and the *p*H's and relative beryllium concentrations were determined. The results of typical experiments were the same after overnight shaking, indicating that the three-hour shaking-time was sufficient to bring about equilibrium. The relative beryllium concentrations were determined by γ-ray counting as previously described.[4]

Table I

Investigation of Sign of Charge on Beryllium–Citrate Complex at 34°

		% of original Be left in aqueous phase after equilibration with			
		Cation-exchange resin[a]			
*p*H	Total citrate, moles/l.	G. of resin	%	Anion-exchange resin,[b] %	No resin, %
1.0	0	0.12	10	..	.....
1.0	0.10	.12	10	..	.....
3.0	0	.070	42	100	.....
3.0	.078	.070	61	100	.....
4.0	0	.20	20	100	.....
4.0	.012	.20	43	100	.....
4.6	0	.60	8	100	.....
4.6	.0089	.60	60	100	.....
7.0	0	.07	11	9	60[c], 19[d]
7.0	.01	3.0	98	89	100[d]
7.5	.07	0.14	99	12	100[d]
7.5	.0001	.8	96	..	95[d]
7.5	0–.0001	.8	(95 but not reproducible)		

[a] At *p*H 1.0; $\mu = 0.10$, hydrogen form of Dowex 50 resin used. At all other *p*H's: $\mu = 0.15$, ammonium form of Dowex 50 used. [b] 0.5 gram of Dowex 1, chloride form, used for each experiment. [c] Solution not centrifuged. [d] Solution centrifuged 15 minutes.

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[1] This publication is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York. Presented at the Gordon Research Conference on Ion Exchange, New Hampton, New Hampshire, July, 1954.

[2] J. Schubert, *J. Phys. Chem.*, **56**, 114 (1952). This paper has an extensive bibliography.

[3] T. Y. Toribara and P. S. Chen, Jr., *Anal. Chem.*, **24**, 539 (1952).

[4] I. Feldman and J. R. Havill, This Journal, **74**, 2337 (1952).

TABLE II

pH	f_1	f_2	$f_3 \times 10^3$	Slope	Relative concn. ratio of mononuclear complexes
3.0	0.50	0.019	0.027	39	14:4:1
3.5	.70	.087	.39	113	1:1:1
4.0	.67	.26	.6	446	1:2:1

Throughout this paper the abbreviations H_3Cit, H_2Cit^-, $HCit^{-2}$ and Cit^{-3} represent, respectively, molecular citric acid and the three citrate ions obtained by its stepwise dissociation. (T·Cit) represents the sum of the molar concentration of all these forms of citrate.

Theoretical Considerations

Thus far, the equations on which the ion-exchange method of studying complex ions is based presuppose that the complex ions under study are mononuclear and that the free metal ions are unpolymerized.[2] The application of this technique to a system which at times, depending on pH, contains polynuclear complex ions and polymerized metal ions has made it necessary for us to formulate a more generalized equation than has previously appeared.

Consider the dissociation of the complex $\{M_xA_y\}^c$

$$\{M_xA_y\}^c \rightleftharpoons (x/p)\, M_p^{+s} + yA^{-v} \qquad (1)$$

The cation M may be polymerized to the extent of p, and the anion is assumed to be in a simple form.

A dissociation constant, K, in terms of concentration units may be written as

$$K = \frac{K_a}{\gamma \text{ ratio}} = \frac{(M_p)^{x/p}(A)^y}{(M_xA_y)} \qquad (2)$$

where K_a is the thermodynamic dissociation constant, γ ratio is the activity coefficient ratio, and parentheses indicate molarities. If charge c is zero or negative and M goes on the resin in the same form in which it exists in solution we obtain the following

$$M_p{}^{+s} + zBR \rightleftharpoons M_pR_s + zB^+ \qquad (3)$$

When no complexing agent is present, the distribution coefficient is

$$K_d^\circ = \frac{\%\text{ M in exchanger}}{\%\text{ M in soln.}} \times \frac{\text{vol. of soln.}}{\text{mass of exchanger}} \qquad (4)$$
$$= \frac{pN_{M_pR_s}}{pN_{M_p}} \times \frac{V}{m} = \frac{N_{M_pR_s}}{(M_p)m}$$

where V is the volume of solution, m is the mass of resin used, and N is the number of moles of indicated substance.

In the presence of the complexing agent, the distribution coefficient is

$$K_d = \frac{pN_{M_pR_s}}{pN_{M_p} + xN_{M_xA_y}} \times \frac{V}{m} = \frac{N_{M_pR_s}}{(M_p) + \frac{x}{p}(M_xA_y)} \times \frac{1}{M} \qquad (5)$$

If the ionic strength is kept constant in the investigation, the γ ratio in equation 2 may be assumed to be constant. Then, dividing (4) by (5), substituting (2), and dividing both sides of the resulting equation by K_d° leaves equation 6.

$$\frac{1}{K_d} = \frac{\frac{x}{p}(M_p)^{(x/p)-1}(A)^y}{K_d^\circ\, K} + \frac{1}{K^\circ} \qquad (6)$$

Only if $x = p$ does equation 6 reduce to the equation of Schubert, *et al.*

$$\frac{1}{K_d} = \frac{(A)^y}{K_d^\circ K} + \frac{1}{K_d^\circ} \qquad (7)$$

In such a case (*i.e.*, $x = p$), y may be determined by a plot of $1/K_d$ *versus* $(A)^y$, in which the proper value of y is that which gives a straight line. Conversely, if $1/K_d$ is plotted *versus* some reasonable power of the ligand concentration and a straight line is obtained, this is evidence that $x = p$. However, neither x nor the ratio y/x between M and A in the complex can be determined unless the value of p is determined by some independent means.

If the metal ion polymer is broken up as it goes onto the resin according to the reaction

$$M_p{}^{+s} + zBR \rightleftharpoons pMR_{s/p} + zB^+ \qquad (8)$$

the final equation obtained is also (6).

If the complex is also adsorbed by the resin (*i.e.*, c is positive) the term $(A)^y$ in equations 6 and 7 must be multiplied by a correction factor $(1 - K_d'/K_d)$, where K_d' = moles complex adsorbed per gram of resin/moles complex per liter of solution.[5] A linear plot of $1/K_d$ *versus* $(A)^y$ would be improbable unless $K_d'/K_d = 0$, as well as $x = p$. A straight-line relationship, therefore, does not indicate conclusively that c is not positive but that the complex is very weakly adsorbed compared to the metal ion.

Consider now a system, $M_p{}^{+s} + A^{-v}$, which reacts completely to form two complex ions, $\{M_bA_q\}^{+w}$ and $\{M_gA_r\}^j$; *i.e.*, only a negligible concentration of uncomplexed metal ion remains. The following equilibrium then exists

$$\{M_gA_r\}^j \rightleftharpoons \frac{g}{b}\{M_qA_q\}^{+w} + yA^{-v} \qquad (9)$$

If the ion $\{M_gA_r\}^j$ is not taken up by the resin but the ion $\{M_bA_q\}^{+w}$ does enter into a typical ion-exchange equilibrium with the resin, reaction 9 should be described by an equation similar in form to equation (6); *i.e.*

$$\frac{1}{K_d} = \frac{g}{b}\,\frac{(M_bA_q)^{(g/b)-1}(A)^y}{K_*^\circ K_e} + \frac{1}{K_d^\circ} \qquad (10)$$

for which K_e is the equilibrium constant of reaction 9 and K_*° is the distribution coefficient of the complex $\{M_bA_q\}^{+w}$ in the absence of any *uncomplexed* ligand. The value of K_*° would have to be obtained by extrapolation since this complex would cease to exist when the concentration of anion A approaches zero.

Results and Discussion

The ion-exchange results presented in Table I, column 4, show that beryllium ions do not react with citric acid molecules but that they do combine with citrate ions. The resulting complex ions are bound less strongly by a cation-exchange resin than are uncomplexed beryllium ions.

In Fig. 1 are plots of $1/K_d$ *vs.* the total citrate concentration, (T·Cit), at various pH's. The lower three curves, for pH 3.0, 3.5 and 4.0, are linear, and all three lines extrapolate to the same K_d° value, which is the K_d° value obtained when no citrate is present.

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(5) J. Schubert and A. Lindenbaum, THIS JOURNAL, **74**, 3529 (1952).

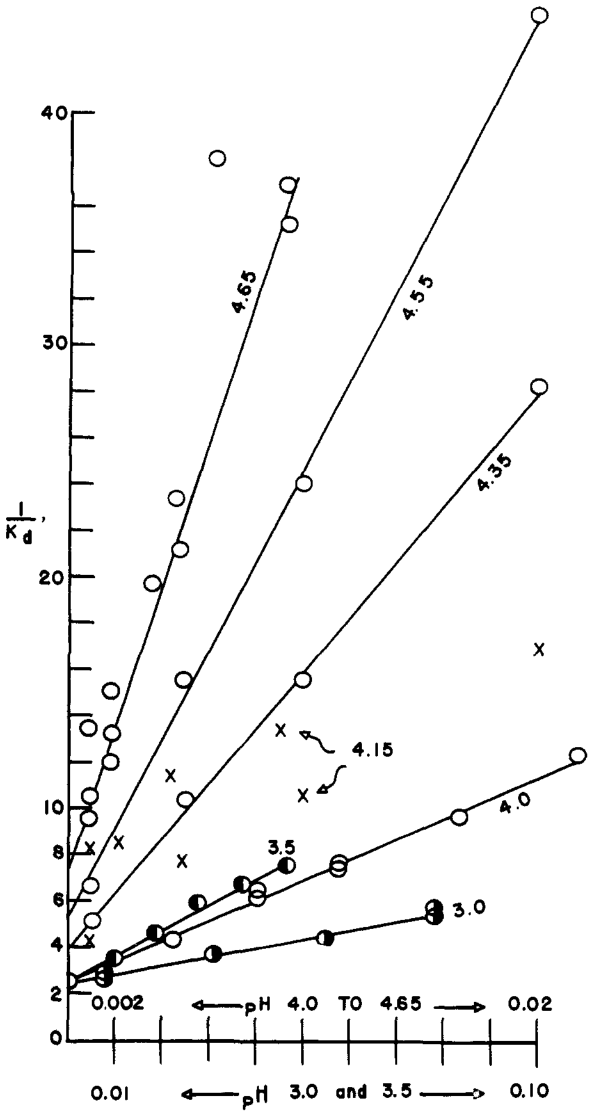

Fig. 1.—Ion-exchange equilibria between Dowex 50 resin, ammonium form, and solutions containing citrate and radioactive Be^7 isotope (see Experimental for details).

At *p*H 4.15, the reproducibility was poor. Straight lines are seen for *p*H 4.35 and 4.55. At *p*H 4.65, the reproducibility was not good. It is obvious that above *p*H 4 none of these lines extrapolates to the experimental K_d° as was the case for the *p*H 3 to 4 curves.

Studies from *p*H 3 to 4.—The data from *p*H 3 to 4 can be explained most simply on the basis of the following set of equilibria

$$\text{BeH}_2\text{Cit}^{+1} \rightleftarrows \text{Be}^{+2} + \text{H}_2\text{Cit}^{-1} \qquad (11)$$

$$\text{BeHCit}^0 \rightleftarrows \text{Be}^{+2} + \text{HCit}^{-2} \qquad (12)$$

$$\text{BeCit}^{-1} \rightleftarrows \text{Be}^{+2} + \text{Cit}^{-3} \qquad (13)$$

When such a system is in equilibrium with the cation-exchange resin, BR, K_d° is given by (14)

$$K_d^\circ = \frac{N_{\text{BeR}_2}}{(\text{Be}^{+2})} \times \frac{1}{m} \qquad (14)$$

because the monovalent BeH$_2$Cit$^+$ ion should not be adsorbed to a significant extent under the conditions of the experiment (high $(\text{NH}_4^+)/N_{\text{NH}_4\text{R}}$). Hence, K_d should be given by (15)

$$K_d = \frac{N_{\text{BeR}_2}}{(\text{Be}^{+2}) + (\text{BeH}_2\text{Cit}^+) + (\text{BeHCit}) + (\text{BeCit}^-)} \times \frac{1}{m} \qquad (15)$$

Dividing (14) by (15) gives (16)

$$\frac{K_d^\circ}{K_d} = 1 + \frac{(\text{BeH}_2\text{Cit}^+) + (\text{BeHCit}) + (\text{BeCit}^-)}{(\text{Be}^{+2})} \qquad (16)$$

Letting K_1, K_2 and K_3 represent the instability constants of (11), (12) and (13), respectively, and f_1, f_2 and f_3 represent the fractions of the total citrate concentration present as (H$_2$Cit$^-$), (HCit^{-2}) and (Cit^{-3}), respectively, at constant *p*H, ionic strength and temperature, (16) transforms into (17)

$$\frac{1}{K_d} = \frac{1}{K_d^\circ} + \frac{1}{K_d^\circ}\left(\frac{f_1}{K_1} + \frac{f_2}{K_2} + \frac{f_3}{K_3}\right)(\text{T·Cit}) \qquad (17)$$

The slope

$$\frac{1}{K_d^\circ}\left(\frac{f_1}{K_1} + \frac{f_2}{K_2} + \frac{f_3}{K_3}\right)$$

of this linear equation varies with *p*H since the f values are *p*H dependent. Determining the slope at three different *p*H's gives three equations which can be solved for the individual K values, if the f values are known at each *p*H.

The f values, calculated from the citric acid dissociation constants determined by Bates and Pinching,[6] and the measured slopes for *p*H 3.0, 3.5 and 4.0 are presented in Table II. The calculated values for K_1, K_2 and K_3 at 34° and $\mu = 0.15$ are 4×10^{-2}, 6×10^{-3} and 3×10^{-5}, respectively.

The relative concentrations of the three mononuclear complexes at a given *p*H may be calculated by the equation

$$(\text{BeH}_2\text{Cit}^+):(\text{BeHCit}):(\text{BeCit}^-) = \frac{f_1}{K_1} : \frac{f_2}{K_2} : \frac{f_3}{K_3}$$

This ratio is *p*H dependent but is independent of either the total citrate concentration or the Be isotope concentration. These ratios are presented (Table II) for two reasons. One, they show that the predominant species varies greatly in a small *p*H interval. Two, they point out the danger in neglecting the effect of a ligand when its concentration seems negligible. At *p*H 3, where $(\text{Cit}^{-3})/(\text{H}_2\text{Cit}^-) = 5 \times 10^{-5}$, the $(\text{BeCit}^-)/(\text{BeH}_2\text{Cit}^+)$ ratio is $^1/_{14}$. At *p*H 4, where $(\text{Cit}^{-3})/(\text{H}_2\text{Cit}^-)$ is 10^{-3}, $(\text{BeCit}^-)/(\text{BeH}_2\text{Cit}^+) = 1.25$.

The belief that a significant amount of the anion BeCit$^-$ exists at *p*H 4 and below is not contradicted by the fact that no beryllium was adsorbed by the anion exchange resin (Table I) at *p*H 4.6 and below. Such a monovalent anion in tracer concentration should not be adsorbed under the conditions of the experiment (high $(\text{ClO}_4^-)/N_{\text{RClO}_4}$.)

Studies above *p*H 4.—The fact that for *p*H > 4 none of the curves in Fig. 1 extrapolates to the experimental $1/K_d^\circ$ value shows that above *p*H 4 the beryllium–citrate system does not contain *merely* Be^{+2} ions and mononuclear complexes. However, beryllium ions below 10^{-5} *M* do not polymerize or hydrolyze below *p*H 4.6 as shown in pre-

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[6] R. G. Bates and G. D. Pinching, This Journal, 71, 1274 (1949).

vious work.[4] Therefore, some polymerization of the complexes is indicated.

It is possible to explain the data qualitatively by postulating that: (i) there exists an equilibrium between two types of polynuclear beryllium–citrate complexes; (ii) both contain the same number of beryllium atoms; (iii) but one complex contains one more citrate group than does the other; (iv) only the complex containing the least citrate is adsorbed by the resin to a significant extent; (v) the adsorbable complex has a smaller distribution coefficient than have beryllium ions.

For such a system, the application of equation 10 would give curves similar to those from *p*H 4.35 to 4.65 in Fig. 1; *i.e.*, linear plots extrapolating to a $1/K^\circ_*$ value higher than $1/K^\circ_d$. To illustrate, the following equilibrium could satisfy the requirements

$$\{Be_2(HCit)_2\}^0 \rightleftharpoons \{Be_2HCit\}^{+2} + HCit^{-2}$$

Other possibilities may be deduced by altering the number of hydrogens in the citrate groups or by adding BeO groups to both complexes.

It seems unlikely that complexes having a Be/citrate molar ratio less than unity (*e.g.*, $Be(HCit)_2^{-2}$ or $BeCit_2^{-4}$) are present to a significant extent in these experiments below *p*H 4.6, because such complexes would introduce a $(T{\cdot}Cit)^2$ term which would prevent linearity of the $1/K_d$ *versus* $(T{\cdot}Cit)$ plot. Furthermore, the adsorption of beryllium by the anion-exchange resin (Table I) was not detected at *p*H 4.6 or below.

However, near *p*H 7 some beryllium was adsorbed by the anion-exchange resin, whereas none was taken up by the cation exchanger. This is shown by the data in rows 9–13 of Table I. A beryllium–citrate anionic complex having a charge more negative than −1 is, therefore, present above *p*H 7.

The poor reproducibility in the *p*H 4.15 region would be expected if the transition from mononuclear to polynuclear complexes were occurring. In this region significant quantities of all complexes would be present and the system would not be expected to follow the mathematics for any one type.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Extraction of Zirconium and Hafnium with Various Fluorinated β-Diketones

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The distribution ratios and equilibrium constants for the extraction of zirconium and hafnium from 4 *M* perchloric acid with various combinations of fluorinated β-diketones and organic solvents have been determined. The separation factors, K'_{Zr}/K'_{HF}, found for this acidity were: 2-thenoyltrifluoroacetone in benzene, 25; 2-thenoyltrifluoroacetone in *o*-dichlorobenzene, 16; benzoyltrifluoroacetone in benzene, 18; isovaleroyltrifluoroacetone in benzene, 13; isovaleroyltrifluoroacetone in *n*-hexane, 13.

The fractional separation of zirconium and hafnium by chelation–extraction with benzene solutions of various β-diketones has been reported previously.[1–3] These studies have been extended in the present work to other fluorinated β-diketones and to other solvents. In order to use more concentrated solutions of zirconium and hafnium, and hence to increase the usefulness of the fractionation method, 4 *M* perchloric acid has been used in these studies instead of 2 *M* acid, as in the previous studies. The concentration of zirconium or of hafnium may be as high as 0.04 *M* in 4 *M* perchloric acid and still be completely extracted, showing that the metal ion is either monomeric or that the monomer and any polymer establish equilibrium rapidly. Attempts were also made, in the case of 2-thenoyltrifluoroacetone, to extract 0.09 *M* zirconium from 5 *M* perchloric acid, a condition which also allows complete removal of zirconium from the aqueous phase, but precipitates formed at the organic–aqueous interfaces for the higher concentrations of diketone and consistent data could not be obtained.

The metal ion species for zirconium and hafnium is mainly M^{+4} for the monomers in 2 *M*, or stronger, perchloric acid,[4] and the extraction reaction may be expressed as

$$M^{+4} + 4HK = MK_4 + 4H^+ \qquad (1)$$

At constant acid concentration the equilibrium constant is then

$$\log K' = \log R - 4 \log [HK] \qquad (2)$$

where R is the extraction coefficient, $[MK_4]/(M^{+4})$, and [HK] is the diketone activity. The equilibrium constants obtained using 4 *M* perchloric acid cannot be compared directly to those[1–3] obtained using 2 *M* perchloric acid because the activity coefficients of the metal ion species at the two different ionic strengths are not known.

The diketones and solvents for which extraction data were obtained were 2-thenoyltrifluoroacetone (HTTA) in benzene and in *o*-dichlorobenzene, benzoyltrifluoroacetone (HBTA) in benzene and isovaleroyltrifluoroacetone (HITA) in benzene and in *n*-hexane. Interference in the form of precipitation at the organic–aqueous interface was encountered when extractions were tried with HTTA in hexone (4-methyl, 2-pentanone) and with 2-naphthoyltrifluoroacetone (HNTA) in benzene. It is probable that satisfactory data for these combinations of reagent and solvent could be obtained at

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(1) E. H. Huffman and L. J. Beaufait, THIS JOURNAL, **71**, 3179 (1949).

(2) B. G. Schultz and E. M. Larsen, *ibid.*, **72**, 3610 (1950).

(3) E. M. Larsen and G. Terry, *ibid.*, **75**, 1560 (1953).

(4) R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).