TABLE I

EFFECT OF ACIDITY LEVEL AND MEDIUM ON THE REACTION OF METHIONINE AND BROMOACETIC ACID

These reactions were run simultaneously. The temperature was 25–28°. Bromide ion was determined as follows: to 1 cc. of the reaction mixture add 25 cc. of H_2O, 3 cc. of 7.5 *M* HNO_3 (which has been boiled to remove free nitrogen oxides) and 0.5 cc. of a 1 *M* solution of $FeNH_4(SO_4)_2$ in 0.1 *N* HNO_3. Cool and add 0.1 or 0.2 cc. of 0.05 *N* KSCN, titrate to colorless with 0.05 *N* $AgNO_3$ and complete titration with 0.05 *N* KSCN. The behavior of analogous reaction mixtures in which alanine was substituted for methionine showed that there are no significant blank values under these conditions.

		$HClO_4 \longrightarrow M$	0.44	0.33	0.22	....	....	....
		$CH_3COONa \longrightarrow M$	....	....	....	....	0.10	0.20
Medium: HCOOH								
+ CH_3COOH	6.6 *M*	49 hr., %	48	45	47	41	42	44
+ H_2O	2 *M*	218 hr., %	87	86	84	84	86	88
Methionine	0.20 *M*	385 hr., %	92	92	91	93	95	96
$BrCH_2COOH$	0.40 *M*							
Medium: HCOOH								
+ CH_3COOH	6.0 *M*	44 hr., %	59	57	57	54	57	58
+ H_2O	7 *M*	93 hr., %	78	75	75	74	76	78
Methionine	0.18 *M*	213 hr., %	95	96	96	93	94	96
$BrCH_2COOH$	0.36 *M*	376 hr., %	97	100		98	99	102

for the study of kinetic factors, because no problems of vapor pressure are encountered over a wide range of solvent composition and temperature. Figure 1 shows examples of reactions between methionine and monoiodo- and monobromoacetic acid. The latter seems to be somewhat more reactive than the former. Monochloroacetic acid, on the other hand, is of extremely low reactivity. A solution of 0.08 *M* methionine and 0.16 *M* monochloroacetic acid in water (which favors sulfonium reactions, see below) containing 0.05 *M* perchloric acid showed a half-time of reaction of approximately fifteen hours at 74°. The results shown in Fig. 2 indicate that among different media the sulfonium reaction is increasingly favored in the following order: acetic acid, formic acid, water, *i. e.*, in the order of increasing dielectric constant.[10] The accelerating effect of water is further borne out by the data of Table I. These data also indicate that in the formeous-aceteous media both strong acids and strong bases (sodium acetate) slightly but definitely catalyze sulfonium formation.

A comparison of the reactivities, with allyl bromide, of methionine and N-formylmethionine, is shown in Fig. 3. Interference of the positive nitrogen charge (HOOC—$CH(NH_3^+)—CH_2—CH_2—S—CH_3$) with the establishment of the positive sulfur charge could explain the slower reaction of the free amino acid.

Summary

A number of alkyl sulfonium salts derived from methionine and N-acyl-substituted methionine have been isolated and certain factors governing their formation have been studied.

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(10) *Cf.* Bost and Everett, THIS JOURNAL, **62**, 1752 (1940).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR, BERKELEY, CALIFORNIA]

Heats of Formation of $NH_4Al(SO_4)_2 \cdot 12H_2O$ and $NH_4Al(SO_4)_2$[1]

BY FRANK E. YOUNG[2]

Several recent thermochemical investigations at the Pacific Experiment Station of the Bureau of Mines have dealt with aluminum compounds of current metallurgical interest. Previous papers by the author described new determinations of the heats of formation of two hydrates of aluminum nitrate,[3] anhydrous and hexahydrated aluminum sulfate, and anhydrous and dodecahydrated potassium aluminum sulfate.[4] Other papers reported low-temperature specific heats, entropies, and high-temperature heat contents of some of these and related compounds.[5] The present paper, a continuation of this work, presents new determinations of the heats of formation of nearly anhydrous (1.80% water) and dodecahydrated ammonium aluminum sulfate and gives an estimate for the completely dehydrated compound.

Materials and Method

J. T. Baker analyzed ammonium sulfate containing 0.02% impurities was dried at 62° and stored over Dehydrite until used. The average of four sulfate analyses[6] indicated 99.96% purity.

Mallinckrodt "Analytical Reagent" ammonium aluminum sulfate dodecahydrate was used without drying or other treatment. Analyses for alumina showed 99.78% purity. Correction was made in the thermal results for the 0.20% alkali sulfate found to be present.

"Anhydrous" ammonium aluminum sulfate[7] was pre-

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(2) Chemist, Pacific Experiment Station, Bureau of Mines.

(3) Young, THIS JOURNAL, **66**, 777 (1944).

(4) Young, *ibid.*, **67**, 257 (1945).

(5) (a) Moore and Kelley, *ibid.*, **64**, 2949 (1942); (b) Shomate and Kelley, *ibid.*, **66**, 1490 (1944); (c) Shomate and Naylor, *ibid.*, **67**, 72 (1945); (d) Shomate, *ibid.*, **67**, 765 (1945).

(6) These analyses were made by E. H. Huffman, formerly metallurgist, Pacific Experiment Station, Bureau of Mines.

(7) This material was prepared and analyzed by A. E. Salo, metallurgist, Pacific Experiment Station, Bureau of Mines.

pared by heating ammonium aluminum sulfate dodecahydrate at 80° for seventy-two hours after which the temperature was raised to 210° during seventeen hours. The material was maintained at 210° for sixty-nine hours, of which the last forty-eight hours were under vacuum. The product was found by analysis to correspond to 95.94% $NH_4Al(SO_4)_2$, 1.87% $Al_2(SO_4)_3$, 0.39% alkali sulfate, and 1.80% water. Aluminum was determined by the 8-hydroxyquinoline method, ammonia by distillation into standard acid, and sulfate by direct weighing after removal of aluminum and ignition to expel ammonium sulfate. Aluminum oxide as such was absent. The water content was obtained by difference. Corrections were made in the thermal results for these impurities. (Further dehydration of this sample was found to be impractical as the ammonium sulfate content decreased, by decomposition, much more rapidly than water was removed.)

The heat of formation of ammonium aluminum sulfate dodecahydrate was obtained by measuring heats of solution in $HCl \cdot 12.68H_2O$ (4 N) prepared by dilution of reagent-quality hydrochloric acid and standardization against sodium carbonate.

To obtain the heat of formation of "anhydrous" ammonium aluminum sulfate it was necessary to measure heats of solution in $KOH \cdot 277.3H_2O$ (0.2 N) because of the low rate of solution of this substance in acid. The potassium hydroxide solution was prepared from reagent-grade material and standardized against sulfuric acid which, in turn, had been standardized against sodium carbonate.

The calorimetric measurements were made in apparatus described by Southard[8] and later by Young.[4] The results are expressed in defined calories (1 cal. = 4.1833 int. joules).[9] All formula weights are in accordance with the 1941 International Atomic Weights. Corrections of weights to vacuum were made using the following densities: ammonium sulfate, 1.77; ammonium aluminum sulfate dodecahydrate, 1.64; and anhydrous ammonium aluminum sulfate, 2.32.

Measurements and Results

The reactions by which the heats of formation of ammonium aluminum sulfate dodecahydrate and ammonium aluminum sulfate containing 1.80% water were obtained are shown in Tables I and II, respectively. These heats of formation were derived using only data obtained by the author, without recourse to the literature. The uncertainties in the last columns are twice the standard deviations of the means of the experimental results.[10] Final values of the heats of formation and corresponding uncertainties have been rounded to the nearest ten calories. It was not necessary to correct the measurements to 25° as the final temperatures were always within a few hundredths degree of this value.

The average sample weights, ammonium sulfate, 1.3214 g., and ammonium aluminum sulfate dodecahydrate, 9.0846 g., correspond to a final concentration of $NH_4Al(SO_4)_2 \cdot 361.6HCl \cdot 4{,}585H_2O$, after making necessary minor corrections. In the measurements in basic solution, the average sample weights, ammonium sulfate, 0.3304 g., and ammonium aluminum sulfate, 1.2358 g., correspond to a final concentration of $NH_4OH \cdot KAlO_2 \cdot 2K_2SO_4 \cdot 67.20KOH \cdot 20{,}024H_2O$.

The temperature changes during solution ranged from 0.70 mμ (0.00060°) for solution of ammonium sulfate in potassium hydroxide to 291.20 mμ (0.24889°) for solution of ammonium aluminum sulfate dodecahydrate in hydrochloric acid. The average time of solution was two minutes for ammonium sulfate and fifteen minutes for anhydrous and hydrated ammonium aluminum sulfate.

Ammonium Aluminum Sulfate Dodecahydrate.—Table I gives the skeleton equations for the reactions measured to obtain the heat of formation of ammonium aluminum sulfate dodecahydrate.

TABLE I

HEAT OF FORMATION OF $NH_4Al(SO_4)_2 \cdot 12H_2O$ (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(1) $Al + 3/2H_2SO_4$ (aq., $26.37H_2O$) + $3H_2O \longrightarrow 1/2Al_2(SO_4)_3 \cdot 6H_2O(c) + 3/2H_2(g)$	−112,292	65
(2) $1/2Al_2(SO_4)_3 \cdot 6H_2O(c) \longrightarrow Al^{+++} + 3/2SO_4^= + 3H_2O$	− 11,542	16
(3) $1/2(NH_4)_2SO_4(c) \longrightarrow NH_4^+ + 1/2SO_4^=$	+ 3,075	5
(4) $NH_4Al(SO_4)_2 \cdot 12H_2O(c) \longrightarrow NH_4^+ + Al^{+++} + 2SO_4^= + 12H_2O$	+ 21,076	19
(5) $Al + 3/2H_2SO_4$ (aq., $26.37H_2O$) + $1/2(NH_4)_2SO_4(c) + 12H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O(c) + 3/2H_2(g)$	−141,840	70

$$\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$$

Reactions (1) and (2) were discussed in a previous paper[4] as reactions (28) and (3), respectively.

Six measurements were made of the molal heat of solution of ammonium sulfate in the final solution of reaction (2) ($1/2Al_2(SO_4)_3 \cdot 361.6HCl \cdot 4{,}585H_2O$), giving +6,150 ± 9 cal. as the mean of +6,159, 6,139, 6,155, 6,163, 6,140, and 6,142. One-half this value, +3,075 ± 5 cal., is taken for ΔH_3.

The value for ΔH_4, +21,076 ± 19 cal. per mole, is the mean of eight measurements of the heat of solution of ammonium aluminum sulfate dodecahydrate in $HCl \cdot 12.68H_2O$. These eight results, which include a directly determined correction of +911 ± 5 cal. for the heat of solution of water of hydration ($\Delta H = -911 \pm 5$), are +21,093, 21,082, 21,038, 21,095, 21,033, 21,081, 21,082, and 21,100 cal. per mole.

The heat of formation of ammonium aluminum sulfate dodecahydrate from aluminum, sulfuric acid (aq., $26.37H_2O$), ammonium sulfate, and water, ΔH_5, is −141,840 ± 70 cal. per mole.

"Anhydrous" Ammonium Aluminum Sulfate.—Because of the difficulty in dehydrating this compound and the uncertainties mentioned below under equation (9), the reactions listed in Table II apply to the heat of formation of ammonium aluminum sulfate containing 1.80% (0.2469 mole) water. A value for the heat of

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[8] Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

[9] Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

[10] Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

formation of the completely dehydrated compound will be estimated from this result.

TABLE II

HEAT OF FORMATION OF $NH_4Al(SO_4)_2 \cdot 0.2469H_2O$ (CAL. PER MOLE)

	Reaction	$\Delta H_{298.16}$	Uncertainty
(6)	$Al + 3/2H_2SO_4$ (aq., $26.37H_2O$) + $3H_2O \longrightarrow 1/2Al_2(SO_4)_3 \cdot 6H_2O(c) + 3/2H_2(g)$	−112,292	65
(7)	$1/2Al_2(SO_4)_3 \cdot 6H_2O(c) + 4OH^- \longrightarrow AlO_2^- + 3/2SO_4^= + 5H_2O$	− 32,808	26
(8)	$1/2(NH_4)_2SO_4(c) + OH^- \longrightarrow NH_4OH + {}^1/_2SO_4^=$	− 227	3
(9)	$NH_4Al(SO_4)_2 \cdot 0.2469H_2O + 5OH^- \longrightarrow NH_4OH + AlO_2^- + 2SO_4^= + 2.2469H_2O$	− 40,522	22
(10)	$Al + 3/2H_2SO_4$ (aq., $26.37H_2O$) + $1/2(NH_4)_2SO_4(c) + 0.2469H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 0.2469H_2O(c) + 3/2H_2(g)$	−104,810	70

$$\Delta H_{10} = \Delta H_6 + \Delta H_7 + \Delta H_8 - \Delta H_9$$

Values of reactions (6) and (7) were listed in a previous paper[4] as reactions (28) and (10), respectively.

Six measurements were made of the molal heat of solution of ammonium sulfate to obtain −454 ± 6 cal. per mole as the mean of −446, −451, −457, −458, −466, and −446 cal. One-half this value or −227 ± 3 cal. is used for ΔH_8.

To estimate the heat of solution of completely dehydrated ammonium aluminum sulfate, heat of solution measurements were made on samples containing 1.89% and 2.11% water in addition to the original material (1.80% water). These samples were prepared by adding weighed amounts of water as small droplets on the walls of flasks containing portions of the original material. The flasks were evacuated quickly and heated at 80° for twenty hours to allow uniform hydration. It was found necessary to stabilize the original material at 80° for twenty hours to obtain consistent results.

Three measurements were made of the heat of solution of the stabilized original material in $KOH \cdot 277.3H_2O$, giving −40,541, −40,503, and −40,454 cal., with a mean of −40,499 ± 36 cal. per mole. Two measurements of the material containing 1.89% water resulted in −40,483 ± 24 cal. per mole as the mean of −40,506 and −40,459. Four values were obtained for the sample containing 2.11% water: −40,304, −40,274, −40,316, and −40,311, with a mean of −40,302 ± 19 cal. per mole. All these results include a +671 cal. correction for impurities.

The mean heats of solution of these three samples lie on a straight line when plotted against water content. This line may be extrapolated to zero water content to obtain ΔH_{9A} = −41,840 for the reaction

(9A) $NH_4Al(SO_4)_2(c) + 5OH^- \longrightarrow NH_4OH + AlO_2^- + 2SO_4^=$

Such extrapolation is subject to several uncertainties attributable to the length of the extrapolation, possibility of error in the water content of the original material, and possibility of a change in slope at low water contents, as was noted for nearly anhydrous potassium aluminum sulfate.[4] Because of this, the heat of formation in Table II has been computed for the compound containing 1.80% water, and thus it is based entirely on actual measurements. The value of ΔH_9 is the mean of measurements of all three samples after correcting to 1.80% water by means of the curve for heat of solution against water content. The corrected values for the sample with 1.89% water are −40,570 and −40,523 cal. per mole; those for the sample with 2.11% water become −40,530, −40,500, −40,542, and −40,537 cal. per mole. The mean of these six results and the three already listed for the sample with 1.80% water, −40,522 ± 22 cal. per mole, is used for ΔH_9.

The heat of formation of ammonium aluminum sulfate containing 0.2469 mole of water from aluminum, sulfuric acid (aq. $26.37H_2O$), ammonium sulfate, and water, ΔH_{10}, is −104,810 ± 70 cal. per mole.

Substituting the estimated heat of solution of the anhydrous compound, ΔH_{9A} for ΔH_9, in Table II yields an estimate of the heat of formation of the completely dehydrated material.

(10A) $Al + 3/2H_2SO_4(aq., 26.37H_2O) + 1/2(NH_4)_2SO_4(c) \longrightarrow NH_4Al(SO_4)_2(c) + 3/2H_2(g)$

ΔH_{10A} = −103,490 cal. per mole (estimated).

Discussion

The results of the present work may be used to obtain heats of several additional reactions without recourse to values in the literature. These reactions, their heats, and method of calculation are given below. No uncertainties have been assigned to the heats of reactions (12) and (16), as they involve the estimate discussed above.

(11) $NH_4Al(SO_4)_2 \cdot 0.2469H_2O(c) + 11.7531H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O(c)$

$\Delta H_{11} = \Delta H_5 - \Delta H_{10}$ = −37,030 ± 100 cal. per mole

(12) $NH_4Al(SO_4)_2(c) + 12H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O(c)$

$\Delta H_{12} = \Delta H_5 - \Delta H_{10A}$ = −38,350 cal. per mole

(13) $1/2Al_2(SO_4)_3 \cdot 6H_2O(c) + 1/2(NH_4)_2SO_4(c) + 9H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O(c)$

$\Delta H_{13} = \Delta H_2 + \Delta H_3 - \Delta H_4$ = −29,540 ± 25 cal. per mole

(14) $1/2Al_2(SO_4)_3(c) + 1/2(NH_4)_2SO_4(c) + 12H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O(c)$

$\Delta H_{14} = \Delta H_{13} + 1/2\,\Delta H_{29}$ (ref. 4) = −48,170 ± 110 cal. per mole

(15) $1/2Al_2(SO_4)_3(c) + 1/2(NH_4)_2SO_4(c) + 0.2469H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 0.2469H_2O(c)$

$\Delta H_{15} = 1/2\,\Delta H_{11}$ (ref. 4) $+ \Delta H_8 - \Delta H_9$ = −11,140 ± 110 cal. per mole

(16) $1/2Al_2(SO_4)_3(c) + 1/2(NH_4)_2SO_4(c) \longrightarrow NH_4Al(SO_4)_2(c)$

$\Delta H_{16} = 1/2\,\Delta H_{11}$ (ref. 4) $+ \Delta H_8 - \Delta H_{9A}$ = −9,820 cal. per mole

Heats of Formation from the Elements

The heats of formation of anhydrous and dodecahydrated ammonium aluminum sulfate from the elements may be calculated using equations (5), (10), and (10A) in conjunction with values from other sources for the heats of formation of ammonium sulfate, sulfuric acid, and water. The method of calculation is illustrated in Table III for the dodecahydrate.

TABLE III

HEAT OF FORMATION OF $NH_4Al(SO_4)_2 \cdot 12H_2O$ FROM THE ELEMENTS (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(17) $Al + 3/2H_2SO_4$ (aq., $26.37H_2O$) $+ 1/2(NH_4)_2SO_4(c) + 12H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O(c) + 3/2H_2$	− 141,840	70
(18) $3/2H_2 + 3/2S + 3O_2 \longrightarrow 3/2H_2SO_4$ (aq., $26.37H_2O$)	− 316,830	115
(19) $1/2N_2 + 2H_2 + 1/2S + O_2 \longrightarrow 1/2(NH_4)_2SO_4(c)$	− 140,870	240
(20) $12H_2 + 6O_2 \longrightarrow 12H_2O$	− 819,816	120
(21) $Al + 1/2N_2 + 2S + 14H_2 + 10O_2 \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O(c)$	−1,419,360	300

$$\Delta H_{21} = \Delta H_{17} + \Delta H_{18} + \Delta H_{19} + \Delta H_{20}$$

Reaction (17) was discussed above as equation (5).

The value for equation (18) is derived from the heat of formation of sulfuric acid reported by Roth, Grau and Meichsner[11] and the dilution data of Becker and Roth,[12] as shown in a previous paper.[4]

The heat of formation of ammonium sulfate at 25°, equation (19), is calculated from the heat of formation of ammonia given by Becker and Roth[13] (−11,050 cal. per mole), the heat of neutralization of sulfuric acid by ammonia gas given by Roth and Zeumer[14] (−65,440 cal. per mole of ammonium sulfate), and the heat of formation of sulfuric acid (−194,150 cal. per mole) determined by Roth, Grau and Meichsner.[11]

Twelve times the heat of formation of liquid water given by Rossini[15] (−68,318 cal. per mole) or −819,816 ± 120 cal. is used as ΔH_{20}.

The heat of formation of ammonium aluminum sulfate dodecahydrate from the elements, $\Delta H_{21} = \Delta H_{17} + \Delta H_{18} + \Delta H_{19} + \Delta H_{20}$, is −1,419,360 ± 300 cal. per mole.

The heat of formation, ΔH_{22}, of ammonium aluminum sulfate containing 1.80% (0.2469 mole) water from the elements (and liquid water) may be calculated in the manner of Table III from the sum of ΔH_{10}, ΔH_{18} and ΔH_{19}.

$$(22)\quad Al + 1/2N_2 + 2S + 2H_2 + 4O_2 + 0.2469H_2O \longrightarrow NH_4Al(SO_4)_2 \cdot 0.2469H_2O(c)$$

$$\Delta H_{22} = \Delta H_{10} + \Delta H_{18} + \Delta H_{19} = -562{,}510 \pm 280 \text{ cal. per mole}$$

The heat of formation of completely dehydrated ammonium aluminum sulfate is obtained similarly by substituting ΔH_{10A} for ΔH_{10}

$$(23)\quad Al + 1/2N_2 + 2S + 2H_2 + 4O_2 \longrightarrow NH_4Al(SO_4)_2(c)$$

$$\Delta H_{23} = \Delta H_{10A} + \Delta H_{18} + \Delta H_{19} = -561{,}190 \text{ cal. per mole}$$

Because of the estimated nature of ΔH_{23}, an uncertainty is not assigned.

Bichowsky and Rossini[16] give −1,417,600 and −531,000 cal. per mole, respectively, as the heats of formation from the elements of dodecahydrated and anhydrous ammonium aluminum sulfate. These results are based on Favre and Silbermann's[17] measurement of the heat of solution of the dodecahydrate and questionable dissociation pressure data of Ephraim and Wagner.[18] Comparison with corresponding results of this paper, −1,419,360 and −561,190 cal. per mole, respectively, illustrates the need for redetermination of thermochemical data antedating modern methods.

Summary

Measurements were made of the heats of solution of ammonium sulfate and ammonium aluminum sulfate dodecahydrate in $HCl \cdot 12.68H_2O$ and of ammonium sulfate and ammonium aluminum sulfate containing 1.80, 1.89, and 2.11% water in $KOH \cdot 277.3H_2O$.

Several heat-of-reaction values involving only data of the author were computed.

Heats of formation from the elements of ammonium aluminum sulfate dodecahydrate and ammonium aluminum sulfate containing 1.80% water were computed from data of this paper and literature values for ammonium sulfate, sulfuric acid; and water.

Heats of solution and formation were estimated for completely dehydrated ammonium aluminum sulfate.

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[12] Becker and Roth, *Z. physik. Chem.*, **A169**, 287 (1934).

[13] Becker and Roth, *Z. Elektrochem.*, **40**, 841 (1934).

[14] Roth and Zeumer, *Z. angew. Chem.*, **44**, 559 (1931).

[15] Rossini, *Bur. Stands. J. Research*, **22**, 407 (1939).

[16] Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[17] Favre and Silbermann, *Ann. chim. phys.*, [3] **37**, 406 (1853).

[18] Ephraim and Wagner, *Ber.*, **50**, 1088 (1917).