THE HEATS OF COMBUSTION OF METAL-ORGANIC COMPOUNDS:

POTASSIUM HYDROGEN PHTHALATE.

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POTASSIUM HYDROGEN PHTHALATE

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Preface

This thesis is based upon work done in partial
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A C K N O W L E D G M E N T

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INTRODUCTION AND HISTORY.

In the thermodynamics of chemical reactions the free energy is of first importance. It may be calculated in various ways:

1. By the measurement of the equilibrium constant in a reversible reaction and the application of the relation $\Delta F = -RT \ln K$.

2. By the determination of the reversible electromotive force of a cell involving the reaction in question, when $\Delta F = -nFE$.

3. By the determination of heat capacities and utilization of these results with heat of reaction data.

4. By the combination of suitable equations with known values of free energy.

The third of these methods is by far the most useful with organic substances. Values for the heats of reaction of organic substances are most readily found from values for their heats of combustion.

The heats of combustion of metal-organic compounds have been studied hardly at all, according to the literature. Parks and Huffman[1] have called attention to this fact, stating:

> "We can present no data whatever for the organic compounds
> containing phosphorus, arsenic, boron or the metallic
> elements. Free energy values for some of these, for
> tetraethyl lead for instance, might prove very interesting
> from a practical standpoint. However, as far as we know
> even the heats of combustion of such compounds are at
> present nonexistent."

A check on the literature shows that little if any change has occurred in the situation since this statement was made.

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[1] Parks and Huffman, _Free Energies of Some Organic Compounds_, p. 196.

A moments reflection on the requirements for a good calorimetric measurement shows the reason for this state of affairs. It is essential in combustion calorimetry that the substance burn smoothly and rapidly, forming a well defined set of products whose quantities can be accurately determined. Combustion in oxygen probably occurs smoothly and rapidly in many cases. When combustion is difficult it may be facilitated by adding substances which themselves yield oxygen, or which raise the temperature to a suitable degree through their heat of combustion. If, however, the products of reaction are solid it becomes difficult to define their nature. This is certainly true for metal-organic substances. It is now generally accepted that on combustion, they yield either oxides or carbonates. These products may react with the water or carbon dioxide or both, which are formed in the bomb; and if they do not, they will certainly adsorb these substances to a greater or less extent. These processes involve thermal changes whose extents may vary from experiment to experiment and whose very nature may be obscure and difficult to determine. It is not surprising that investigators have hesitated to attempt thermochemical work with them.

Satisfactory combustion methods have long since been worked out for hydrocarbons and for compounds containing only carbon, hydrogen and oxygen. Much progress has been made in the combustion calorimetry of sulfur and nitrogen containing compounds. Something is also being accomplished with the organic halides. The metal-organic compounds, while they do not bulk very large in organic chemistry as a whole, are often highly important. This makes the development of methods for determining their heats of combustion highly desirable.

EXPERIMENTAL.

PRELIMINARY CONSIDERATIONS.

The metal-organic salts seemed more promising as materials to use in a preliminary investigation than the other metal-organic compounds. They can be prepared in well crystallized form and in a high state of purity. Potassium hydrogen phthalate ($KHC_8H_4O_4$) was chosen for this study since it is a well characterized salt, readily available in very pure form, anhydrous and nonhygroscopic. It seems probable that water of hydration in any substance will act as a serious hindrance to its combustion. It seemed, also, that the preponderance of carbon and hydrogen in it would make it readily combustible. This expectation was borne out by preliminary experiments in which it was found to burn much more readily than do many organic substances containing no metal.

Pure potassium carbonate is prepared by the incineration of organic salts of potassium according to Ephraim[2]. Ephraim[3] states that its dissociation pressure is less than one millimeter of mercury at $800^{\circ}C$. and that it is only 27 mm. of mercury at $1200^{\circ}C$. It seems safe, therefore, to proceed upon the assumption that it is the salt which is first formed on combustion of potassium hydrogen phthalate, especially since there is a relatively high concentration of carbon dioxide in the bomb at that time.

The temperatures reached in combustion calorimetry run relatively high. In one experiment a piece of heavy pyrex tubing was laid across the top of a crucible in which benzoic acid was burned in the

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[2] Fritz Ephraim, Inorganic Chemistry, p. 822.

[3] Ibid., p. 812.

combustion bomb in the usual way. The tubing sagged to the bottom of the crucible and melted together in the middle. Since the softening temperature of pyrex glass is 820°C. and the fusion temperature must be still higher, this indicates that the temperature reached was well above this. The potassium carbonate resulting from the combustion of potassium hydrogen phthalate in our experiments was always fused. This indicates that the temperature reached was above 900°C., the approximate melting point of this substance. This high temperature is sharply localized, however. Potassium carbonate placed in a crucible and suspended 4.4 centimeters above another in which benzoic acid was burned in a bomb showed no signs of melting. Crystals of pyrogallol (melting point 133°C.) which were placed on the bottom of a dry bomb did not fuse during a combustion of potassium hydrogen phthalate. If any evidence of the sort were needed, this would indicate that the temperature in the crucible is certainly sufficiently high to bring about complete combustion in oxygen. Any material which escapes it must be projected out of the crucible.

Potassium carbonate will react with the gaseous carbon dioxide and water in contact with it in the bomb to form potassium hydrogen carbonate:

$$K_2CO_3 + CO_2(g) + H_2O(g) = 2KHCO_3.$$

The quantities of carbonate and hydrogen carbonate in the products must be determined, and a correction for the heat of this reaction must be made. Kelly and Anderson[4] find that the free energy of


[4] Kelly and Anderson, Bureau of Mines Bulletin 384, p. 31.

this reaction is given by the expression:

$$\Delta F^{\circ} = -30,850 + 21.07\ T \log_{10}T - 12.75\text{x}10^{-3}T^2 - 19.06\ T.$$

From this it follows that the free energy of the reaction is -10,620 calories at 27°C. Setting ΔF° equal to zero and solving for T it is found that the free energy of the reaction is zero at 443°K. or 170°C. Thus the formation of $KHCO_3$ does not start until the temperature of the reacting materials in the bomb has fallen to about 170°C., and it proceeds as the temperature falls. The calorimetric reaction, then, involves the combustion of potassium hydrogen phthalate in oxygen to form at first potassium carbonate, carbon dioxide, and water.

$$KHC_8H_4O_4(s) + 15/2\ O_2(g) = 1/2\ K_2CO_3(s) + 15/2\ CO_2(g) + 5/2\ H_2O(1).$$
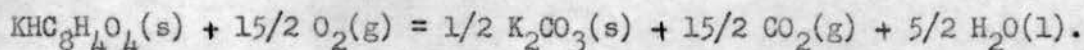
A further reaction then occurs to form potassium hydrogen carbonate to an extent which must be determined.

$$K_2CO_3(s) + CO_2(g) + H_2O(g) = 2KHCO_3(s).$$
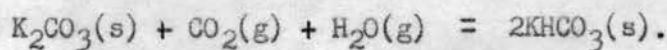
The sum of the heat effects of these two reactions is the overall heat effect which is determined. If x ion moles of potassium go to the formation of $KHCO_3$, there remain $(.5 - x/2)\ K_2CO_3$. There are x moles of $KHCO_3$ formed, and this takes x/2 moles of CO_2 and x/2 moles of H_2O. The overall reaction becomes:

$$KHC_8H_4O_4(s) + 15/2\ O_2(g) = (.5 - x/2)\ K_2CO_3(s) + xKHCO_3 + (7.5 - x/2)CO_2(g) + (2.5 - x/2)\ H_2O(1).$$
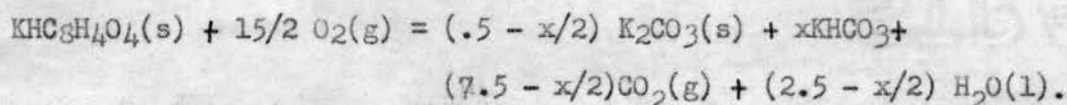
This is the reaction whose heat effect is measured. When x has been determined, the heat effect of the potassium bicarbonate reaction may be applied as a correction factor to give the heat effect of the original reaction.

The potassium hydrogen phthalate used in these experiments was
all taken from the same container. It was "reagent grade", lot 15,
made by the General Chemical Company and certified by them as meeting
A. C. S. requirements. The label certifies it as 99.9% pure, losing
not more than 0.05% at 100°C. and containing impurities whose maximum
limits were: water insoluble, 0.005%; Cl, 0.003%; sulfur, 0.002%;
Fe, 0.001% and heavy metals (as Pb) 0.0005%. It was not purified
further. Phthalic acid, from which it was presumably prepared, is
commonly made by the partial oxidation of naphthalene, which yields
the ortho acid. Beilstein[5] in discussing the preparation of the meta
and para acids gives only methods which are much more laborious and
expensive. The preparation, therefore, was probably a salt of the
ortho acid. This was confirmed by preparation of the acid by acidifying
the salt and recrystallizing it. It was found to decompose at 206°C.,
which is characteristic of the ortho acid. The meta acid melts at
347-8°C., and the para acid sublimes at 300°C. and above.

The salt possessed such low adhesive properties, due to its
purity and possibly to its intrinsic nature, that it could not be
pressed into pellets for use in combustion experiments. It was
simply spread in a layer over the bottom of the crucible. The
crystals were found to be irregular, of approximate diameter 1 mm.,
and containing a very small proportion of "fines". It burned
completely without projection from the crucible, under proper
conditions, as it probably would not have done if it had been very

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[5] Beilstein, Volume IX, pp. 791, 833, 841 (1926).

fine or pressed into dense pellets. It burned completely before becoming encapsulated with molten K_2CO_3. This was shown by applying the test for phthalate[6] in which it is made to combine with resorcinol to give fluorescein. This test was positive with very small quantities of phthalate, but invariably negative with the residues from these combustions. It has been found that encapsulation of a material by an added salt of low melting point, such as $K_2S_2O_7$, will commonly prevent its complete combustion.

No organic residues of any kind resulted from these combustions, since the residues would never reduce either $KMnO_4$ or $K_2Cr_2O_7$ in hot acid solutions.

[6] R. E. Andrew, J. Ind. Eng. Chem., 15, 838 (1923).

THE CALORIMETER AND ITS OPERATION.

An adiabatic Parr calorimeter was used in this investigation. Both a single and a double valve bomb were used. The latter bomb is designed for ready removal of the gases from combustion for analysis - an essential feature in combustion work. The bombs, in use, are submerged in water held in an oval pail, chromium plated and highly polished on the outside. A collar of nonconducting material at the top of the outer jacket provides a shoulder for suspending the pail so that there is an air gap one half inch in thickness on all sides and above and below it. This gap reduces thermal leakage due to conduction. The outer jacket, about two inches thick on sides and bottom, is also oval and everywhere equally distant from the pail within. It is chromium plated and highly polished inside. The cover of the calorimeter which is of the same thickness as the jacket permits the circulation of water by means of a rotary lift pump through it from the jacket and back to it through a discharge port. This provides complete circulation of water on all sides of the pail and insures constancy of temperature throughout. Power for the pump and the stirrer in the pail is supplied by means of a suitable constant speed motor. The pump and stirrer pulleys are connected by means of a belt so as to run at corresponding rates at all times. This calorimeter embodies the best features of modern calorimeter construction except that it lacks a convection shield midway of the air gap and a cover for the pail. These features, hard to incorporate in a calorimeter for general commercial use, would have added to its value.

Other accessories used with the calorimeter were an automatic water heater and an ignition unit to provide current for igniting the charge. Cold water from the tap, passed first through a cooling constant temperature bath in hot weather, was also available. Either hot or cold water could be introduced into the jacket by turning suitable taps. The overflow was conducted to the sink.

The calorimeter was operated in a nonadiabatic manner for convenience. White[7] in his book The Modern Calorimeter after discussing the various calorimetric methods, infers that with ordinary calorimetric equipment and with external temperatures which are reasonably constant the more ordinary calorimetric methods have fully paralleled the more refined adiabatic method for ordinary experiments. After discussing the merits of nonadiabatic (regular) and adiabatic methods he states:

> "Hence it is not surprising that as calorimetric precision
> has been increased the regular method has given as great
> precision as the special ones."

The constant temperature jacket provides the best possible environment for the regular calorimeter.

Differences in temperature in the pail were measured by means of a Beckmann thermometer calibrated by the Bureau of Standards. (Bureau of Standards number 63426.) The calibrated Fahrenheit thermometers provided with the calorimeter are more convenient, but they cannot be read with greater accuracy than $\pm 0.01^{\circ}F$. With the Beckmann thermometer there is little excuse for an error in reading greater than $\pm 0.001^{\circ}C$.

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[7] Walter P. White, The Modern Calorimeter, pp. 23, 24.

This greater accuracy is essential for modern calorimetry. The Parr thermometer is adequate for keeping track of temperatures in the jacket, and it was used for this purpose. With it the jacket temperature could be kept constant to within $\pm 0.006^{\circ}C$. It takes a very good control device to maintain temperatures in pail and jacket the same within $0.01^{\circ}C$. in the best adiabatic calorimeters. Water in the jacket was held at $80^{\circ}F \pm 0.01^{\circ}F$. This is $26.66 \pm 0.006^{\circ}C$.

Both thermometers were read by means of a thermometer reader. This device eliminated error from parallax. The thermometers were tapped before reading to prevent sticking of the mercury thread.

Further improvement in temperature measurements in the pail could have been gained by using a platinum resistance thermometer and a Mueller bridge, or by using a thermocouple and a high precision potentiometer. The advantage of these devices lies in the fact that they are not subject to minor aberrations as a mercury thermometer which is calibrated at only a few points may be. Their use requires freedom from vibrations, which will affect the operation of their galvanometers, and the services of a second operator. The precision of the much more convenient Beckmann thermometer was quite sufficient for these experiments.

In each run the sample to be burned was weighed in a previously weighed platinum crucible. Two of them were used indiscriminately in all these experiments. They differed in weight by only 0.04 grams, which corresponds to a difference in heat capacity of only 0.0013 calories per degree.

A standard iron fuse wire as supplied by the Parr Instrument Company was used to ignite the sample. Ten centimeters of this wire

was taken in assembling the bomb, and the length remaining after the combustion was measured. A correction of 2.8 calories per centimeter of wire burned was applied to the heat output of each run.

In the earlier experiments the bomb was filled to a pressure of 30 atmospheres with oxygen after assembling. In the later ones it was filled to 25 atmospheres pressure and blown down to one atmosphere pressure and refilled with oxygen to 25 atmospheres pressure, for reasons which will be explained later. The assembled bomb was then placed in the calorimeter pail and approximately 2000 grams of water, adjusted to 25°C. in a constant temperature bath and weighed with an accuracy of ±0.01 gram on a balance of large capacity, was poured into it. The calorimeter was then assembled.

The jacket was filled with water after starting the stirring motor, and its temperature was adjusted to 80°F. This temperature was checked frequently during the run and brought back to 80°F. if necessary. After the calorimeter had been running for some minutes to smooth out the energy flow a preliminary rating period of ten minutes was taken, the temperature being read each minute as measured by a stop watch. The charge was then fired on the tenth minute. The reading of the temperature was continued until it had passed through a maximum and had fallen at a uniform rate for ten minutes more. This last is the second rating period.

A method of finding the corrected temperature rise which has not been commonly used in calorimetry, if a reading of the literature may be trusted, was employed in these experiments. To illustrate it the

data taken in a typical run chosen at random among those performed are given in Table I below. The data are plotted in the graph of Figure 1.

TABLE I
Temperature-Time Data For a Typical Experiment

	Time	Temperature	Δt	
	0	2.253	+ .005	
	1	2.258	.004	
First	2	2.262	.004	
Rating	3	2.268	.004	
Period	4	2.272	.005	
	5	2.277	.005	
	6	2.282	.005	
	7	2.287	.004	
	8	2.291	.005	
	9	2.296	.005	Average = + .0048°/min.
Fired	10	2.301		
	11	3.700		
	12	4.550		
	13	4.767		
	14	4.828		
	15	4.846		
	16	4.850		
	17	4.851		
	18	4.849	− .005	
	19	4.844	.005	
	20	4.839	.005	
	21	4.835	.004	
Second	22	4.831	.004	
Rating	23	4.827	.004	
Period	24	4.823	.004	
	25	4.819	.004	
	26	4.815	.004	
	27	4.811	.004	Average = − .0042°/min.
	28	4.807		

The corrected rise may be found either graphically (the usual method) or by mathematical analysis. The contents of the can were brought initially to a temperature which, as experience showed, was about as far below the jacket temperature as read from the Beckmann thermometer as it would be above this temperature at the end. This

Figure 1 Temperature-Time Relationship For a Typical Experiment
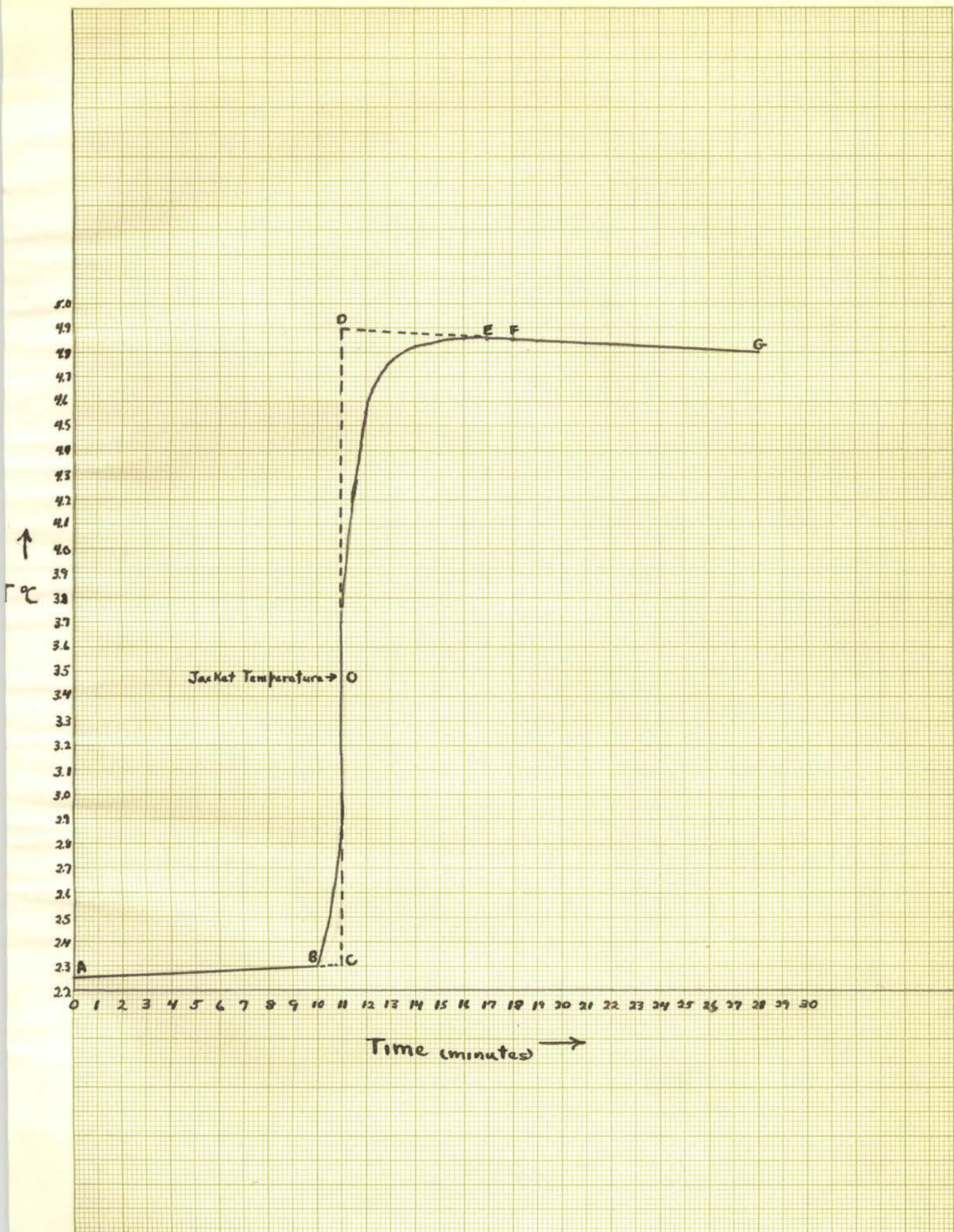
procedure was adopted for all runs so as to make them regular and reproducible. The corrected rise is found by the graphical method by drawing a vertical line through the point on the curve of Figure 1 corresponding to the jacket temperature and extrapolating the two lines representing temperatures during the initial and final rating periods to cut it. The length of this line in degrees between the points where these extrapolated lines cut the vertical line is the corrected rise. This length on the graph is that of the line C – D.

The accuracy of this method for finding the corrected rise is limited by the accuracy with which the points can be plotted and read. This accuracy is not great where values must be plotted to thousandths degree unless a very large piece of graph paper is used. The mathematical method gives the result more simply. Referring to Table I, the temperature is found to be rising at the average rate $0.0048^\circ C./min.$ during the first rating period. The temperature of the jacket is reached one minute after firing, that is, one minute after reading number 10. If the leak of heat into the pail had gone on as in the first rating period until the time when the temperature of the jacket was reached, the temperature as read on the thermometer would have been $2.301 + 0.005^\circ = 2.306^\circ C.$ If this hypothetical temperature is calculated from the temperature of reading #9 it is $2.296 + 2 \times 0.0048$ or $2.306^\circ C.$, and so on. Taking the last rating period we proceed in the same manner, noting that the first reading of the final rating period was taken 7 minutes after the temperature

of the jacket was reached. The tables embodying the calculations are given below.

TABLE II
Data Used in Finding the Corrected Temperature Rise

First Rating Period

0(A)	2.253	+ 11(.0048)	=	2.306
1	2.258	+ 10(.0048)	=	2.306
2	2.262	+ 9(.0048)	=	2.306
3	2.268	+ 8(.0048)	=	2.306
4	2.272	+ 7(.0048)	=	2.306
5	2.277	+ 6(.0048)	=	2.306
6	2.282	+ 5(.0048)	=	2.306
7	2.287	+ 4(.0048)	=	2.306
8	2.291	+ 3(.0048)	=	2.305
9	2.296	+ 2(.0048)	=	2.306
10(B)	2.301	+ 1(.0048)	=	2.306
		Average	=	2.306 (Temperature C)

Second Rating Period

18(F)	4.849	+ 7(.0042)	=	4.878
19	4.844	+ 8(.0042)	=	4.878
20	4.839	+ 9(.0042)	=	4.877
21	4.835	+ 10(.0042)	=	4.877
22	4.831	+ 11(.0042)	=	4.877
23	4.827	+ 12(.0042)	=	4.877
24	4.823	+ 13(.0042)	=	4.878
25	4.819	+ 14(.0042)	=	4.878
26	4.815	+ 15(.0042)	=	4.878
27	4.811	+ 16(.0042)	=	4.878
28(G)	4.807	+ 17(.0042)	=	4.878
		Average	=	4.878 (Temperature D)

The averages of the corrected initial and final readings are now found. These are, respectively, $4.878°$ and $2.306°$. The difference between them, $2.572°$, is the corrected rise. These calculations may be carried out very rapidly with the aid of a calculating machine. Other methods for finding the corrected rise have been given by Regnault-Pfaundler, and others[8]. They are much more cumbersome than this, but offer

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[8] Walter P. White, The Modern Calorimeter, pp. 39-58.

little or no advantage from the point of view of accuracy. They are little used at present.

To the corrected rise as found the scale correction, the setting factor correction and the emergent stem correction for the Beckmann thermometer must be added. These corrections were applied as outlined in the certificate for the thermometer used. This final corrected temperature rise multiplied by the total capacities of water, bomb and calorimeter accessories gives the quantity of heat evolved in the reaction.

The heat of a reaction at a given temperature is the difference between the heat contents of its products and the heat contents of the reactants at that temperature. The heat of combustion is the energy released on starting from a given temperature and bringing the products back to that starting temperature. Strictly speaking, the calorimetric procedure does not give exactly this heat of combustion, but the difference between this correct value and that which is found is negligibly small. The results for the present experiments will be stated to be for $26.66^{\circ}C.$, the jacket temperature and also the median temperature of the calorimetric runs. They may equally well be taken as at $25^{\circ}C.$ Dickinson[9] states:

> "To be exact, the temperature at which the reaction takes place should also be specified, but the change of the heat of combustion with temperature is so small that this is not necessary for a temperature range between $15^{\circ}C.$ and $30^{\circ}C.$, temperatures at which experimental results are usually obtained. In practice, also, the initial and final temperatures are not the same, but differ from 2 to 4 degrees. The effect of this difference is small and is usually neglected - -."

[9] H. C. Dickinson, Bulletin #2 Vol. 11 of the U. S. Bureau of Standards, Department of Commerce, March 1, 1915.

HEAT CAPACITIES OF BOMBS AND CALORIMETER ACCESSORIES.

The heat capacities of two bombs and a common set of calorimeter accessories were determined by the combustion of a standard sample of benzoic acid (sample 39g) furnished by the National Bureau of Standards of the United States Department of Commerce. The certification accompanying this sample stated:

> "this lot of benzoic acid was prepared to insure material of high purity and uniformity. Although it is known to contain a small amount of impurity, its heat of combustion has been found to be the same, within the estimated uncertainty of the measurements, as that of specially purified samples of benzoic acid. On the basis of titration, a purity of 99.9% is indicated. It has also been found that this material will not absorb moisture from the atmosphere if the relative humidity does not exceed 90 per cent. The heat of combustion and the acidimetric value of this sample will not change with time if adequate precautions are taken to avoid the introduction of impurities."

> "The quantity of heat evolved by combustion of Standard Sample 39g of benzoic acid has been found to be 26.4338 abs. kj/g mass with an estimated uncertainty of 0.0026 kj/g, when the sample is used under the following conditions:

> A. The combustion reaction is referred to 25°C.
> B. The sample is burned in a bomb of constant volume in pure oxygen at an initial absolute pressure of 30 atm. at 25°C.
> C. The number of grams of sample burned is equal to three times the volume of the bomb in liters.
> D. The number of grams of water placed in the bomb before combustion is equal to three times the volume of the bomb in liters.

Heat capacities of the bombs were at first carried out according to the above directions. The heat of combustion of this benzoic acid is 26.4338/ 0.0041840 calories per gram. Certain modifications of the procedure, described later, were found to be necessary in determining the heat of combustion of potassium hydrogen phthalate.

The procedure for determining the heat capacities of the bombs was then altered to make it correspond as closely as possible to that used in the determinations. The chief modifications of the procedure were as follows:

1. Commercial oxygen which was found by analysis to be 99.5% pure was used.

2. The runs were made at 25 atmospheres pressure.

3. The quantity of nitric acid formed in the course of the combustion reaction was determined.

4. The bomb was filled with oxygen, blown down and refilled again to 25 atmospheres pressure.

Item 3 requires further discussion. It was found in these standardization runs that nitric acid always formed. Its quantity had to be determined and a correction for its heat of formation and solution applied. It was absorbed by the water which was present in the bomb at the end. It was determined by titrating the washings of the bomb with a solution of sodium carbonate, described in the Parr manual on combustion methods, of such concentration that a titre of one ml. represented a total heat evolution of one calorie in the formation and solution of nitric acid. Methyl orange was used as indicator. It was thought that the correction could be reduced if the nitrogen from the air originally in the bomb were removed as completely as possible by flushing it. It was found that the heat evolved by nitric acid formation was about 8 to 10 calories if the bomb was not flushed. Flushing it once and refilling reduced this quantity of heat to less than one calorie. For a simple standardization of

the bomb a better correction could be made without flushing. It was found, however, that this flushing was advantageous in connection with the runs on the salt; so it was included in the determination of the heat capacities of the bombs.

The certification provided the following formula for making a correction to the heat of combustion when deviations from the given procedure were made. The heat of combustion is to be multiplied by this factor if it is found to be significant:

$$\text{Factor} = 1 + 10^{-6} \left[20(P-30) + 42(M_s/v - 3) + 30(M_w/v-3) - 45(t-25) \right]$$

where:

P = initial absolute pressure of oxygen in atmospheres at the temperature t,
M_s = mass of sample in grams,
M_w = mass of water in grams placed in bomb before combustion,
v = volume of bomb in liters,
t = temperature to which the reaction is referred, in degrees Celsius.

This factor was determined and found to be 1.0001, leaving the heat of combustion value still within its own estimated uncertainty.

The results of the determination of the heat capacities of the bombs gave the following results.

TABLE III

Heat Capacities of Bombs.

Bomb #1 and Accessories		Bomb #2 and Accessories	
Run	Heat Capacity	Run	Heat Capacity
1	437.1	1	424.9
2	436.1	2	426.4
3	436.0	3	428.4
4	437.5	4	426.5
5	438.1	5	428.3
6	436.3	6	427.4
7	436.9	7	427.5
8	437.0	8	427.0
9	436.7	9	427.1
10	436.7		
11	436.1		
Average	436.7 ± .5 Calories	Average	427.1 ± .7 Calories
Average deviation ± .11%		Average deviation ± .16%	

There is a considerable difference between the heat capacities of the bombs. This is to be expected since bomb #1 weighs 3046.4 grams and bomb #2 weighs 2895.2 grams. The ratio of weights of these two bombs is 1.052, while the ratio of their heat capacities is 1.023. We infer that the two bombs have been constructed of two different types of illium.

A check on the standardizations was run by using the values there obtained and determining the heat of combustion of a sample of naphthalene which was purified in the laboratory by recrystallization from ethanol and subsequent fusion and heating to remove the last traces of solvent. The results of four runs which were made are given in Table IV.

TABLE IV

Naphthalene Runs

Run #	Bomb #	Heat of Combustion($-\Delta E$)
1	1	1229.6 Kcal/mole
2	2	1230.9
3	1	1228.2
4	2	1228.3

Average 1229.2 = .8 Kcal/mole
Average deviation = .065%

On converting the value here found to the heat of reaction, ΔH, we find $\Delta H = -1230.4 = .8$ Kcal/mole as compared with the value of -1232.5 Kcal/mole found by Kharasch[10]. This indicates that the heat capacities of the two bombs as determined are correct. They were used indiscriminately in the determination of the heats of combustion.

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[10] Kharasch, Bureau of Standards Journal of Research 2, 359 (1929).

HEAT OF COMBUSTION OF POTASSIUM HYDROGEN PHTHALATE.

SPECIAL CONSIDERATIONS.

It was found early in the runs made with potassium hydrogen phthalate that the presence of nitrogen in the bomb was important. On analyzing the solid combustion products for potassium carbonate and potassium hydrogen carbonate it was found that not all of the potassium input was accounted for, the results being as much as 5% short of the theoretical amount when the bomb was not flushed. It was suspected that the loss might be due to the formation of potassium nitrate which could not be detected by this analysis. The brown ring test showed that nitrate was present. The runs were then carried out after flushing the bombs once with oxygen. The test now failed to show the presence of nitrate. The brown ring test is not highly accurate, so it is not surprising that it should fail to detect a small quantity of nitrate, if present. The analysis for potassium carbonate and potassium hydrogen carbonate now accounted for very nearly all the potassium introduced. Quantitative analysis to determine the quantity of potassium nitrate present would be very difficult. A part of the nitrate formed, too, probably went to the water in the bomb as HNO_3. Since the quantity of nitrate formed was certainly small, no attempt was made to correct for it.

As has been stated, analysis of the oxygen which was used showed it to be 99.5% pure. The impurity was probably nitrogen. Calculation shows that the concentration of nitrogen in the atmosphere of the bomb; filled, with air originally present, to a total pressure of 25 atmospheres, and using oxygen containing 0.5% of nitrogen by volume, is

about 3.64 mole precent. Flushing the bomb to a pressure of one
atmosphere and refilling to 25 atmospheres reduces the concentration
of nitrogen to about 0.63 mole percent. A second similar flushing
and refilling reduces it to about 0.50 mole percent; a relatively
unimportant gain. As has been stated under the discussion of the
standardization of the bombs, a single flushing reduces the correction
for nitrate formed to about one calorie. It was decided to carry out
the determinations with one flushing of the bombs, filling to 25
atmospheres. It is estimated that this probably introduces an error
of about one calorie in these determinations.

Modern directions for combustion calorimetry specify that one
ml. of water be added to the bomb when assembling it for a run. In
the combustion of coal, which may contain sulfur and nitrogen, these
elements are converted to sulfuric acid and nitric acid, respectively.
The water is added to absorb them. Washing of the bomb and titration
of the washings enables one to make corrections for their formation.
Nitric acid forms in the absence of nitrogen containing compounds,
however, if the bomb contains nitrogen from air originally present
or added with the oxygen, as has been noted in the discussion of
standardization. It was thought that some error due to adsorption of
nitric acid by the added water in these runs could be avoided if this
water were not added. It was found, however, that this added water
plays an essential part in the actual combustion. If it were not
added originally at either 25 or 30 atmospheres, combustion was
incomplete both in the standardization with benzoic acid and in the
runs with potassium hydrogen phthalate. This was evident because
a small residue of unburned carbon was always found in the crucible

and upon the top and walls of the bomb to which it had been projected in combustion. This was never found when water was added in assembling the bomb. The initial addition of water was, therefore, made a regular part of the procedure.

Incomplete combustion giving carbon monoxide has often been found to occur with organic substances. This did not occur in our experiments as was shown by passing the gases from the bomb after combustion through a solution of palladous chloride. Voiret and Bonaime[11] have found that this test, involving the formation of a black-brown precipitate, will detect as little as one part of CO in 1000 parts of gas. It was negative in our work. The presence of K_2CO_3 in the residues of these combustions was probably advantagious. It has been found that it is a positive catalyst for the oxidation of carbon monoxide.[12]

The total pressure in the bomb was found to be important. It was found that combustion was sometimes incomplete at pressures as high as 30 atmospheres, carbon remaining in the crucible and being projected to the top and sides, and even the bottom of the bomb. This effect has often been found in combustion calorimetry. The remedy lies in the reduction of the pressure of oxygen in the bomb. This promotes turbulence in the gases. This turbulence brings oxygen more readily to the surface of the burning particles and also assists in the transfer of heat to the walls of the bomb. The manual furnished

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[11] E. G. Voiret and A. L. Bonaime, Ann. chim. anal. 26, 11-12 (1944).

[12] C. A. 32, 4865 (1938) Japanese paper abstracted in Met. Abstracts 2, No. 1, 22 (1939).

by the Parr Instrument Company recommends that combustions be carried
out at as low pressures of oxygen as possible. It was found that
combustions were complete at 25 atmospheres pressure, so this pressure
was adopted for our experiments.

With these details in hand, the problem of determining the
quantity of potassium hydrogen carbonate formed in the bomb when the
thermochemical process is complete and correcting for it remained.
Analysis of the residual gases for carbon dioxide by absorption
methods, allowing the gas to flow from the bomb, took some hours
and were not very accurate. Any such method which required a long
time will be inadmissable. The only feasible method seems to be to
open the bomb as soon as may be after the completion of combustion
and to determine the quantities of $KHCO_3$ and K_2CO_3 which are present.
The solid residues are readily recovered since they remain in the
crucible. The precaution of washing out the bomb and adding the
washings to the main solution was always observed, however. Titration
of the solutions with acid to the phenolphthalein end point, followed
by titration to the methyl orange and point serves to determine the
quantities of carbonate and bicarbonate.

The time factor still remains, for the reaction goes on
continuously until the crucible with its contents is removed from
the bomb. The kinetics of the reaction

$$K_2CO_3(s) + CO_2(g) + H_2O(g) = 2KHCO_3(s)$$
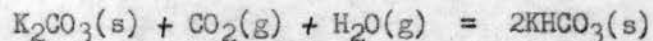
have never been investigated, so far as we know; certainly not for
such conditions as previal in our experiments. We, therefore,
studied it in some detail. Potassium hydrogen phthalate was burned
in the combustion bomb in the manner which had been fixed upon for

our combustions, using approximately constant quantities of the substance, the bombs were removed and blown down at definite times after the moment of firing and the residues were analyzed for carbonate and bicarbonate content. The results are shown in the data of Table V and in the graph of Figure 2.

TABLE V

Data From Kinetic Study of Potassium Hydrogen Carbonate Formation

Time after firing	%Potassium Occurring as $KHCO_3$
5 minutes	12.00
15 minutes	14.65
30 minutes	16.79
1 hour	20.26
2 hours	22.54
4 hours	23.15

Some sources of error are readily recognized in this procedure. The reaction occurs at the surface of the potassium carbonate in the crucible, and its rate will depend upon the extent of this surface. The layer of potassium hydrogen phthalate was spread as uniformly as possible over the bottom of the crucible, but the surface tension of molten K_2CO_3 drew it up so that the exposed area was not constant from experiment to experiment. We believe, however, that the area exposed was sufficiently nearly constant to make this error negligible. Formation of $KHCO_3$ does not begin immediately after the completion of combustion but only, as we have seen, when the temperature of the reacting materials (that is, the surface of the K_2CO_3) has fallen to about 170°C. This temperature will be reached rather promptly after the completion of the combustion, and the time required should be nearly constant with the same quantities of reagents taken initially. It seems that this factor will be essentially constant, and that it

Figure 2   Kinetic Study of $KHCO_3$ Formation
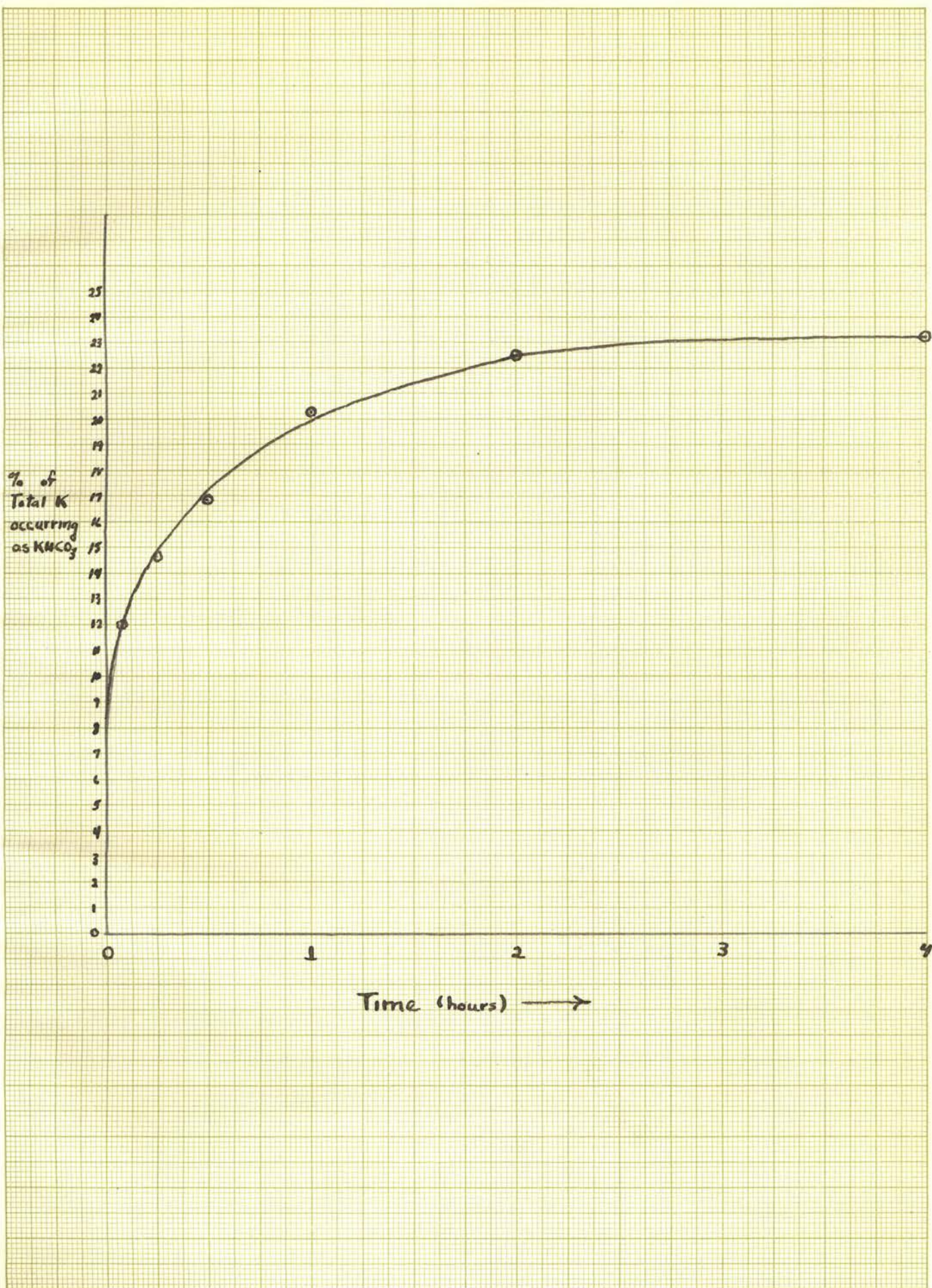
may be included in the total time from the moment of firing to the time when the crucible is removed from the bomb without seriously complicating the overall time of reaction. As will be seen, the percents of potassium converted follow a consistent course as a function of time. We have, therefore, used this curve in estimating the extent of this reaction for these experiments. It has been assumed that the time of completion of the reaction as it was carried out may be taken as twenty minutes after the time at which the charge was fired, for the purpose of the calculation. At this time, reading from the curve shows that fifteen percent of each ion mole of potassium present will have been converted to $KHCO_3$. The further application of this result will be given in the calculations which follow.

Another possibility of estimating the quantity of heat evolved in the formation of $KHCO_3$ might be found in the respective courses of temperature change when it occurs, as with potassium hydrogen phthalate, and when it does not occur as in the combustion of benzoic acid. In Figure 3 are given two curves resulting from combustion of such quantities of potassium hydrogen phthalate and of benzoic acid as would give approximately equal quantities of heat. As will be seen, these curves are not significantly different. The lag between the time of evolution of heat in the bomb and the time when it becomes apparent upon the thermometer is such that it would pretty certainly cover up any such change, especially since this quantity of heat is relatively small.

It is believed that, due to the high concentration of CO_2 in the bomb, hydration of K_2CO_3 as taken apart from the reaction to

Figure 3 Comparison of Time-Temperature Relationships for C_6H_5COOH and $KHC_8H_4O_4$ Runs
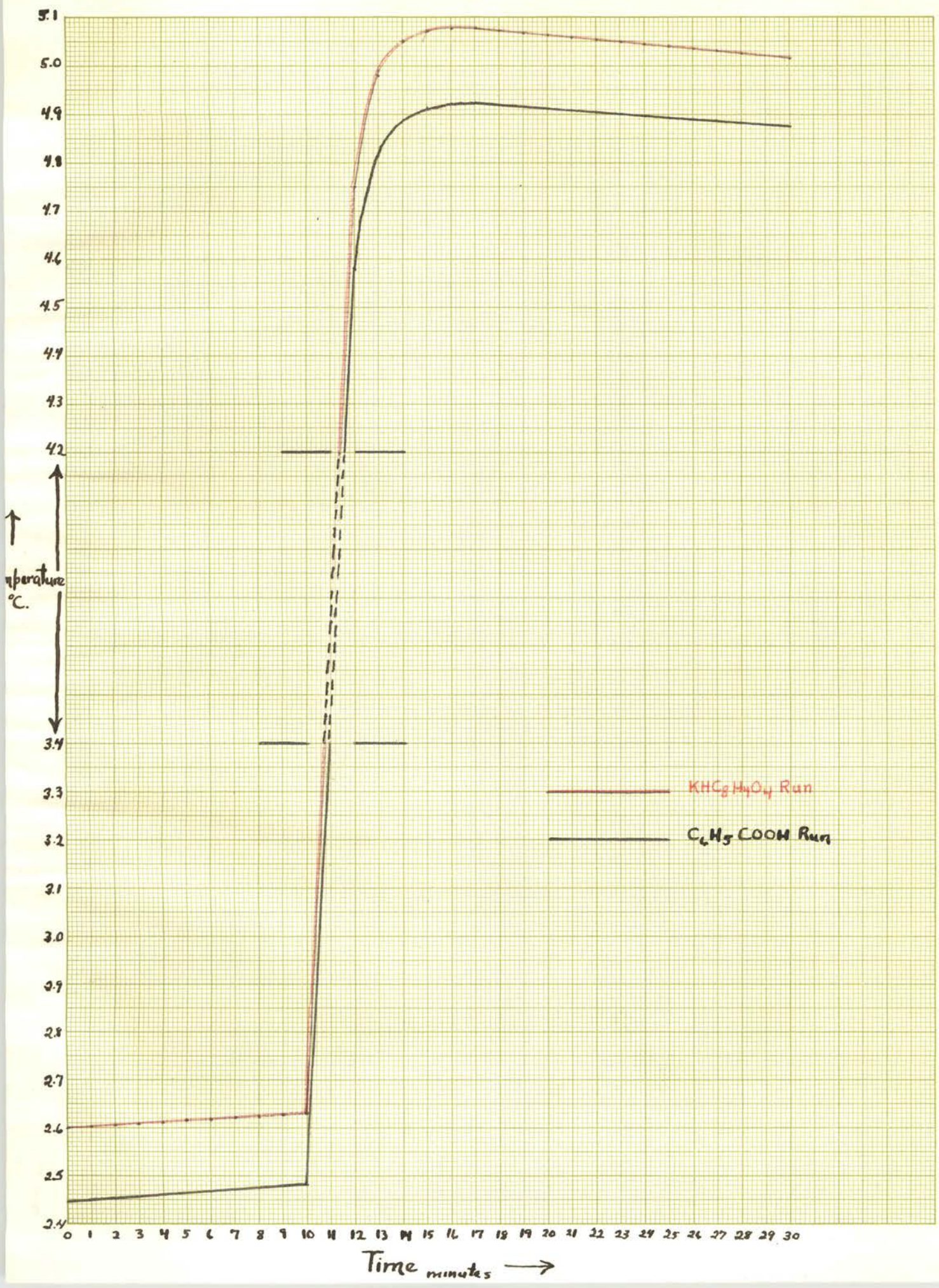
form $KHCO_3$ did not occur in these experiments. Adsorption of the
gases as such was probably not a factor, either. In any case, if they
did occur, they were included in the overall heat evolved in the
reaction. They would constitute a source of error which cannot be
estimated. It has been assumed that they do not occur.

CORRECTION FOR THE HEAT OF FORMATION OF $KHCO_3$.

For the reaction:

$$K_2CO_3(s) + CO_2(g) + H_2O(g) = 2KHCO_3(s)$$
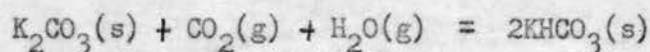
Δ H is -33.69 calories per mole of K_2CO_3 reacting. This calculation employs the values of heats of formation of the respective substances given by Bichowsky and Rossini[13]. These values are for 18°C. They are adopted for these calculations since heat capacity data for some of these substances, which are probably as accurate as the values themselves, are not available. It seems that the heat of reaction at 26.66°C. will not be significantly different from that at 18°C., considering the probable accuracy of these experiments. Assuming that 15 percent of each ion mole of potassium is converted to $KHCO_3$, the correction is .15/2 x -33.69 or -2.53 Kcal. per mole of potassium carbonate formed in the combustion. This correction is to be subtracted algebraically from the heat of the reaction as found to give the heat of the reaction:

$$KHC_8H_4O_4(s) + 15/2\ O_2(g) = 1/2\ K_2CO_3(s) + 15/2\ CO_2(g) + 5/2\ H_2O(l)$$

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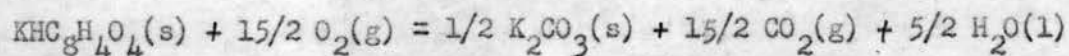
[13] Bichowski and Rossini, Thermochemistry of the Chemical Substances.
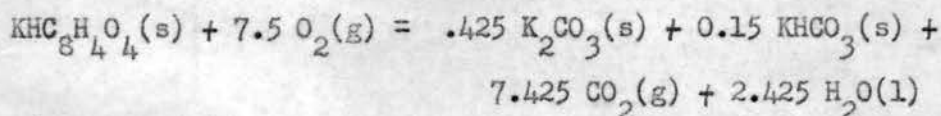
THE HEAT OF THE REACTION.

The combustion of potassium hydrogen phthalate, since it occurs in a bomb (that is, at constant volume) is ΔE in the notation of Lewis and Randall[14]. The complete reaction as it occurs in the bomb is actually:

$$KHC_8H_4O_4(s) + 7.5\ O_2(g) = .425\ K_2CO_3(s) + 0.15\ KHCO_3(s) + 7.425\ CO_2(g) + 2.425\ H_2O(l)$$
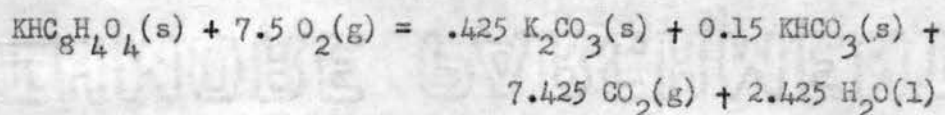
There is a decrease of 0.075 moles in the quantity of gas in the reaction. Since $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta nRT$, ΔH of the reaction is numerically greater than the change in internal energy of the reaction as measured by ΔnRT. Taking Δn as 0.075 this correction is numerically 0.075 x 299.9 x 1.987 or 44.7 calories. This is 0.04 Kcal. per mole. The heat of reaction as measured divided by the fraction of one mole of $KHC_8H_4O_4$ which was burned gives ΔE per mole for the reaction. We then have for the heat of combustion, forming only K_2CO_3:

$$\Delta H = \Delta E + 0.04 - 2.53\ Kcal/mole$$

Alternately, the heat of the reaction:

$$KHC_8H_4O_4(s) + 7.5\ O_2(g) = .425\ K_2CO_3(s) + 0.15\ KHCO_3(s) + 7.425\ CO_2(g) + 2.425\ H_2O(l)$$

may be calculated. It will be $\Delta H = \Delta E + 0.04$ Kcal/mole, where ΔE is the heat of the reaction as measured. This value will be equally satisfactory for many purposes, though it lacks the simplicity which commonly is incorporated in thermochemical equations.

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[14] Lewis and Randall, Thermodynamics and Free Energy of Chemical Substances

RESULTS AND CONCLUSIONS.

In the course of this work numerous determinations of the heat capacities of the bombs and calorimeter accessories and of the heat of combustion of potassium hydrogen phthalate were made straight-forwardly without introducing the various refinements which have been discussed. Though they cannot be reported, it is interesting to note that, though different from these latter values, their inner consistency was equally good. This indicates that the reaction involved proceeded in a highly reproducible manner.

The values found for the heat capacities of the bombs and calorimeter accessories have been presented in a preceding section.

The heats of combustion of potassium hydrogen phthalate, employing all refinements, were eleven in number. They are given in Table VI.

TABLE VI
Heats of Combustion of Potassium Hydrogen Phthalate

Experiment #	Heat of Combustion ($-\Delta E$) in calories/gram
1	3750.9
2	3752.4
3	3754.5
4	3748.4
5	3755.8
6	3753.4
7	3756.6
8	3755.8
9	3754.5
10	3752.0
11	3753.9

Average $-\Delta E = 3753.4 \pm 1.9$ calories/gram

$= 766.52 \pm .39$ Kcalories/mole

For ΔE for the reaction as it occurs in the bomb reaction we find
-766.52 ±0.39 Kcal., the average deviation being that for the
experimental results. It seems probable that the deviations due to
specific sources of error will fall within the limits of the
deviation as here given. Applying the corrections as discussed in
a former section the value of ΔH for the reaction

$$KHC_8H_4O_4(s) + 7.5\ O_2(g) = 0.5\ K_2CO_3(s) + 7.5\ CO_2(g) + 2.5\ H_2O(l)$$

is -764.03 ± 0.39 Kcal./mole.

From this value it follows that the heat of formation of this
salt from its elements is -252.58 ±.39 Kcal./mole.

SUMMARY.

Methods for the determination of the heats of combustion of metal-organic compounds have been studied in a preliminary way by an investigation of the heat of combustion of potassium hydrogen phthalate.

A new and convenient method for arriving at the corrected temperature rise in a calorimetric experiment is presented.

Some of the modifications of usual combustion methods which are necessary in this new field have been studied, particularly as they apply to this salt; and a method for determining the heats of combustion of such salts has been worked out.

The heat of combustion of potassium hydrogen phthalate has been found to be $\Delta H_{(combustion)} = -764.03 \pm 0.39$ Kcal./mole.

Its heat of formation from the elements has been found to be $\Delta H_{(formation)} = -252.58 \pm 0.39$ Kcal./mole.

BIBLIOGRAPHY

Andrew, R. E. "A Modified Test for Phthalates." Journal of Industrial and Engineering Chemistry, 15, 838 (1923).

Beilstein. "Phthalsaure." "Isophthalsaure." "Terephthalsaure." Volume IX, pp. 791, 833, 841. Berlin: Julius Springer, 1926.

Bichowski, F. Russell and Rossini, Frederick D. Thermochemistry of the Chemical Substances, New York: Reinhold Publishing Company, 1936.

Dickinson, H. C. "Combustion Calorimetry and The Heats of Combustion of Cane Sugar, Benzoic Acid, and Naphthalene." Bulletin of the Bureau of Standards, Department of Commerce, Volume 11, No. 2, p. 190. March 1, 1915.

Ephraim, Fritz. Inorganic Chemistry. New York: Interscience Publishers, Inc.

Kelly, K. K. and Anderson, C. T. "Metal Carbonates – Correlations and Applications of Thermodynamics." Bulletin of the United States Department of the Interior, Bureau of Mines, Bulletin #384 (1935).

Kharasch, M. S. "Heats of Combustion of Organic Compounds." Bureau of Standards Journal of Research, 2, 359 (1929).

Lewis, G. N. and Randall, Merle. Thermodynamics and Free Energy of the Chemical Substances. New York: McGraw-Hill, 1923.

Parks, G. S. and Huffman, H. M. The Free Energies of Some Organic Compounds. New York: Chemical Catalog Company, 1932.

Takahashi, E.
    Nippon Kinzoki Gakukai-Si 1, 26-40, 104-12 (1937).
    Abstracted in: Metallurgical Abstracts (in Metals and Alloys) 9, No. 1, 22 (1938).
    Abstracted in: Chemical Abstracts, 32:4865.

Voiret, E. G. and Bonaime. "Improvement in Use of Palladous Chloride as Reagent for CO." Ann. chim. anal. 26, 11-12 (1944).
    Abstracted in: Chemical Abstracts 40, 1105 (1946).

White, Walter P. The Modern Calorimeter, New York: Chemical Catalog Company, 1928.

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