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Heats of Solution and Formation of Oxalic Acid and Some Alkali Metal Oxalates

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By Mary H. Brown and Arthur R. Taylor, Jr.

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BUREAU OF MINES

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CONTENTS

TABLES

HEATS OF SOLUTION AND FORMATION OF OXALIC ACID AND SOME ALKALI METAL OXALATES

by

Mary H. Brown[1] and Arthur R. Taylor, Jr.[2]

ABSTRACT

The heats of formation of oxalic acid and sodium, potassium oxalates, and lithium oxalates were related by solution calorimetry to the heat of formation of $(COOH)_2 \cdot 2H_2O$, a value believed to be reliable as reported in the literature. The following heats of formation were determined: $(COOH)_2(\alpha)$, -198.1±0.1; $(COOH)_2(\beta)$, -197.8±0.1; $Li_2C_2O_4$, -328.7±0.4; $Na_2C_2O_4$, -316.2±0.1; $K_2C_2O_4$, -321.9±0.2; and $K_2C_2O_4 \cdot H_2O$, -393.5±0.2 kcal/mole. The heat of the crystalline transformation $(COOH)_2(\alpha) \rightarrow (COOH)_2(\beta)$ was determined to be 0.30±0.02 kcal/mole at 298.15° K.

INTRODUCTION

The Bureau of Mines is conducting a series of studies to determine accurate thermodynamic properties of compounds of metallurgical interest. Although oxalic acid and its salts are well known to chemists and metallurgists, accurate values for the thermochemical properties of these compounds are lacking. Various investigators (12, 16-18, 22-23, 25)[3] have reported values for the heat of formation of oxalic acid ranging from 196 to 205 kcal/mole. Even though anhydrous oxalic acid is known to exist in two crystalline modifications, only Wilhoit and Shiao (25), the most recent investigators, made any attempt to ascertain the crystalline form of their samples. The method of sample preparation and the refractive indices reported by Wilhoit and Shiao indicate that they measured the enthalpy of combustion of alpha (α) oxalic acid. Their results, however, are based on sample weights rather than the amount of carbon dioxide liberated during combustion; hence, a small amount of moisture in the sample (anhydrous oxalic acid is very hygroscopic) could have caused their reported values for the heat of formation to be excessively negative.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

From vapor pressure measurements, Bradley and Cotson (6) determined an average value over the temperature range of 37° to 52° C for the heat of transformation of alpha to beta oxalic acid to be 1.17 kcal/mole. Their measurement indicates that a significant error could be present in the reported heat of formation values if the sample crystallinity was not properly identified. This Bureau of Mines investigation, however, has established the heat of the transformation to be only 0.3 kcal/mole, indicating that improper crystal identification would cause a relatively small error in the heat of formation value for oxalic acid.

To obtain a reliable value upon which to base a determination of the heat of formation of oxalic acid, the work of Becker and Roth (2) on the heat of combustion of oxalic acid dihydrate was selected. Combustion data of the dihydrate were considered more accurate than the value for the anhydrous compound because the dihydrate exists in only one crystalline form and can be handled and stored with only moderate care to avoid decomposition or absorption of moisture. From the heat of combustion reported by Becker and Roth, the heat of formation of oxalic acid dihydrate was calculated to be -341.0±0.1 kcal/mole, and this value was used as the fundamental quantity for calculating the enthalpies of formation of the other oxalates in this report.

APPARATUS AND PROCEDURE

Enthalpies of solution at 298° K were measured in an isothermal solution calorimeter described in detail elsewhere (10). Essentially, the calorimeter consisted of a glass dewar with a volume of about 750 ml. The thermal leak modulus averaged about 0.002 per minute, and the heat capacity was approximately 725 cal/deg when full of solvent. During a run, the dewar was immersed in a 40-gallon thermostatically controlled water bath. The temperature of the water bath would remain constant at any setting between 20° and 30° C to within ±0.001° C during a typical 3-hour run.

A stainless steel insert, holding the temperature measuring thermistors, the sample breaking mechanism, the stirrer assembly, and the calibration heater, was attached to the stopper used to seal the reaction dewar. The temperature measuring device consisted of two 1,000-ohm probe-type thermistors connected in opposite arms of a Wheatstone bridge circuit. A potentiometer was used to oppose part of the bridge output; the remainder was fed through a dc amplifier to a recorder. Temperature changes of about $1° \times 10^{-5}$ K could be detected above the noise level of the circuit. The calibration heater was a 100-ohm calibrated coil of manganin wire wound around the calorimeter insert. Before and after each sample dissolution, the energy equivalent of the calorimeter was determined by passing a current from lead storage cells through the calibration heater.

Samples for the solution runs were weighed to 10^{-4} g, and solvent was weighed to 10^{-2} g. All weights were corrected to vacuum, 1961 atomic weights were used (14), and the heats of solution were expressed in defined calories (1 cal = 4.184 joules).

MATERIALS

Primary standard and reagent-grade oxalic acid dihydrate were used interchangeably, without purification, both for solution studies and for preparation of the anhydrous oxalic acid. Analyses of both grades of dihydrate were identical within experimental error. Titration with standardized sodium hydroxide and potassium permanganate gave the theoretical percentages for hydrogen ion and oxalate ion. Titration with Karl Fisher reagent gave the theoretical water content, and the X-ray powder pattern agreed with that given in the ASTM File (1).

The beta form of anhydrous oxalic acid was prepared by vacuum sublimation in an apparatus similar to that described by Mallory (11). A charge (approximately 12 g of partially dehydrated oxalic acid dihydrate) was sublimed at 105° C over a period of about 3 days.

The indices of refraction were checked with a polarizing microscope and compared with published data on β oxalic acid (26). X-ray analysis yielded "d" values that agreed with those reported by Gérard and coworkers (9). A mineral oil suspension was used for the X-ray analysis because the fine grinding necessary to fill the 0.7-mm quartz capillaries appeared to trigger the conversion of the crystals into the alpha form. Microscopic examination and X-ray spectra of samples ground in the dry box without using oil showed almost complete reversion of beta to alpha after a few days. The same type of chemical analyses used for the dihydrate yielded theoretical results for hydrogen ion and oxalate ion for the beta crystals.

Samples of alpha oxalic acid were prepared by recrystallization of the freshly sublimed beta form from anhydrous ethyl ether and from anhydrous acetone. Alpha crystals were also obtained from a concentrated solution of oxalic acid dihydrate in acetic acid and water by evaporation at 50° C. All three procedures gave some samples of alpha oxalic acid which were identical according to heat of solution results and X-ray and chemical analysis. The ethyl ether recrystallization appeared to be the least reliable preparation procedure, producing alpha, beta, and mixtures of these depending upon minor variations of procedure. The acetic acid-water procedure was used by Strassburger and Torgesen (19) at the Bureau of Standards to prepare single crystals; however, some difficulty was experienced with sublimation of the oxalic acid from the solution and in removing the acetic acid from the pure crystals. The method described by Bradley and Cotson (6) for obtaining alpha crystals from acetone was found to be the easiest and most reliable procedure. Slow removal of the acetone by magnesium perchlorate usually produced well-formed crystals; however, if the acetone was allowed to remain too long, a yellow compound, phorone, was formed by an aldol condensation of the acetone (21). Rapid evaporation of the acetone by a vacuum produced a fluffy amorphous material which gave erratic heats of solution. Samples of alpha and beta oxalic acid were examined by infrared spectroscopy, and the spectra were found to agree with the spectra reported by Bellamy and Pace (3).

Primary standard sodium chloride, potassium chloride, and sodium oxalate, and reagent-grade lithium chloride, lithium oxalate, and potassium oxalate monohydrate were used without additional purification. From spectrographic and chemical analyses, the lithium chloride was estimated to be 99.52 percent LiCl, 0.33 percent $CaCl_2$, 0.14 percent NaCl, and 0.01 percent KCl; the lithium oxalate was estimated to be 99.69 percent $Li_2C_2O_4$, 0.26 percent CaC_2O_4, 0.04 percent $Na_2C_2O_4$, and 0.01 percent $K_2C_2O_4$. Spectrographic and chemical analyses indicated that the impurities in the other compounds were less than 0.01 percent. X-ray powder patterns for all of these compounds agreed with the data reported in the ASTM File (1).

Anhydrous potassium oxalate was obtained by dehydrating the monohydrate at temperatures between 100° and 150° C. Weight loss at these temperatures was equal to the theoretical loss expected for the dehydration of the monohydrate, and oxalate ion determinations were within experimental error of the theoretical values for anhydrous potassium oxalate. The X-ray powder pattern determined for these samples, however, differed significantly from the pattern given in the ASTM File (card 14-757) (1) for anhydrous potassium oxalate. Potassium carbonate, an expected decomposition product of potassium oxalate, was not detected in the powder patterns. The pattern reported on the ASTM card for the anhydrous material was very similar to that reported for the monohydrate, indicating that the sample used for the ASTM data was contaminated with monohydrate. This conclusion was further strengthened by examination of patterns for samples of the anhydrous potassium oxalate which were handled without precaution to prevent moisture absorption from the air. The "d" values obtained for the anhydrous potassium oxalate are reported in table 1.

TABLE 1. - X-ray data for anhydrous potassium oxalate[1]

"d" values	Intensity	"d" values	Intensity	"d" values	Intensity
4.15	Weak	2.141	Weak	1.564	Weak
4.07	Medium	2.108	Weak	1.509	Weak
3.75	Weak	2.036	Weak	1.486	Weak
3.453	Weak	2.004	Weak	1.474	Weak
3.126	Medium	1.933	Weak	1.457	Weak
3.063	Weak	1.910	Medium	1.415	Weak
2.950	Strong	1.821	Weak	1.399	Weak
2.889	Very strong	1.776	Weak	1.385	Weak
2.730	Strong	1.743	Weak	1.279	Weak
2.671	Medium	1.722	Medium	1.177	Weak
2.629	Strong	1.670	Weak	1.160	Weak
2.491	Strong	1.634	Weak	1.135	Weak
2.312	Very strong	1.610	Weak	1.122	Weak
2.238	Strong	1.579	Medium		

[1] The anhydrous potassium oxalate was obtained by dehydrating potassium oxalate monohydrate at 100° C. It was ground in petroleum jelly to protect it from moisture while in the diffractometer sample holder.

RESULTS AND DISCUSSION

Oxalic Acid

Table 2 presents the reactions for the heats of solution of oxalic acid and its hydrate, together with the reactions which represent the heat of hydration and enthalpy of formation of each anhydrous form and the heat of transition from the beta form to the more stable alpha form. Reaction 1 represents the average heat of solution of 16 samples of alpha oxalic acid weighing from 2.1 to 4.6 g in 763.4 g of water. Reaction 2 represents the average heat of solution of 13 samples of beta oxalic acid weighing from 2.1 to 3.1 g in 763.4 g of water. Reaction 3 represents the average heat of solution of seven samples of oxalic acid dihydrate weighing from 4.2 to 5.0 g in 763.38 g of water. The large number of anhydrous samples were run to check various preparation procedures for the different crystal modifications. All of the heats of solution measured were independent of sample size. The difference between the heats of reactions 1 and 3 is the heat of hydration of alpha oxalic acid, -6.245 kcal/mole, as shown by reaction 4. The difference between the heats of reactions 2 and 3 is the heat of hydration of beta oxalic acid, -6.544 kcal/mole, as shown by reaction 5. Using data from table 3 and the heat of reaction 4, the heat of formation of alpha oxalic acid was calculated to be -198.1±0.1 kcal/mole as shown by reaction 6. Using reaction 5 and data from table 3, the heat of formation of beta oxalic acid was calculated to be -197.8±0.1 kcal/mole, as shown in reaction 7. The difference between the heats of reactions 1 and 2 is the heat of the transition from the beta form to the alpha form, -0.30±0.02 kcal/mole, as shown in reaction 8.

TABLE 2. - Reactions concerning oxalic acid

Reaction			$\Delta H_{298.15}$, cal
(1) $(COOH)_2$ (α) + 1284 H_2O (ℓ)	→	$(COOH)_2 \cdot 1284\ H_2O$	2,438±12
(2) $(COOH)_2$ (β) + 1284 H_2O (ℓ)	→	$(COOH)_2 \cdot 1284\ H_2O$	2,139±18
(3) $(COOH)_2 \cdot 2\ H_2O$ (c) + 1282 H_2O (ℓ)	→	$(COOH)_2 \cdot 1284\ H_2O$	8,683±14
(4) $(COOH)_2$ (α) + 2 H_2O (ℓ)	→	$(COOH)_2 \cdot 2\ H_2O$ (c)	-6,245±19[a]
(5) $(COOH)_2$ (β) + 2 H_2O (ℓ)	→	$(COOH)_2 \cdot 2\ H_2O$ (c)	-6,544±23[b]
(6) 2 C (graphite) + H_2 (g) + O_2 (g)	→	$(COOH)_2$ (α)	-198,125±110
(7) 2 C (graphite) + H_2 (g) + O_2 (g)	→	$(COOH)_2$ (β)	-197,826±112
(8) $(COOH)_2$ (β)	→	$(COOH)_2$ (α)	-299±22[c]

[a] $\Delta H_4 = \Delta H_1 - \Delta H_3$.
[b] $\Delta H_5 = \Delta H_2 - \Delta H_3$.
[c] $\Delta H_8 = \Delta H_2 - \Delta H_1$.

This heat of transition of beta to alpha is only about one-fourth that obtained from Bradley and Cotson's (6) vapor pressure studies and indicates very little energy difference between the two crystalline forms of anhydrous oxalic acid. This conclusion is further confirmed by phenomena such as either alpha or beta crystals being deposited from ethyl ether solutions during attempts at sample preparation.

TABLE 3. - Selected heat of formation values used in calculations

Compound	ΔHf, kcal/mole	Reference
$(COOH)_2 \cdot 2\ H_2O$ (c)	-341.0 ±0.1	(2)
H_2O (ℓ)	-68.315± .020	(24)
$HCl \cdot 27.75\ H_2O$ (ℓ)	-39.321± .020	(24)
LiCl (c)	-97.58 ± .27	(8)
NaCl (c)	-98.26 ± .08	(8)
KCl (c)	-104.37 ± .06	(8)

Becker and Roth (2) also measured the heat of solution of oxalic acid dihydrate and anhydrous oxalic acid, but they made no mention of the crystalline form of their anhydrous sample. They obtained values of 8.62±0.1 kcal/mole for the dihydrate and 2.03±0.01 kcal/mole for their anhydrous sample at 20.5° C in a final concentration of 2,100 moles of water per mole of oxalic acid. From these data, they calculated the heat of hydration of their anhydrous oxalic acid to be -6.59 kcal/mole, which compares favorably with -6.54±0.03 kcal/mole obtained in this study for the beta form of oxalic acid.

Lithium and Sodium Oxalates

The value of the heat of formation of sodium oxalate in Circular 500 (15) is based on heat of solution measurements reported by Berthelot (4) in 1875. Lithium oxalate is not listed in Circular 500. The heats of formation reported in this work are the first values obtained from a single experimental study for these oxalate compounds.

For all of the solution measurements in this study, 2.000 M HCl was used as solvent. The acid was prepared by diluting reagent-grade concentrated acid with distilled, deionized water. The acid was standardized with sodium hydroxide solution which had been standardized with primary standard potassium hydrogen phthalate. Adjustments were made until an exact concentration of 2.000 M was reached.

Although the heat of formation of lithium oxalate was determined in a prior study in this laboratory (10), evidence from the present investigation indicated that the anhydrous oxalic acid samples used in the older study were mixtures of two crystal forms. To avoid problems of sample crystallinity, a new reaction scheme based on oxalic acid dihydrate was selected.

Table 4 gives the equations, average heat effects, and uncertainties for the reactions used to determine the heat of formation of lithium oxalate. Reaction 1 represents the average heat of dissolution of five samples of LiCl (c) weighing from 2.5 to 4.0 g in 796.9 g of 2.000 M HCl. Reaction 2 represents the average heat of dissolution of eight samples of $(COOH)_2 \cdot 2\ H_2O$ in a solution equivalent to the final solution of reaction 1. The heat absorbed in reaction 2 was independent of the presence of LiCl. Reaction 3 represents the average of the heats of dilution when four samples of H_2O (ℓ) weighing from 14.3 to 30.8 g are added to a solution equivalent to the final solution of reaction 2. Reaction 4 represents the average heat of dissolution of seven samples of $Li_2C_2O_4$ (c) weighing from 2.4 to 5.3 g in 796.9 g of 2.000 M HCl. Reaction 5 represents the heat of mixing when an appropriate amount of 2.000 M HCl is added to a solution equivalent to the final solution of reaction 4 to make it equivalent to the final solution of reaction 3. Only one run was made to show that the heat of this reaction was negligible. All heats of solution were independent of sample size. Reaction 6 in table 4 is obtained by adding reactions 1, 2, and 3 and subtracting reactions 4 and 5. The heats of formation of all the compounds and solutions in reaction 6, with the exception of $Li_2C_2O_4$ (c), are reliably known. Combining the necessary heats of formation from table 3 with the calculated heat of reaction 6 and keeping only the significant digits yields the heat of formation of $Li_2C_2O_4$, -328.7±0.4 kcal/mole.

TABLE 4. - Reaction scheme for $Li_2C_2O_4$ (c)

Reaction	$\Delta H_{298.15}$, cal
(1) $LiCl\ (c) + 21.84\ HCl \cdot 27.75\ H_2O \rightarrow \begin{bmatrix} LiCl \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix}$	-7,776±4
(2) $1/2\ H_2C_2O_4 \cdot 2\ H_2O + \begin{bmatrix} LiCl \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix} \rightarrow \begin{bmatrix} 1/2\ Li_2C_2O_4 \\ 22.84\ HCl \\ 607.06\ H_2O \end{bmatrix}$	4,515±6
(3) $\begin{bmatrix} 1/2\ Li_2C_2O_4 \\ 22.84\ HCl \\ 607.06\ H_2O \end{bmatrix} + 26.75\ H_2O\ (\ell) \rightarrow \begin{bmatrix} 1/2\ Li_2C_2O_4 \\ 22.84\ HCl \\ 633.81\ H_2O \end{bmatrix}$	-407±2
(4) $1/2\ Li_2C_2O_4 + 21.84\ HCl \cdot 27.75\ H_2O \rightarrow \begin{bmatrix} 1/2\ Li_2C_2O_4 \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix}$	243±5
(5) $\begin{bmatrix} 1/2\ Li_2C_2O_4 \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix} + HCl \cdot 27.75\ H_2O \rightarrow \begin{bmatrix} 1/2\ Li_2C_2O_4 \\ 22.84\ HCl \\ 633.81\ H_2O \end{bmatrix}$	0±2
(6) $LiCl\ (c) + 1/2\ (COOH)_2 \cdot 2\ H_2O\ (c) + 26.75\ H_2O\ (\ell) \rightarrow 1/2\ Li_2C_2O_4\ (c) + HCl \cdot 27.75\ H_2O$[a]	-3,911±10
(7) $2\ Li\ (c) + 2\ C\ (graphite) + 2\ O_2\ (g) \rightarrow Li_2C_2O_4\ (c)$	-328,706±403

[a] $\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$.

Table 5 gives the equations, average heat effects, and uncertainties for the reactions used to determine the heat of formation of sodium oxalate. The scheme is identical to the one presented in table 4 for lithium oxalate. Reaction 1 represents the average heat of dissolution of six samples of NaCl (c) weighing from 4.2 to 4.9 g in 796.9 g of 2.000 M HCl. Reaction 4 represents the average heat of dissolution of 11 samples of $Na_2C_2O_4$ (c) weighing from 4.1 to 5.1 g. Reactions 2, 3, and 5 in table 5 are identical to similar reactions in table 4. Combining the necessary heats of formation from table 3 with the calculated heat of reaction 6 yields the heat of formation of sodium oxalate, -316.2±0.2 kcal/mole.

TABLE 5. - Reaction scheme for the determination of the standard heat of formation of $Na_2C_2O_4$ (c)

Reaction	$\Delta H_{298.15}$, cal
(1) $NaCl\ (c) + 21.84\ HCl \cdot 27.75\ H_2O \rightarrow \begin{bmatrix} NaCl \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix}$	1,418±4
(2) $1/2\ (COOH)_2 \cdot 2\ H_2O\ (c) + \begin{bmatrix} NaCl \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix} \rightarrow \begin{bmatrix} 1/2\ Na_2C_2O_4 \\ 22.84\ HCl \\ 607.06\ H_2O \end{bmatrix}$	4,515±8
(3) $\begin{bmatrix} 1/2\ Na_2C_2O_4 \\ 22.84\ HCl \\ 607.06\ H_2O \end{bmatrix} + 26.75\ H_2O\ (\ell) \rightarrow \begin{bmatrix} 1/2\ Na_2C_2O_4 \\ 22.84\ HCl \\ 633.81\ H_2O \end{bmatrix}$	-407±2
(4) $1/2\ Na_2C_2O_4\ (c) + 21.84\ HCl \cdot 27.75\ H_2O \rightarrow \begin{bmatrix} 1/2\ Na_2C_2O_4 \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix}$	2,501±6
(5) $\begin{bmatrix} 1/2\ Na_2C_2O_4 \\ 21.84\ HCl \\ 606.06\ H_2O \end{bmatrix} + HCl \cdot 27.75\ H_2O \rightarrow \begin{bmatrix} 1/2\ Na_2C_2O_4 \\ 22.84\ HCl \\ 633.81\ H_2O \end{bmatrix}$	0±2
(6) $NaCl\ (c) + 1/2\ (COOH)_2 \cdot 2\ H_2O\ (c) + 26.75\ H_2O\ (\ell) \rightarrow 1/2\ Na_2C_2O_4\ (c) + HCl \cdot 27.75\ H_2O^a$	3,025±12
(7) $2\ Na\ (c) + 2\ C\ (graphite) + 2\ O_2\ (g) \rightarrow Na_2C_2O_4\ (c)$	-316,198±159

$^a \Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$.

Potassium Oxalate and Potassium Oxalate Monohydrate

The heat of formation of anhydrous potassium oxalate reported in Circular 500 is based on the heat of solution measurements made by Berthelot in 1875 (4), and the heat of formation of potassium oxalate monohydrate is based on heat of solution measurements made by Berthelot (4), Thomsen (20), and Perreu (13).

For convenience, distilled, deionized water was used as the solvent instead of the 2.000 M HCl used as the solvent for the sodium oxalate studies. The use of water as the solvent necessitated a few minor changes from the reaction scheme used for sodium oxalate. These changes are evident from table 6. Reaction 1 represents the average heat of dissolution of eight samples of oxalic acid dihydrate weighing from 4.2 to 5.0 g in 763.4 g of water. Reaction 2 represents the average heat of dissolution of five samples of potassium chloride in a solution equivalent to the final solution of reaction 1. Reaction 3 represents the heat of dilution of the final solution of reaction 2 with water. Only one run was necessary to show that the heat of this reaction was negligible. Reaction 4 represents the average heat of dissolution of five samples of potassium oxalate monohydrate weighing 6.2 to 7.4 g in 763.4 g of water. Reaction 5 represents the average heat of mixing six samples of

2.000 M HCl with a solution equivalent to the final solution of reaction 4 to make it equivalent to the final solution of reaction 3. Reaction 6 was obtained by adding reactions 1, 2, and 3 and subtracting reactions 4 and 5; the heat of reaction 6 was obtained in a like manner from the heats of reactions 1, 2, 3, 4, and 5. The heats of formation of all the compounds and solutions in reaction 6, with the exception of $K_2C_2O_4\cdot H_2O$ (c), are reliably known. Using the heats of formation listed in table 3 and the heat of reaction 6, the heat of formation of $K_2C_2O_4\cdot H_2O$ (c) was calculated to be -393.5±0.2 kcal/mole.

TABLE 6. - Reaction scheme for determining the standard heat of formation of $K_2C_2O_4\cdot H_2O$ (c)

Reaction	$\Delta H_{298.15}$, cal
(1) $(COOH)_2\cdot 2\,H_2O$ (c) + 1246 H_2O (ℓ) → $\begin{bmatrix}(COOH)_2\\ 1248\ H_2O\end{bmatrix}$	8,683±14
(2) 2 KCl (c) + $\begin{bmatrix}(COOH)_2\\ 1248\ H_2O\end{bmatrix}$ → $\begin{bmatrix}K_2C_2O_4\\ 2\ HCl\\ 1248\ H_2O\end{bmatrix}$	8,322±9
(3) $\begin{bmatrix}K_2C_2O_4\\ 2\ HCl\\ 1248\ H_2O\end{bmatrix}$ + 54.50 H_2O (ℓ) → $\begin{bmatrix}K_2C_2O_4\\ 2\ HCl\\ 1302.5\ H_2O\end{bmatrix}$	0±2
(4) $K_2C_2O_4\cdot H_2O$ (c) + 1246 H_2O (ℓ) → $\begin{bmatrix}K_2C_2O_4\\ 1247\ H_2O\end{bmatrix}$	7,127±14
(5) $\begin{bmatrix}K_2C_2O_4\\ 1247\ H_2O\end{bmatrix}$ + 2 $HCl\cdot 27.75\ H_2O$ → $\begin{bmatrix}K_2C_2O_4\\ 2\ HCl\\ 1302.5\ H_2O\end{bmatrix}$	578±13
(6) $(COOH)_2\cdot 2\,H_2O$ (c) + 2 KCl (c) + 54.50 H_2O (ℓ) → $K_2C_2O_4\cdot H_2O$ (c) + 2 $HCl\cdot 27.75\ H_2O$[a]	9,300±26
(7) 2 K (c) + 2 C (graphite) + H_2 (g) + 5/2 O_2 (g) → $K_2C_2O_4\cdot H_2O$ (c)	-393,483±165

[a] $\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$.

The heat of formation of anhydrous potassium oxalate may be calculated from the reactions representing the heats of solution of potassium oxalate monohydrate and anhydrous potassium oxalate given in table 7. Reaction 1 is identical with reaction 4 of the previous scheme. Reaction 2 represents the average heat of solution of six samples of anhydrous potassium oxalate weighing from 4.9 to 5.7 g in enough water to make the final solution equivalent to that obtained in reaction 1. Reaction 3, the hydration of $K_2C_2O_4$, was obtained by subtracting reaction 1 from reaction 2. Using the heat of formation of water from table 3, the heat of formation of $K_2C_2O_4\cdot H_2O$ (c) determined in this study, and the heat of reaction 3, the heat of formation of $K_2C_2O_4$ (c) was calculated to be -321.9±0.2 kcal/mole.

According to Bichowsky and Rossini (5), the data of Berthelot yield +7.57 kcal/mole for the heat of solution of potassium oxalate monohydrate at a final concentration of 400 moles of water per mole of potassium oxalate, and those of Thomsen yield +7.52 kcal/mole at a final concentration of 800 moles of water per mole of potassium oxalate. Perreu (13) measured the heat of solution of potassium oxalate monohydrate as a function of concentration for several solutions. At the same final concentration used in this study, Perreu measured a heat of solution of +7.42 kcal/mole. All of these previous measurements of the heat of solution of $K_2C_2O_4 \cdot H_2O$ (c) were made at 18° C. In this study, the heat of solution measured at 25° C and at a final concentration of 1,247 moles of water per mole of $K_2C_2O_4 \cdot H_2O$ is +7.13 kcal/mole, somewhat less than the older measurements. This may explain the difference between the values of the heats of formation of $K_2C_2O_4 \cdot H_2O$ (c) and $K_2C_2O_4$ (c) found in this work and in Circular 500 (15).

TABLE 7. - Reactions for the determination of the standard heat of formation of $K_2C_2O_4$ (c)

Reaction	$\Delta H_{298.15}$, cal
(1) $K_2C_2O_4 \cdot H_2O$ (c) + 1246 H_2O (ℓ) → $K_2C_2O_4 \cdot 1247\ H_2O$	7,127±14
(2) $K_2C_2O_4$ (c) + 1247 H_2O (ℓ) → $K_2C_2O_4 \cdot 1247\ H_2O$	3,897±10
(3) $K_2C_2O_4$ (c) + H_2O (ℓ) → $K_2C_2O_4 \cdot H_2O$ (c)[a]	-3,230±18
(4) 2 K (c) + 2 C (graphite) + 2 O_2 (g) → $K_2C_2O_4$ (c)	-321,938±167

[a] $\Delta H_{10} = \Delta H_9 - \Delta H_8$.

SUMMARY

Table 8 summarizes the heats of formation determined from this study. These heats of formation are based on the heat of formation of $(COOH)_2 \cdot 2\ H_2O$, -341.0±0.1 kcal/mole determined by Becker and Roth (2).

TABLE 8. - Heats of formation of several oxalates

Compound	Heat of formation, kcal/mole
$(COOH)_2$ (α)	-198.1±0.1
$(COOH)_2$ (β)	-197.8±0.1
$Li_2C_2O_4$	-328.7±0.4
$Na_2C_2O_4$	-316.2±0.1
$K_2C_2O_4$	-321.9±0.2
$K_2C_2O_4 \cdot H_2O$	-393.5±0.2

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