2. Structure calculations, based on the Kelvin equation, result in curves showing the distribution of pore volume over a large range of pore radii. Radius values taken from the maxima of these curves show increase with activation temperature, and are of the same magnitude and vary in the same order as the "geometrical" average pore radius based on the relationship 2 × pore vol./surface area.

3. A relationship between the differential thermal curve and the behavior of the adsorbent upon activation is presented, and the conclusions are supported by the experimental data. The relationship also serves to explain tentatively the discontinuity in properties noted between 340 and 400°.

WARREN, PA. RECEIVED FEBRUARY 28, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Stability of Chelate Compounds. IV. Effect of the Metal Ion[1]

BY MELVIN CALVIN AND NORTEN C. MELCHIOR[2]

In the first paper[3] of this series it was shown that there are at least two components of the forces which bind cupric ion in chelate molecules. One component is of the same character as for hydrogen ion; the other is dependent upon the nature of the ion of the organic portion, and is different for cupric ion and for hydrogen ion. This second component was ascribed to homopolar binding of copper, which allowed the resonance in the ion to extend to copper, thus making the stability of the chelate sensitive to changes in the resonance of the ion.

It was therefore of interest to compare the stabilities of chelates formed from a given organic ion and a series of metal ions. The ions cobaltous, nickelous, cupric and zinc were selected for comparison, and the dinegative ion of 5-salicylaldehydesulfonic acid[4] was chosen as the organic portion. This selection gave water soluble chelates, thus eliminating difficulties due to low solubility as well as any question about the interpretation of the readings of the glass electrode.[3] To determine the relative stability of these chelates the titration method of Calvin and Wilson[3] was used, with a modification intended to avoid difficulties which might be caused by the presence of small amounts of impurities.

Experimental

Materials.—Sodium 5-salicylaldehydesulfonate was prepared essentially as described by Blau[4] and recrystallized ten times from water. The metal salts used in titrations were reagent grade nitrates. The sodium hydroxide solution was carbonate-free, carefully standardized. The nitric acid was standardized against the sodium hydroxide solution used.

Titrations.—All titrations were made under purified nitrogen gas in a glass vessel immersed in a thermostat controlled to ±0.01°. The vessel was provided with openings for the electrodes, a stirrer, the buret and the nitrogen gas. Standard sodium hydroxide was added from a buret which could be read to 0.002 ml. *p*H readings were made using a Beckman model "G" *p*H meter equipped with extension electrodes. To eliminate any effect of traces of impurities the following procedure was adopted: 50 ml. of a water solution of sodium 5-salicylaldehydesulfonate (0.2 or 0.02 *M*) was pipetted into the titration vessel, the solution purged with nitrogen, and the electrodes inserted. When the *p*H reading became constant, 5 ml. of 0.01 *M* nitric acid which was 0.002 to 0.005 *M* in the desired metal ion was added by pipet, and the titration begun. The control titrations were carried out using 0.01 *M* nitric acid containing no metal ion. Careful comparison titrations showed exactly the same results with either solution in the absence of a chelating agent up to *p*H 6, whereas all comparisons were made at *p*H's less than 6. Typical titration curves are shown in Fig. 1.

Preparation of Chelate Compounds: Nickelous, Cobaltous, Cupric.—To 30 ml. of a water solution containing 0.02 mole of sodium 5-salicylaldehydesulfonate, 19 ml. of 1.0 *M* sodium hydroxide and 10 ml. of 1.0 *M* metal chloride solutions were added in succession. The solution, protected from air, was heated on the steam-bath for three hours, then allowed to cool overnight. The solid was filtered on a Büchner funnel, washed with two 10-ml. portions of 50% alcohol and dried over fused calcium chloride *in vacuo*.

$(C_7H_4O_5SNa)_2Ni \cdot 2H_2O$, light green. Calcd.: C, 31.1; H, 2.24; H_2O, 6.7. Found[5]: C, 30.5; H, 2.62; residue, 41.3; H_2O,[6] 6.7. $(C_7H_4O_5SNa)_2Co \cdot 2.5H_2O$, light orange. Calcd.: C, 30.6; H, 2.38; H_2O, 8.2. Found: C, 30.7; H, 2.63; residue, 47.4; H_2O, 7.6. $(C_7H_4O_5SNa)_2Cu \cdot 3H_2O$, pea green. Calcd.: C, 29.8; H, 2.50; H_2O, 9.6. Found: C, 29.7; H, 2.64; residue, 43.2; H_2O, 9.6.

Zinc.—The preparation method described above gave only a small amount of solid, but by decreasing the total amount of water slightly (from 59 to 43 ml.) a yellow crystalline solid was obtained which was washed and dried as before. Calcd. for $(C_7H_4O_5SNa)_2Zn$: C, 32.7; H, 1.57. Found: C, 31.8; H, 1.95; residue, 48.3; H_2O, *nil*.

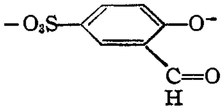
Results

If we write the reaction of chelate formation as two successive reactions

$$\mathrm{Me^{++} + Ke^{=} \rightleftarrows MeKe} \qquad (1)$$

$$\mathrm{MeKe + Ke^{=} \rightleftarrows MeKe_2^{=}} \qquad (2)$$

Me represents the metal being considered and $Ke^{=}$ refers to the ion



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[1] Abstracted from the thesis of N. C. Melchior, submitted in partial fulfillment of the requirements for the Ph.D. degree, at the University of California, Berkeley, California, September, 1946.

[2] Shell Research Fellow in Chemistry, 1945-1946; present address: Northwestern University, Evanston, Illinois.

[3] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[4] F. Blau, *Monatsh.*, **18**, 123 (1897).

[5] Microanalyses by Charles Koch.

[6] H_2O = weight loss at 140°. 0.001 mm.

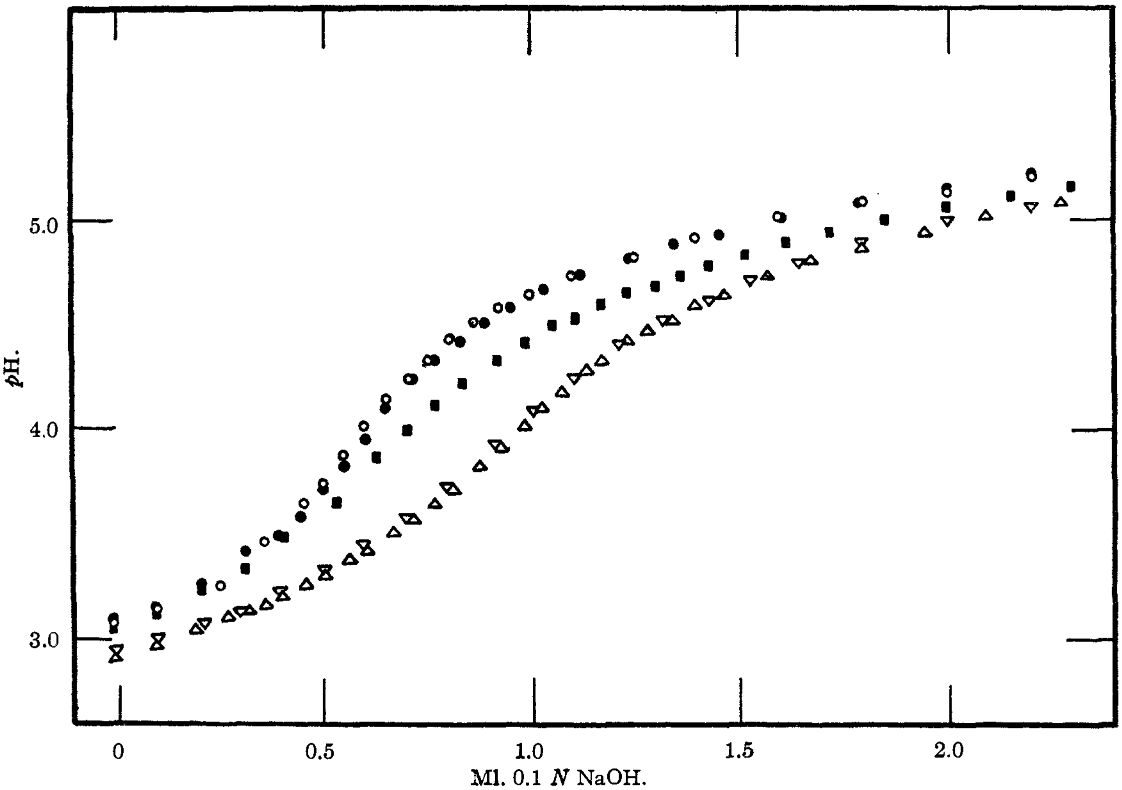

Fig. 1.—Typical titration curves: ○, ●, 0.2 *M* sodium 5-salicylaldehydesulfonate, 0.0009 *M* HNO_3; ■, acid and chelation agent as before, 0.0004 *M* Ni^{++}; △, ▽, acid and chelation agent as before, 0.00045 *M* Cu^{++}.

The sum of reactions (1) and (2) is

$$Me^{++} + 2\ Ke^{=} \rightleftarrows MeKe_2^{=} \qquad (3)$$

We have chosen to express the stability of the chelates in terms of the equilibrium constant for this last reaction

$$K = (MeKe_2^{=})/(Me^{++})\ (Ke^{=})^2 = k_1k_2$$

where k_1 and k_2 are the equilibrium constants for reactions (1) and (2).

Bjerrum[7] has developed a method for the evaluation of the equilibrium constants of reaction of this type (*i.e.*, stepwise successive addition) which involves the quantity $\bar{n}$, the average number of $Ke^{=}$ bound to a Me^{++}. He has shown that at $\bar{n} = 0.5$, $1/(Ke^{=}) \simeq k_1$; at $\bar{n} = 1.5$, $1/(Ke^{=}) \simeq k_2$; and for this simple case (only two steps), at $\bar{n} = 1.0$, $1/(Ke^{=})^2 \simeq K$.

The evaluation of $\bar{n}$ in these experiments was simple. Referring to Fig. 1, at any *p*H, the horizontal distance between the reference curve and the curve determined in the presence of a metal ion measures quite accurately the additional base consumed by the reactions

$$Me^{++} + HKe^- + OH^- \rightleftarrows MeKe + H_2O \qquad (4)$$

$$MeKe + HKe^- + OH^- \rightleftarrows MeKe_2^- + H_2O \qquad (5)$$

or the total number of moles of $Ke^{=}$ bound. This number divided by the total Me^{++} added is n.

At any *p*H the value of $(Ke^{=})$ can be calculated from the known amount of HKe^- present and its dissociation constant, determined in this case from the *p*H of the half titration point of a sample of the substance. If the values of $\bar{n}$ are plotted against log $1/(Ke^{=})$, approximate values for log k, etc., are easily read from the curve. These values are collected in Table I.

TABLE I

FORMATION OF CHELATE IONS OF 5-SALICYLALDEHYDESULFONATE

Ion	Temp., °C.	log k_1[a]	log k_2[b]	log K[c]	log K[d]
Cu^{++}	40	5.64	4.15	9.80	9.79
Cu^{++}	25	5.35	3.92	9.20	9.27
Ni^{++}	25	3.79	2.77	6.54	6.56
Co^{++}	25	3.42	[e]	5.6	[e]
Zn^{++}	25	3.0	[e]	5.4[f]	[e]

K_{HKe^-} (40°) = 3.6×10^{-8}

K_{KHe^-} (25°) = 4.3×10^{-8}

[a] Log $1/(Ke^{=})$ at $\bar{n} = 0.5$. [b] Log $1/(Ke^{=})$ at $\bar{n} = 1.5$. [c] Log $1/(Ke^{=})^2$ at $\bar{n} = 1.0$. [d] Log k_1k_2. [e] Not determined. [f] Maximum value.

From the values determined at 25 and at 40° we calculate for the reaction

$$Cu^{++} + 2\ Ke^{=} = CuKe_2^{=}$$

$$\Delta H \sim +\ 17\ \text{kcal.}$$

$$\Delta S \sim +\ 100\ \text{cal./deg.}$$

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[7] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

Discussion

The order of decreasing stability found for the chelates studied is Cu^{++}, Ni^{++}, Co^{++}, Zn^{++}. To understand this order it is desirable to know the type of binding in the chelate, as well as much as possible about the metal ions. Some of the data available are given in Table II. The only correlation between chelate stability and these data is the parallelism with the second ionization constants of the gaseous atoms. This is illustrated in Fig. 2.

TABLE II

Ion	Radius,[a] Å.	Heat of hydration,[b] kcal.	Partial molal entropy[c]	Ionization potential, volts[c] 1e⁻	2e⁻
Fe^{++}	0.76	468	−25.9	7.83	16.16
Co^{++}	.74	497	....	7.81	17.3
Ni^{++}	.73	507	....	7.61	18.2
Cu^{++}	..	507	−26.5	7.68	20.2
Zn^{++}	.72	491	−25.7	9.36	17.89

[a] Kordes, *Z. physik. Chem.*, **B48**, 91 (1940). [b] Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1938. [c] Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938.

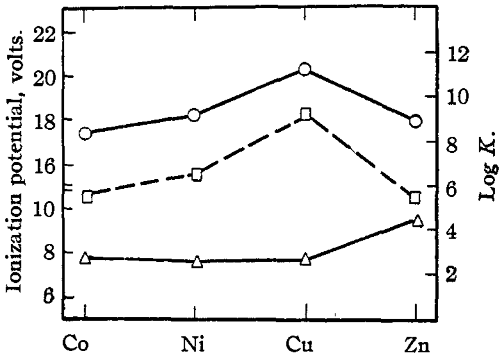

Fig. 2.—△—△, first ionization potential; ○—○, second ionization potential; □—□, log *K*.

With the exception of zinc, the ionization involves the removal of an electron from a d orbital; and one would expect the order Cu > Ni > Co in the energy available to a reaction which replaces this electron. Thus, we are led to the suggestion that a d orbital is somehow involved in the binding of salicylaldehyde and closely related derivatives by Co^{++}, Ni^{++} and Cu^{++}. The magnetic criterion is of no use in the case of Cu^{++} since planar dsp^2 covalent binding with a promoted electron in 4p, tetrahedral sp^3 covalent, and pure ionic binding would all three result in a single unpaired electron. However, the solid chelates of Co^{++} and Ni^{++} with salicylaldehyde, as well as the dihydrate of the nickel chelate, have a magnetism corresponding to three unpaired electrons for the cobalt compound and two for the nickel compounds,[8,9] indicating quite clearly that they cannot be exclusively covalent planar dsp^2 compounds. Since we feel that the correlation with second ionization potentials indicates an involvement of a d orbital, we suggest that the structure of the Co^{++}, Ni^{++}, and Cu^{++} chelates is a planar one and the binding a hybrid between dsp^2 and ionic, involving one promoted electron in 4d in each case. When two of the chelated oxygen atoms are replaced by the much more basic nitrogen atoms as in the corresponding salicylaldimines (methylimines, and ethylenediamines) the tendency for the coördinating electron pairs to enter the d orbitals is enhanced forcing the molecule into the pure dsp^2 planar covalent binding. This has been shown by both magnetic and X-ray measurements.[9] It is also of interest to note that the single related case for which X-ray data are available,[10] namely, bis-(benzoylacetone)-copper, is planar in the solid state.

Entropy of the Reaction.—The large increase in entropy in the formation of the copper chelate was suprising. A portion of this increase is due to the increase in the number of particles. If we write reaction (6) more accurately

$$Cu(H_2O)_6^{++}(aq) + 2\,Ke(H_2O)^-_n(aq) \rightleftarrows CuKe_2(H_2O)^-_m + (6 + 2n - m)H_2O \qquad (7)$$

it is apparent that there is an increase in the number of particles in chelate formation. A somewhat similar case studied in this Laboratory[11] gives the order of magnitude of the entropy change to be expected. For the reaction

$$Ni(NH_3)_6^{++}(aq) + 3\,(CH_2NH_2)_2(aq) \rightleftarrows Ni([CH_2NH_2]_2)_3^{++}(aq) + 6\,NH_3(aq) \quad \Delta S \sim +24\text{cal./deg.}$$

This effect is accentuated in the reaction we are considering since one dipositive ion and two mononegative ions[12] are removed from solution in the formation of a chelate molecule. This causes a large increase in the entropy of the solvent, since the water surrounding an ion is oriented to a degree which depends on the ionic charge and the distance from the charged center, and most, if not all, of this order is lost in chelate formation. Similar results have been reported by Rabinowitch and Stockmayer[13] who found

$$Fe^{+++}(aq) + Cl^-(aq) \rightleftarrows FeCl^{++}(aq) \quad \Delta S \sim +35\ \text{cal./deg.}$$

$$Fe^{+++}(aq) + Br^-(aq) \rightleftarrows FeBr^{++}(aq) \quad \Delta S \sim +23\ \text{cal./deg.}$$

$$Fe^{+++}(aq) + OH^-(aq) \rightleftarrows FeOH^{++}(aq) \quad \Delta S \sim +50\ \text{cal./deg.}$$

Summary

The order of stability in aqueous solution was determined for the chelates formed from 5-salicyl-

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[8] Mellor and Craig, *Proc. Roy. Soc. N. S. Wales*, **75**, 475, 495 (1939).

[9] Calvin and Bakelew, THIS JOURNAL, **68**, 2267 (1946).

[10] Cox and Webster, *J. Chem. Soc.*, 731 (1935).

[11] M. Calvin and R. H. Bailes, THIS JOURNAL, **68**, 949 (1946).

[12] The sulfonate part of the organic residue remains the same in both sides and does not enter into consideration.

[13] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

aldehydesulfonate and zinc, cobaltous, nickelous and cupric ions. The sodium salts of these compounds have been isolated. The entropy of formation of bis-(5-salicylaldehydesulfonate)-copper was determined.

EVANSTON, ILLINOIS RECEIVED JANUARY 7, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Stability of Chelate Compounds. V. The *o*-Formylnaphthoxide Chelates[1]

BY MELVIN CALVIN AND NORTEN C. MELCHIOR[2]

A previous report[3] from this Laboratory showed that the stability of cupric chelates of salicylaldehyde and its derivatives, or of β-diketones, varies, within a given group, inversely as the acid strength of the organic portion. Further, it was shown that the stability of cupric chelates is also related to the degree of "doublebondedness" in the ion of the organic portion, thus indicating a partial extension of the resonance in the negative ion to the cupric ion. A study[4] of the stability of the zinc, cobaltous, nickelous and cupric derivatives of 5-salicylaldehydesulfonate has shown that the stability of these chelates increases in the order given, and this order has been shown to be in accord with this idea.

In order to study these related effects more closely the three possible *o*-formylnaphthols were prepared, and the preparation of their metal derivatives was studied.

Experimental

1-Formyl-2-naphthol.[5]—This compound was prepared as described in "Organic Syntheses." The product was further purified by precipitating the cupric chelate by treatment with cupric acetate in alcoholic solution. The washed chelate was decomposed with a slight excess of 2 *N* sulfuric acid and the naphthol distilled with steam; very light yellow-green needles, m. p. 82.2–82.5 uncor.

3-Formyl-2-naphthol.[6]—Thirty-eight grams of purified 3-acetoxy-2-naphthoyl chloride was placed in a three-necked flask with 200 ml. of C. P. xylene, 6.0 g. of palladium on barium sulfate and 0.6 ml. of quinoline–sulfur poison. The reduction at 150–155° (bath temperature) was 91% complete in two hours, and was stopped after three hours. The catalyst was filtered from the hot solution and the cooled filtrate treated with 600 ml. of 1 *N* sodium hydroxide. A heavy orange precipitate formed immediately. The mixture was heated under reflux until all the solid had dissolved (twenty-five minutes), then indirectly steam distilled until the distillate was clear. The clear, deep red solution was cooled and the orange crystals which separated were isolated and washed with a little ice-water. A second crop was obtained by concentrating the mother liquor. The wet sodium 3-formyl-2-naphthoxide was treated with 200 ml. of water and 15 ml. of acetic acid on the steam-bath and the precipitated solid recrystallized from ethanol–water in bright yellow crystals, m. p. 97–98°; yield 20.6 g., 81%. Boehm and Prafft report 40%.

1-Hydroxy-2-naphthoic Acid.—This acid, prepared by passing carbon dioxide into a suspension of sodium 1-naphthoxide in boiling toluene,[7] was recrystallized from toluene and found to melt at 204–205° (dec.) uncor. Since the highest melting point reported for this compound is 191°,[8] a sample of the acid was titrated potentiometrically. No titratable phenolic group was found. The lower melting points reported are probably due to small amounts of impurities, since the compound decomposes rapidly as low as 180° when in the liquid phase, and thus would appear to give a sharp melting point.

1-Acetoxy-2-naphthoyl Chloride.—Preparation of this compound by usual methods was not satisfactory. A procedure modeled after Fischer[9] was successful. 1-Hydroxy-2-naphthoic acid was acetylated with acetic anhydride in acetic acid, recrystallized from acetic acid and dried *in vacuo*. The dry ester was stirred in an ice-bath with ten times its weight of acetyl chloride and treated with 1.1 equivalents of phosphorus pentachloride in small portions. The mixture was then allowed to warm to room temperature, filtered to remove a small amount of solid, and reduced to one-half volume under vacuum at room temperature. The crystals which formed when the residue was cooled to 0° were filtered off, washed with two small portions of cold petroleum ether and dried *in vacuo*. A second crop was obtained by removing everything volatile at 20° and 1.0 mm. from the mother liquor, dissolving the residue in acetyl chloride at room temperature, and cooling at 0°; yield 86% of white crystals, m. p. 112–113°.

2-Formyl-1-naphthol.—1-Acetoxy-2-naphthoyl chloride was reduced under the same conditions used in the preparation of 3-formyl-2-naphthol above, and the acetoxyaldehyde hydrolyzed as before, substituting 0.5 *N* sodium hydroxide for the 1 *N* base. Since preliminary experiments had shown that 2-formyl-1-naphthol was very easily oxidized, the calculated amount of 6 *N* sulfuric acid was added to the reaction mixture as soon as all the xylene had been removed, and the aldehyde steam distilled. The distillate was stored overnight at 0° and the aldehyde which separated was filtered off and dried over calcium chloride as very light green crystals, m. p. 59–60°; yield based on acetoxyacid chloride, 60%. Weil[10] obtained 27%, based on the hydroxy acid.

***o*-Formylnaphthoxide Chelates.**—Fifty ml. of 95% alcohol containing 1 g. of the desired formylnaphthol was heated to boiling in a round-bottom flask. Ten ml. of 1.2 *M* sodium acetate and 10 ml. of a water solution which was 0.29 *M* in the desired metal ion acetate were added in succession. A rubber stopper fitted with a stopcock was inserted and the system evacuated until the alcohol boiled vigorously. The stopcock was closed and the mixture heated on the steam-bath for from two to ten hours, cooled to room temperature and filtered. The precipitate was washed well with water and dried over calcium chloride *in vacuo*. Analyses and other data are collected in Table I.

Cupric 3-Formyl-2-naphthoxide.—Preparation by the method above gave a red precipitate upon addition of the

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(1) Abstracted from the thesis submitted by N. C. Melchior in partial fulfillment of the requirements for the Ph.D. degree at the University of California, Berkeley, California, September, 1946.

(2) Shell Research Fellow in Chemistry, 1945–1946; present address: Northwestern University, Evanston, Illinois.

(3) M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

(4) M. Calvin and N. C. Melchior, *ibid.*, **70**, 3270 (1948).

(5) "Organic Syntheses," **22**, 63 (1942).

(6) T. Boehm and E. Prafft, *Arch. Pharm.*, **269**, 25 (1931).

(7) "Beilstein," Vol. IV, **10**, p. 331.

(8) R. T. Arnold and J. Sprung, THIS JOURNAL, **60**, 1163–1164 (1938).

(9) E. Fischer, *Ber.*, **38**, 612 (1905).

(10) H. Weil, *ibid.*, **54**, 3217 (1921).