nent for thirty seconds is obtained. In addition to the poor end-point, a small amount of reagent is used up by the aldehyde. As much as 10% of aldehyde does not seriously affect the analysis of alcohols. 50% solutions of isobutyraldehyde and 2-methylpenten-2-al-1 both gave unsatisfactory results even when the above precautions were taken. Nevertheless, the acetyl chloride procedure is definitely superior to the acetic anhydride procedure for the analysis of samples containing aldehydes. The latter reagent seems to combine with aldehydes to an appreciable extent and so lead to erroneous hydroxyl determinations.

Ketones produce only slight effects which are readily corrected by control experiments. Analyses of pure samples of acetone, 2-methylpentanone-4 and 2,4-dimethylpentanone-3 showed 1.4, 1.1 and 0.1% reaction calculated as the isomeric unsaturated alcohols.

The authors extend their thanks to Mr. W. A. Morgan for part of the analytical work connected with this research and to Mr. J. B. Evans for analyses of isobutanol and castor oil.

Summary

1. A rapid and precise method for the determination of primary and secondary hydroxyl groups in organic compounds, based on the use of acetyl chloride and pyridine, has been developed. Analytical results for more than thirty alcoholic and phenolic substances are reported.

2. Comparative experiments employing the new method and an accepted form of the acetic anhydride–pyridine method show that the results of the two methods are entirely comparable.

3. Under similar conditions of reagent concentration and temperature and in the presence of pyridine, acetyl chloride is a more reactive acetylating agent than acetic anhydride.

4. The matter of interfering substances is discussed briefly.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Heats of Organic Reactions. I. The Apparatus and the Heat of Hydrogenation of Ethylene

BY G. B. KISTIAKOWSKY, H. ROMEYN, JR., J. R. RUHOFF, HILTON A. SMITH AND W. E. VAUGHAN

The majority of those who have met with the necessity of computing the heat of some organic reaction have probably felt discouraged because of the unreliability of the result obtained, due to uncertainty in the combustion data. Often not even the sign of the heat change, much less its magnitude, can be predicted for small structural change in the molecule. Although the newer work, particularly that of Rossini, greatly exceeds in precision the classical measurements of Thomsen and Berthelot, it is an inherent feature of the method that, as the molecular weight of the substance studied increases, the absolute error in the molar heat of combustion becomes proportionately larger. For this reason, Dr. J. B. Conant and one of the present writers—in common with many others, undoubtedly—have felt the need for a calorimetric procedure capable of yielding more accurate thermal data for higher molecular weight compounds. The direct measurement of the heat of an organic reaction rather than the determination of the difference of the heats of combustion of the reactants and products offers many possibilities. Although this method has been used occasionally in the past, it has never been developed systematically—probably for the reason that not many reactions have been sufficiently quantitative and clean-cut for calorimetric work. However, with catalysts and methods known today, a sufficient number of compounds and reactions can be investigated to make this method worthy of a thorough test.

Catalytic hydrogenations, in particular, seem likely to give interesting and valuable data. Not only can the heat of hydrogenation itself be determined, but by a combination of several such measurements, thermal data for other reactions can be obtained indirectly. The advantage of this device, quite analogous to the combustion method, of course, is that since the heat of hydrogenation is a much smaller quantity than the heat of combustion, more accurate values for the differences in heat content of organic compounds can be obtained, although the calorimetric procedure is less precise. Of course, the method as outlined has many limitations and cannot replace combustion calorimetry. It is hoped, however, that it may complement combustion measurements, particularly where there is a dearth of accurate data.

Through a generous grant from the Rockefeller Foundation it has now become possible to put the outlined suggestions to a practical test under conditions which should ensure the best possible results.

The present paper describes the method adopted for the study of catalytic hydrogenations and halogenations in the vapor phase at atmospheric pressure and at temperatures below 150°. The first phase of the work is the study of the effect of structural changes on the heat of hydrogenation of the carbon-to-carbon double bond, this paper dealing specifically with the results obtained in the hydrogenation of ethylene.

The Method

The standard calorimetric procedure of observing the temperature of the calorimeter before and after the actual run, and computing the temperature rise after applying certain corrections to these observations, is not well suited for use with the large masses of catalyst necessary for rapid and complete hydrogenation in the vapor phase. The adsorption of the reactants and the products, and their subsequent desorption in the after-period, a process which is usually very slow, would cause thermal effects for which it would be very difficult to correct; furthermore, the danger would always be present that some of the substances may have been lost by irreversible adsorption on the body of the catalyst. The method here adopted attempts to minimize these sources of error by the study of the temperature rise over a period during which the catalyst is in a steady state, in so far as processes of adsorption are concerned.

A constant stream of the reactant gases is passed over a catalyst contained in an adiabatic calorimeter, and the products are discharged as waste until the calorimeter has reached a state of steady change, and the time-temperature relationship has become linear. A short time later, without disturbing in any way the flow, the effluent gases are directed to the measuring unit, and the temperature of the calorimeter is noted at the instant of change. During the ensuing interval the quantity of gases which pass through the calorimeter is measured. After the desired temperature rise in the calorimeter has occurred, the gas flow is changed instantaneously from the measuring device to waste and the temperature of the calorimeter is again noted. These operations give the temperature rise caused by the heat evolved from the measured quantity of reacting gases. The electrical energy equivalent of the calorimeter is obtained by supplying electrical energy at a constant rate and determining the rate of temperature change. This is done by measuring the temperature rise for an arbitrary time interval during which the time-temperature relationship is linear, and for which the total energy input is known. From these data, after a correction has been applied, the heat of the reaction can be calculated. A method of this type probably is not capable of being developed to such high precision as the standard calorimetric procedure. However, results have been obtained which are precise to nearly 0.1%. Since this is sufficient for the purpose in hand, the method has proven satisfactory, and seems to be free from the gross systematic errors which probably would have been present if the standard calorimetric procedure had been used.

Apparatus

The calorimeter proper is a conventional gold-plated cylindrical copper can of about 1.5 liters volume, with a tightly fitting cover. It is suspended in a gold-plated calorimeter jacket of the Richards "submarine"[1] design by three thin rods of low conductivity chrome-nickel steel which provide a rigid mount; the interspace is about 3 cm. wide on all sides. The calorimeter contains a central propeller-stirrer driven by a synchronous motor through a positive drive; a glass reaction vessel, containing the catalyst; an electric heater; and two multiple junction thermocouples, denoted in the following as thermels. The reaction vessel (see Fig. 1) of elongated annular shape, is followed by a glass spiral containing 2 meters of 5-mm. tubing, through which the gases must pass before leaving the calorimeter. Experiments with electrically preheated gases have shown that the length of this spiral is more than sufficient to ensure heat exchange which is complete within the experimental error. The vessel is mounted coaxially with the stirrer and acts as a baffle, distributing the flow of liquid uniformly throughout the calorimeter. The electric heater, of some 40 ohms resistance, modeled after Gucker's[2] design, is mounted flush with the inner wall of the reaction vessel. The potential wires, as usual, are attached at the midpoint between the calorimeter and the jacket. One of the thermels, containing 12 junctions,

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(1) Walter P. White, "The Modern Calorimeter," Chemical Catalog Co., N. Y., 1928, p. 150.

(2) Gucker, THIS JOURNAL, 50, 1005 (1928).

serves to maintain the adiabaticity; the other, having 16 junctions, acts as the thermometer. The copper–constantan thermels are made of carefully selected wire,[3] and are insulated with silk and cellulose acetate. Wherever rapid heat exchange with the surroundings is needed, the thermels are encased in thin silver tubes, 4 junctions to the tube, the interspace being filled with an 80–20% Cumar wax–rubber mixture melting at about 180°.[4] Other parts of the thermels are encased in glass. These thermels will stand prolonged heating to 150° and a brief heating to 200° without deterioration. The outer ends of the adiabatic thermel project some distance above the cover of the calorimeter jacket into the liquid of the bath, which is rapidly circulated. All other connections to the calorimeter are also immersed for some distance into the liquid of the bath before coming in contact with the outside air. The bath, of some 30 liters capacity, contains, besides the stirrer, a very low lag bare-wire electric heater. The response of the adiabatic thermel to this heater lags by about ten seconds.

From the outset of the work it was felt that the calorimeter should be so designed as to work satisfactorily at elevated temperatures, 150° being set as the tentative limit. Thereby the use of less powerful catalysts is made possible, and the usefulness of the method is extended to substances boiling well over 100°. Such a requirement eliminates water as the calorimeter liquid; after some trials diethylene glycol was found to satisfy the needs not only for the calorimeter but also for the bath. It has a very low vapor pressure, low viscosity at elevated temperatures, and quite a high volume-heat-capacity. Its great disadvantage, as we have found, is its chemical reactivity, which has caused much trouble and delay and is not much lessened by the addition of inhibitors. The difficulties were overcome, finally, by coating all soft-soldered joints and all silk- and cellulose-acetate-covered wires with a layer of high melting asphalt which prevents corrosion and short-circuits.

The apparatus, including the calorimeter and a reference temperature bath, is mounted within a large air thermostat maintained steady to ±0.1°, just below the working range of the calorimeter. This ensures that no considerable temperature gradients are present near the vital parts of the apparatus, so that the working conditions approximate more nearly those at room temperature.

Since only temperature changes, and not absolute temperatures, are measured by the thermometer thermel, the temperature of the reference junctions need not be known very accurately, but need only be kept constant. It is obviously advantageous that this temperature be very near the working temperature of the calorimeter, since the total e. m. f. of the thermel will be small and the changes can be measured more accurately. The reference junctions are immersed in a 2-liter narrow-necked Dewar flask filled with diethylene glycol. The Dewar itself is immersed in a thermostat filled with oil and maintained approximately 2° above the temperature of the surrounding air. The temperature of the thermostat varies less than 0.002° during any one day and drifts at the rate of about 0.02° a month. The contents of the Dewar are stirred gently; the heat of stirring keeps the Dewar liquid steady at 0.25° above the thermostat. When the stirring is stopped, the steady state of the Dewar is 0.003° below the temperature of the thermostat. Since the surroundings, *i. e.*, the air above the Dewar, are 2° colder, the heat exchange between the Dewar and the surroundings is clearly very small. The heat leak from the Dewar to the thermostat causes the temperature of the former to change by 3% of the temperature difference per hour. These details are given to show that even should the Dewar temperature drift, the rate is nearly constant over the few hours necessary to execute all the measurements of associated chemical and electrical runs.

Thermels are provided for reading the temperatures of the calorimeter bath, the Dewar and the oil thermostat.

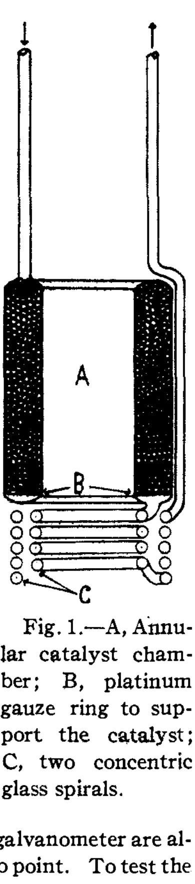

Fig. 1.—A, Annular catalyst chamber; B, platinum gauze ring to support the catalyst; C, two concentric glass spirals.

The adiabaticity of the calorimeter is maintained almost automatically. The adiabatic thermel is connected to a stable, short-period, Moll galvanometer operating a relay through a photocell–amplifier device.[5] The function of the relay is a double one: it operates a small on-and-off current for the calorimeter bath and also a magnetic reversing clutch on a drive from a motor which slowly turns a variable autotransformer,[6] on the secondary of which is the main heating current of the calorimeter bath. When the on-and-off current is on, the transformer is uniformly increasing the energy input and when the auxiliary current is off, the main energy input is decreasing. Clearly, when left to itself, the tendency of this device is to adjust the energy input to such a value that the auxiliary current is half of the time on and half of the time off.[7] In the beginning of a run the energy input is adjusted manually but within a few minutes the automatic mechanism corrects the error of the setting and later supplies increased energy as the temperature of the calorimeter rises above the temperature of the surrounding air thermostat. Thus the swings of the Moll galvanometer are always quite symmetrical around the zero point. To test the effectiveness of the adiabatic mechanism, the photocell was shifted sideways from its usual position a distance about equal to double the amplitude of the galvanometer swings. An electric energy equivalent determination then made differed by less than 0.1% from the value obtained with the normal setting of the photocell, corresponding to zero temperature difference between the calorimeter and the outer bath. This was to be expected from a consideration of the following numerical data. The heat leak from the calorimeter to the jacket amounts to 1.6 × 10^{-5} of the

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(3) Walter P. White, *Rev. Sci. Inst.*, **4**, 142 (1933), gives a detailed description of thermel construction.

(4) We are greatly indebted to the Barrett Co. for generously supplying us with this and other insulating materials.

(5) Constructed by the G. M. Laboratories.

(6) The Variac of General Radio Co.

(7) We are greatly indebted to Dr. A. L. Loomis of Tuxedo Park for suggesting the idea of this temperature control method.

temperature difference per second (when the temperature difference is small). The displacement of the photocell was equivalent to 0.028° temperature difference between the calorimeter and the bath. The run occupied 1700 seconds, during which time the temperature of the calorimeter changed by 1.4°. Thus the leak accounted for 0.0008° temperature change, or 0.06% of the total. Further evidence, for the proper functioning of the adiabatic mechanism, is furnished by the observation that, within experimental error (see Fig. 3), the electrical energy equivalent of the calorimeter does not depend on the rate of electric energy supply during calibrations.

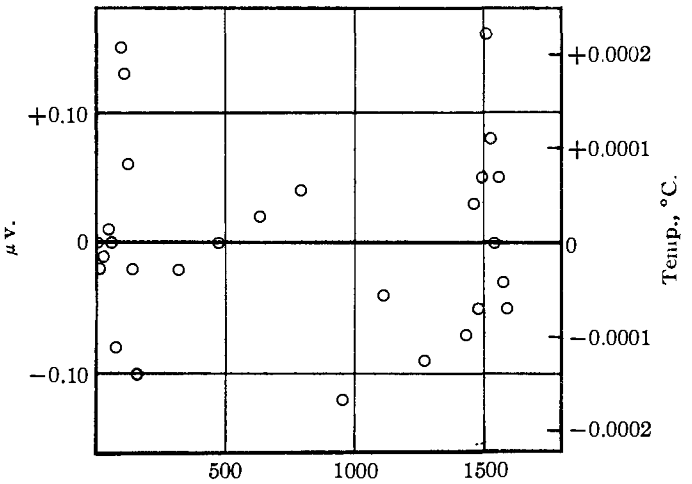

Fig. 2.—Deviations from linearity for a single calibration run.

The power input for the electrical energy equivalent calculations is obtained from current and voltage measurements made by means of a calibrated standard resistance and a calibrated potential divider on a Diesselhorst potentiometer constructed by Wolff. The energy supplied changes linearly and by less than 0.05% during the half hour or so of the run; its value is checked at regular intervals and the average used. Time is measured by means of a master clock which registers one-second intervals on a paper tape. The temperature of the calorimeter is measured with the aid of a low-range Wenner potentiometer,[8] made by Leeds and Northrup. The potentiometer is set each time at a certain reading, and at the instant the galvanometer crosses the zero line, by means of a tapping key the observer sends a signal to the timing tape. Such measurements are registered on the tape at regular intervals during the entire run. When the electromotive force of the thermometer thermel is found to change strictly linearly with time, the rate of this change divided into the power input gives the electrical energy equivalent of the calorimeter, a microvolt being chosen as the unit of temperature. For the actual calculations, the exact degree-equivalent of the microvolt is immaterial. As a matter of fact, 720 microvolts are about equal to one degree at 82°, the average working temperature of the calorimeter, but this ratio increases slowly with temperature.

All external electrical circuits are made of inspected copper wire and switching or reversing is done by oil immersed copper switches.

The type of results thus obtained is shown in Fig. 2, which gives single readings of an electric run chosen at random. Here, to bring out the errors, a linear function of time has been deducted from all e. m. f. measurements; the plot covers a temperature change of the calorimeter equivalent to 1000 microvolts or 1.4°.

Hydrogen used in the hydrogenations is supplied from a tank.[9] After passing through the usual and then through a fine adjustment reduction gage, it is led into a long furnace filled with platinized asbestos at 300°, then through long tubes filled with moisture and carbon dioxide absorbers (Dehydrite and Ascarite) and thence a flowmeter followed by a tube of catalyst identical with that used in the calorimeter. The purpose of this catalyst tube—and a similar one used for the other gas—is to remove catalyst poisons from the gases, which have caused some difficulties in the early stages of the work. With the tubes in, the catalyst in the calorimeter was found to remain active even after more than two months of continuous experimentation and heating to 80–90°.

The gas to be hydrogenated—ethylene in the present case—after passing a reduction gage, flows through an automatic flow-regulating device capable of maintaining the rate constant even though the back pressure may be changing slowly. This device was found necessary as the reduction gages were inadequate to maintain the flow to the constancy desired. Small variations in the flow of hydrogen, which is present in excess, are immaterial and thus a reduction gage is sufficient. Ethylene passes a flowmeter, a tube filled with the catalyst and is then mixed with the hydrogen. Both gases flow through a glass spiral 2 meters long immersed in the calorimeter bath to be heated to the temperature of the calorimeter before entering it. Hydrogenation occurs on about 100 g. of copper catalyst prepared by reduction of Kahlbaum copper oxide, analytical grade, in hydrogen at 180–200°. After reduction, the copper is not brought into contact with the air. This catalyst is sufficiently active to hydrogenate 50 cc. or more of ethylene per minute even at 0° to the extent of 99% or more. Nevertheless, it is probably the mildest catalyst[10] in that no cracking or carbonization of hydrocarbon accompanies the hydrogenation of the double bond. This is clearly a debatable point and evidence will be presented later to substantiate this contention.

It seemed essential to determine whether the maintained constancy of the ethylene flow—which can be estimated to 0.2% or better for periods up to an hour—was sufficient for our purposes. Experiments were made therefore in which the ethylene flow was changed in the middle of the runs (Nos. 11A and 11B of Table IV). An increase of the flow by 10% caused an increase of the apparent heat of hydrogenation by 0.32%; a decrease of the flow by 10% also an increase, this time by 0.17%. Although we

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(8) Described by Leo Behr, *Rev. Sci. Inst.*, **3**, 109 (1932).

(9) Electrolytic hydrogen of Ohio Chem. and Mfg. Co.

(10) *Cf.* Rideal and Taylor, "Catalysis," Macmillan Co., N. Y., 1926.

are unable to account for these results completely, since from a simple consideration of the effect of thermal lags in the calorimeter it seems that an increase and then a decrease of rate of flow should change the heat of hydrogenation in opposite directions from the mean, still it is clear that the small variations in the ethylene flow present in regular experiments cannot have an appreciable effect on the final results.

After leaving the calorimeter, the gases pass through a special double needle valve, a half-turn of the handle sufficing to send the stream either to the outside or into the gas-measuring system. The flow of the gases is not interfered with in the instant of turning and flow resistances are balanced in both paths of the gases. At the instant of turning the valve an electric contact automatically sends a signal to the same tape on which is recorded the time and the temperature of the calorimeter. Suitable devices provide that even should the needle valve leak, no loss of gas from the measuring system occurs during the run and none enters it during the fore- and the after-periods.

During the fore-period in each chemical run a sample of the effluent gases is collected in a one-liter flask for a test of the completeness of the reaction. The analytical method devised is capable of detecting fairly accurately as little as 0.1 cc. of ethylene in one liter of hydrogen–ethane mixture. A small ampoule containing a weighed quantity of bromine is broken in the flask and the mixture is exposed for one minute to radiation from a 500-watt lamp at 15 cm. distance. Potassium iodide solution is then added and iodine titrated in the usual way. Table I shows some of the results selected at random.

TABLE I

DETERMINATION OF ETHYLENE

Ethylene used, cc., N. T. P.	Bromine added, mg.	Bromine found, mg.	Bromine lost, mg.	Ethylene found, cc.	Other gases present
None	4.9	4.8	0.1	0.01	H_2
None	14.9	15.0	− .1	− .01	H_2
None	14.3	13.7	.6	.09	C_2H_6
None	15.6	15.0	.6	.09	C_2H_6
1.02	15.6	8.9	6.7	.94	H_2
0.29	9.7	7.3	2.4	.32	H_2
.74	14.6	10.2	4.4	.67	90% H_2 10% C_2H_6

No substitution reaction was found to occur when ethylene and ethane were used, but a correction for this becomes of importance when applying this method to higher hydrocarbons, as has been done now and will be described in a later paper. The ethylene found in ethane, when none was added, is due not to substitution reaction but to traces of impurities in the commercial ethane used, which were reduced but not completely eliminated by the process of purification to which it was subjected before use. The chief errors of the method are those in weighing the bromine, and in losses of bromine when introducing the potassium iodide; they could be further reduced if desired.

The hydrogenation of ethylene in the calorimeter has always been found by this method to be complete and the procedure adopted to determine the amount of reaction during a run consisted in burning the effluent gases and determining carbon dioxide gravimetrically. Upon leaving the special needle valve the gases are burned at a nozzle in a stream of purified tank oxygen and immediately enter a furnace filled with platinized pieces of quartz[11] heated to about 800°. The flame is started by a spark and to prevent backfire at the start and the finish, a stream of purified nitrogen flows through the nozzle until the needle valve is turned on and the nitrogen is again started a few seconds before the valve is turned off. The presence of nitrogen in the flame even during a short time results in the formation of nitrogen oxides which are afterward weighed as carbon dioxide. It has been found necessary therefore to standardize the amount of nitrogen passing through the flame so as to apply a consistent correction to the weights. Table II shows tests made to determine the cause of the formation of nitrogen oxides.

TABLE II

FORMATION OF NITROGEN OXIDES

Gas flow, cc./min. H_2	O_2	N_2	Procedure	Duration of flame, minutes	Increase, mg.
330	400	on-and-off	Standard	30	4.6
320	440	on-and-off	Standard	30	1.8
320	380	on-and-off	Standard	30	2.6
320	400	on-and-off	Standard	60	2.5
				Average	2.9
...	400	200	No flame; spark only for 2.5 minutes		0.5
300	400	200	Flame on for a few seconds only		1.1
320	390	50	Continuous flow of nitrogen	30	11.9
320	390	50	Continuous flow of nitrogen	60	41.0

Apparently nitrogen oxides are formed in the flame and not in the spark alone. The uncertainty of the weight correction may be as large as 1 mg. or slightly more, but this uncertainty (which we purposely overestimate) would amount to but 0.03% error in even the smallest weights of carbon dioxide.

Upon leaving the furnace, most of the water vapor is condensed in a trap cooled with ice and the remainder is removed by two large tubes filled with Dehydrite, the second of which is systematically weighed for constancy to ensure efficiency of the first. Carbon dioxide is absorbed in special tubes containing Ascarite, three of which are used in the train, although most of the absorption always occurs in the first and none in the third. These tubes are provided with Dehydrite to prevent losses of moisture. Methods of assembly, handling, weighing and bringing to constant weight of all tubes, as developed by Professor G. P. Baxter, have been utilized freely in the present work and the detailed procedure may be found in his publications. After a run, water condensed in the trap is boiled, of course, while air is led through the train to bring the tubes to constancy. Vacuum corrections are applied to all weighings. For all calculations the molecular weight of carbon dioxide has been assumed to be

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(11) Unsatisfactory results were experienced with furnaces containing ceric oxide on pumice and with platinized asbestos.

44.000. To determine the accuracy of the analytical method, sealed tubes containing known amounts of pure *n*-heptane were broken in a stream of hydrogen, and the gases burned in precisely the same manner as above. To conserve space, no further details will be given, except to remark that the accuracy thus obtained is about 0.05% on one-gram samples of heptane—these giving about the same amount of carbon dioxide as the calorimetric runs with ethylene.

It has been found that chemical runs show larger average deviations than the electrical energy equivalent determinations. This is to be expected because in the latter the only error of significance is that of temperature measurement, while in chemical runs a variety of other errors such as those in weighing, and in starting and stopping the flame, are also of importance.

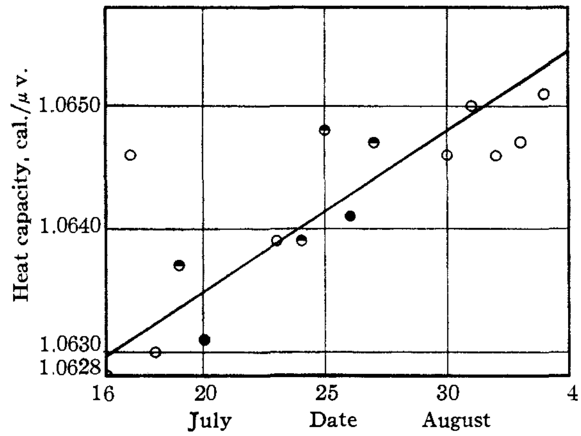

Fig. 3.—Change of heat capacity with time (for all chemical experiments). ○, 10 volt heating; ◓, 8 volt heating; ●, 12 volt heating.

Since, furthermore, there is very little change in the electrical energy equivalent (in calories per microvolt of the thermometer thermel) over the temperature range used and since only three runs can be made every day, the following procedure has been adopted; namely, that of making two chemical runs with an intervening electrical determination. This latter is used for both chemical runs. Even should there be a steady change in the electrical energy equivalent while the calorimeter is gradually warming during the day, the average of the two chemical runs would still be correct, as their mean temperature coincides closely with the mean temperature of the electrical experiment. The change of the electrical energy equivalent per μ v. with temperature has been investigated and found to be less than 0.1% over the 7° range used in experiments, a slight *decrease* with increasing temperature having been observed. Between all runs determinations of the heat of stirring are made. These form the only correction applied to the electric temperature measurements. They amount to 1–2% of the total temperature change in various runs and represent the combined correction not only for the actual heat of stirring, but also for possible slow drifts in the temperature of the reference bath. They would also rectify errors caused by the incomplete preheating of the entering gases, but it has been found that the heat of stirring is completely independent of gas flow. The heats of stirring are reproducible to about 15% over long intervals of time, and show a slight upward drift during each day. As the stirring correction is applied in the same manner to the electrical determinations and to the chemical runs, the correction nearly cancels out in the final result. It would disappear completely if the same rate of temperature change was maintained in electrical and in chemical runs; this, however, is inconvenient for practical reasons, although the two rates are usually within 10% of each other. In Fig. 3 are shown electrical energy equivalent determinations made during work on ethylene. Aside from an unmistakable trend, which has been traced definitely to a trivial cause, these measurements show mean deviation of about 0.03%.

It has been found that the time necessary for the calorimeter to reach a steady state in the electrical calibrations—for the temperature to change linearly with time—is only a few seconds. In the chemical runs the lag is considerably greater but even this amounts to only about two minutes as Fig. 4 shows. To be quite certain, ten minutes from the start was allowed in both the electric calibrations and the chemical runs before measurements were taken.

In chemical runs a systematic error due to adsorption of gases on the catalyst may be present because the material changes its temperature during a run and is thus not quite in a stationary state. All electrical energy equivalents were determined therefore with the usual rate of hydrogen flowing through the calorimeter, although no difference could be noticed between this procedure and runs without hydrogen. Further evidence of the absence of this error is offered by the following experiments. A duplicate of the catalyst vessel in the calorimeter, filled with active copper in the same manner, was placed in the path of the mixed gases before they enter the calorimeter and was maintained at 80°, so that hydrogenation occurred on this first catalyst. An electrical determination was made when only hydrogen was flowing; it gave 1.0655 cal./microvolt. Then, while a typical ethylene–hydrogen mixture was passed through the catalysts, a second electrical determination yielded 1.0649 cal./μ v. Finally, another run, with hydrogen only, gave 1.0649 cal./μ v. Clearly, since the thermal effects of adsorption are too small to be noticeable, our general procedure is justified. It is perhaps too much to claim that this experiment gives additional confirmation to the chemically established completeness of the reaction or proves that no degradation or polymerization of the hydrocarbon takes place; but on the other hand it would be rather unusual if all these thermal effects just cancelled each other, and it is much more probable that none of them is present.

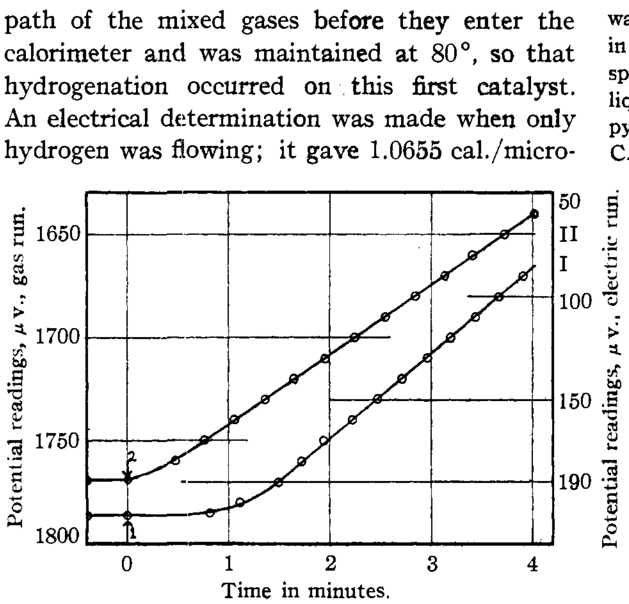

Fig. 4.—I, Chemical run with ethylene at 26 cc./min.; hydrogen at 300 cc./min.; ethylene flow through calorimeter begun at point 1. II, Electric calibration with 10 volts on heater; heating begun at point 2.

The Ethylene

Three samples of ethylene have been used in the course of the present studies. One is a commercial ethylene, made from ethyl alcohol and rated 99.5% pure by the makers. They suggest air as the impurity; in addition we found some diethyl ether to be present. The next sample was made from petroleum products by the Linde Air Products Company, who carefully purified it by fractional distillation. It was rated 99.8 + % pure. The third sample was prepared here from the commercial ethylene by double fractional distillation. The still used was designed to work at constant pressure of one atmosphere, the column being modeled after those of Podbielniak.[12] It is one meter long and 8 mm. in diameter with a spiral of No. 18 nichrome wire as packing. The head was designed for partial return and is shown in Fig. 5 in which shaded parts represent copper. The annular space, A, during operation is constantly being filled with liquid air, while B is filled with liquid hydrocarbon (propylene and propane were used), stirred by the ring plunger, C. The rate of stirring was found to provide a very convenient method of controlling the supply of cold to the centrally located still head, this depending only slightly on the level of the liquid air in A, provided that the intervening wall was made of sufficiently heavy copper (about 4 mm. thick). The temperature was measured with a four-junction thermel in the well, E. The still is attached to an all-glass apparatus consisting of several bulbs for collecting the fractions, a provision for a double bulb-to-bulb distillation *in vacuo* (the last stage being carried out in the absence of stopcock grease), an attachment for transferring *in vacuo* the ethylene to Monel metal cylinders for storage, and the usual high vacuum pumping system. The device described by Shepherd[13] for comparing vapor pressures of different fractions is also present. After ethylene is placed in the still pot for the first distillation, it never comes in contact with air, an atmosphere of pure nitrogen being maintained in the apparatus during the fractionation; later vacuum is maintained. The distillations were carried out with a 10:1 reflux ratio. The middle fraction of the first two distillations, comprising about 50% of the total used, was returned to the pot for the second distillation, 50% again comprising the middle fraction. Before the distillation which produced the material used in the reported hydrogenation experiments, the still head was broken; during the emergency repairs, the thermel well was accidentally misplaced from the central position in the head. This caused irregular fluctuations of temperature amounting to 0.3° during the distillation of the middle fraction. A better idea of the boiling range of the middle fraction is gained from a comparison with an earlier distillation (the products of which were used up in preliminary experiments), which was carried out under precisely identical conditions. Here the boiling range was 0.08° and even this figure chiefly represents irregular fluctuations dependent more on the slight variations in the rate of distillation, than on the amount already distilled. The boiling point was −103.9° at 767.5 mm. The differential vapor pressures of the first cc. of the first

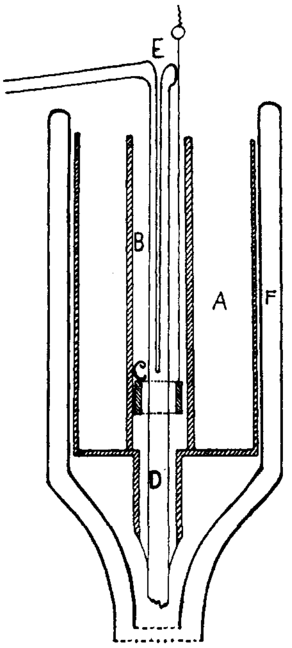

Fig. 5.—A, Liquid air jacket; B, hydrocarbon jacket; C, stirrer; D, column; E, thermocouple well; F, Dewar jacket.

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(12) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

(13) Shepherd, *Bur. Stand. J. Research*, **2**, 1156 (1929).

fraction from the second distillation and of the last cc. from the last fraction were studied, but without much success, perhaps because this was done at the end of distillations lasting twenty hours. The differences were irregular, sometimes one, sometimes the other, fraction having the greater vapor pressure and we can only say that the differences are less than 1 mm. at −112° and below.

The freezing points of the several ethylene samples were determined; precautions were taken that they came into contact with no gases. Stirring was done magnetically at a constant rate. Temperature was read with a copper–constantan thermocouple and was reproducible with different fillings taken from the same sample to 1.0μ v. or 0.05°. This and the four-junction thermel were calibrated with sodium sulfate decahydrate, freezing mercury, subliming carbon dioxide and boiling oxygen and the temperatures computed from "International Critical Tables"[14] to which a quadratic correction was applied. Table III gives the freezing points and shows that they all are, almost within the error of measurement, the same.

TABLE III

FREEZING POINTS OF ETHYLENE SAMPLES

Sample	Temperature, °C.
Middle fraction from double distillation	−169.44
Last fraction	−169.50
Linde Company sample	−169.51
Commercial sample	−169.50

From the reproducibility of the calibrations at standard temperatures and the accuracy of interpolation, we believe that the absolute values of the melting points are correct to about 0.1°.

Heat of Hydrogenation of Ethylene

Table IV presents all experiments made on the heat of hydrogenation of ethylene with the final form of the calorimeter. No runs have been omitted from the table for any reason whatsoever. Many earlier runs made before some of the refinements were introduced agree substantially with the data of Table IV, but show greater scattering of single values. The calorie used in this table and the following calculations is defined as being equal to 4.1833 international joules. It will be observed that a fifteen-fold variation of the ethylene–hydrogen ratio, a three-fold variation of the ethylene rate and a more than 1.5-fold variation of the total amount hydrogenated under otherwise identical conditions, have no effect on the heat of hydrogenation. This, in itself, constitutes good evidence that the reaction as studied is a clean hydrogenation to form ethane and is not accompanied by side reactions. To substantiate this point further tests appeared desirable. Two reactions seem to be possible: a polymerization, and a degradation with formation of methane. The first, however, is very improbable to judge from the experiences of others with copper as catalyst;[15] besides, a test for very small amounts of higher hydrocarbons in the effluent gases is an almost hopeless task. Tests for this reaction have therefore been relinquished. If this reaction should be shown to occur, the heat of hydrogenation of ethylene as given in Table IV would have to be increased by 0.1% for each 0.6% ethylene polymerized to yield butane. These figures are deduced from the combustion data of Rossini.[16] Formation of methane, although also very improbable, is more in the realm of possibilities, since it has been observed to occur on nickel. This reaction is more exothermic than hydrogenation to ethane and to lower the results of Table IV by 0.1, 0.3% of ethylene must form methane. A test for methane appeared possible and was carried out in the following manner: between the double valve on the gas line from the calorimeter and the nozzle of the flame was placed a stopcock and a large and efficient trap cooled with liquid air. When a 3:1 hydrogen–ethylene mixture was passed through the calorimeter and was directed to the flame through the trap, almost all ethane (and some of the potentially present methane) was condensed in the trap. The vapor pressure of ethane at liquid air temperature can be estimated as 0.03 mm. and this should give, after one hour of running, with 10 liters of hydrogen passing through the trap, about 1.5 mg. weight increase of the carbon dioxide absorption tubes. The actually observed increase was 1.3 mg. A similar run was now made, but 30 cc. of methane (corresponding to 0.3 mole per cent. of ethylene hydrogenated) was gradually added (throughout the entire hour of the run) to the effluent gases before they entered the cold trap. The weight increase of the absorption tubes was now found to be 19.1 mg. In these tests the flame was started and stopped in the absence of nitrogen and the weight increases found represent the actually formed carbon dioxide. A calculation assuming that methane and ethane form an ideal solution indicates that 14 mg. of carbon dioxide should have been found in the second run. The conclusion to be drawn is that insignificant amounts of methane are formed in the present hydrogenation over copper.

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(14) "I. C. T.," Vol. I, p. 58.

(15) *Cf.* Rideal and Taylor, *loc. cit.*

(16) Rossini, *Bur. Stand. J. Research*, **13**, 21 (1934).

TABLE IV

ΔH OF THE REACTION $C_2H_4 + H_2 \longrightarrow C_2H_6$

Run	Flow C_2H_4, cc./min.	Flow H_2, cc./min.	Moles C_2H_4 converted	Mean temp. of calorimeter in μv.; 82° = 0μ v.	ΔH	ΔH corrected to 355°K. in calories
			Commercial Ethylene, 99.5% pure			
1A	32	289	0.032027	− 450	−32,698	−32,701
1B	32	289	.031881	3300	−32,882	−32,863
2A	32	290	.032005	− 500	−32,852	−32,855
2B	32	288	.038284	2900	−32,836	−32,819
3A	32	292	.047991	− 200	−32,760	−32,761
3B	32	290	.028736	3250	−32,781	−32,762
4A	23	144	.038190	− 800	−32,769	−32,774
4B	23	143	.031736	2600	−32,789	−32,774
5A	49	294	.045039	0	−32,750	−32,750
5B	49	294	.038476	4100	−32,812	−32,788
15A	33	305	.038508	− 700	−32,814	−32,818
15B	34	302	.038545	800	−32,842	−32,837
					Average value −32,792	± 39 calories per mole
			Our Middle Fraction			
6A	34	296	0.038462	− 800	−32,784	−32,789
6B	34	294	.038295	2500	−32,820	−32,806
7A	24	150	.038203	− 700	−32,770	−32,775
7B	24	150	.038083	2400	−32,851	−32,837
8A	24	306	.038167	− 650	−32,889	−32,893
8B	24	304	.038108	2450	−32,874	−32,860
9A	48	216	.044856	− 300	−32,885	−32,887
9B	50	214	.038395	4400	−32,883	−32,856
10A	11	450	.034818	− 750	−32,823	−32,828
10B	11	450	.034758	2150	−32,809	−32,796
					Average value, −32,833	± 34 calories per mole
			Linde Ethylene, 99.8 + % pure			
13A	37	295	0.035297	− 750	−32,802	−32,807
13B	37	296	.035235	2650	−32,842	−32,825
14A	38	296	.035325	− 850	−32,787	−32,792
14B	38	298	.035273	2500	−32,815	−32,801
					Average value, −32,806	± 10 calories per mole
			Our Last Fraction			
12A	36	298	0.035216	− 700	−32,857	−32,862
12B	36	296	.035167	2500	−32,889	−32,875
			Our Middle Fraction, with Ethylene Flow Changed at Midpoint of Run			
11A	32 and 36	300	0.035078	− 750	−32,935	−32,940
11B	36 and 32	298	.035074	2650	−32,905	−32,890

Returning to Table IV, one will notice that the heats of hydrogenation, after correction to 82° (ΔC_p being taken as -4.2 cal.) show average deviations of about 0.1%. A comparison of all "A" with all "B" runs shows that the average of the latter is slightly the higher. This is probably due to the earlier-mentioned decrease of the electrical energy equivalent of the calorimeter with increasing temperature. Since the effects are well within our experimental error, we prefer not to make the very uncertain correction for them and to leave the results in the present form. The number of "A" and of "B" runs being equal, the resultant error is certainly near zero. The "errors" computed from Table IV by the method of Rossini[17] amount also to about 0.1% or slightly less, but there seems to be no particular advantage in using them instead of mean deviations, only a limited number of experiments being available for each sample. The differences in the heats of hydrogenation of the three important samples studied are, we believe, real. In forming the final mean, the commercial sample was disregarded as undoubtedly containing impurities (their amount may be considerably greater than

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(17) See for example *Bur. Stand. J. Research*, **12**, 735 (1934).

indicated by these results since oxygen and diethyl ether compensate for each other in the present method of procedure) and double weight was given the fraction prepared in this Laboratory. This results in the value $\Delta H_{355} = -32{,}824$ cal. We consider the probable error of this figure, including the uncertainty of ethylene purity, to be of the order of 0.15% or 50 cal.

Some reliable determinations of the heat capacities of gaseous ethane and ethylene have been made recently by Eucken and Parts[18] and by Eucken and Weigert[19] and, of course, very accurate values for hydrogen are available from the calculations of Giauque[20] for lower temperatures and from older experimental measurements for ordinary temperatures. Using these figures and interpolating graphically, the heat capacities of ethylene and ethane, the heat of hydrogenation is readily and accurately corrected to standard temperatures. For 25° is obtained: $\Delta H_{298} = -32{,}575$ and for 0°, $\Delta H_{273} = -32{,}460$ cal. The calculations do not contribute significantly to the already present probable error of 50 cal. A correction to absolute zero is of considerable interest, but cannot be executed as accurately as the above, chiefly because of the uncertainty in the heat capacity of ethane, which at the lowest temperature studied by Eucken (143°K.) is in excess of the classical heat capacity of translation and rotation by more than one calorie. Eucken attributes this to the internal rotation of the CH_3 groups and shows agreement with the theoretically calculated heat capacities for this type of internal motion.[21] The extrapolation in the case of ethylene presents fewer difficulties, since at the lowest temperatures employed by Eucken and Weigert, the heat capacity has reached essentially the value demanded classically for translation and rotation. Using Eucken's theory for ethane, adding a small correction for the nonclassical behavior of rotational heat capacities of ethane and ethylene at the lowest temperatures roughly calculated as 10 cal., and also using Giauque's calculated heat content of hydrogen, the following value is obtained

$$\Delta H_0 = -31{,}000 \pm 150 \text{ cal.}$$

The increased error is that allowed for the uncertainties in the heat capacities.

Several determinations of the heats of combustion of the participants in the present reaction have been recorded in the literature. A nondiscriminating use of figures obtained by different investigators for the three substances involved gives an array of figures ranging from about 27 to about 47 kcal., but such a procedure does considerable injustice to the combustion method. Consistent use of Thomsen's data[22] results in a value of 30.7 kcal., the data of Berthelot[22] yield 38.4 kcal. The former figure is usually considered the more accurate one, but an error of several kcal. is not out of the question for both of them.

A direct calorimetric determination, also involving a catalytic hydrogenation, has been carried out by v. Wartenberg and Krause,[23] who obtained $\Delta H_{298} = -30{,}600 \pm 300$ cal. As catalyst they used palladium in colloidal suspension, working at room temperature. The reaction was incomplete and ethylene in effluent gases was removed by reaction with bromine and subsequent cooling of the gases to 0°, which was supposed to remove ethylene bromide formed. The removal thus effected, however, may be quite incomplete, ethylene bromide having a vapor pressure of about 3.5 mm at 0°. The amount of reaction was determined by combustion and weighing of carbon dioxide formed and the ethylene bromide which might remain in the gases can more than account for the low value for the heat of hydrogenation obtained by v. Wartenberg and Krause. Insufficient data are given in the paper, however, to attempt an accurate evaluation of the resulting error. Furthermore, no effort has been made to show that adsorption phenomena do not cause a systematic error in their determinations.

The study of the thermal equilibrium constants in the dissociation of ethane to yield ethylene and hydrogen has also provided some values for the heat of this reaction.

Pease and Durgan[24] studied the equilibrium in the temperature range 600–700° and from the temperature coefficient obtained: $\Delta H_{923} = -31{,}244$ cal. The uncertainty of this value is probably several thousand calories because of the short temperature range, small number of experiments and the presence of complicating side reactions. The extrapolation to room temperature is also rather uncertain and usually a value

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[18] Eucken and Parts, *Z. physik. Chem.*, **20B**, 184 (1933).

[19] Eucken and Weigert, *ibid.*, **23B**, 265 (1933).

[20] Giauque, This Journal, **52**, 4808, 4816 (1930).

[21] Teller and Weigert, *Nachr. Götting. Ges.*, 218 (1933)

[22] Landolt-Börnstein, "Tabellen," 4th edition.

[23] v. Wartenberg and Krause, *Z. physik. Chem.*, **151A**, 105 (1930).

[24] Pease and Durgan, This Journal, **50**, 2715 (1928).

$\Delta C_p = -4$ cal. is used.[25] This would give $\Delta H_{298} = -28{,}744$ cal.

Frey and Huppke[26] studied the same equilibrium, using catalysts to accelerate the reaction, in the temperature range 400–500°. Combining their own and Pease's results they arrive at a value $\Delta H_{823} = -31{,}100$ cal., which should be considerably more accurate because of the very wide temperature interval covered. We believe, however, that these data should be reinterpreted. An inspection of Fig. 3 of Frey's paper will show that in arriving at the equilibrium concentrations they extrapolated to infinite contact time, giving all weight to long contact time experiments. Such a procedure is unavoidable in the case of homologs of ethane, also discussed in the paper, because at shorter contact times the equilibrium is not established. In case of ethane, however, because of the higher temperatures employed, the equilibrium is clearly established (see Fig. 3 of their paper) even at shorter contact times and it is these values, not distorted by secondary reactions, which should preferably be used to compute equilibrium constants.[27] Proceeding in this manner one obtains at 400°$K = 8.2 \times 10^{-5}$, at 450°$K = 5.6 \times 10^{-4}$, and (with greater uncertainty) $K = 2.4 \times 10^{-3}$ at 500°. A plot of these new values is shown in Fig. 6 and it will be seen that they are still consistent with measurements of Pease, also plotted. The heat of reaction is obtained now, however, to $\Delta H_{823} = -33{,}900$. Extrapolating, as before, to room temperature, one obtains: $\Delta H_{298} = -31{,}800$. This is in complete agreement with the now determined value when the uncertainties of the thermal work and of the extrapolation are considered.

This paper would be incomplete without thanks being expressed to several persons whose advice and criticism materially aided our progress. We wish in particular to thank Dr. J. B. Conant, Professor E. P. Kohler and Professor G. P. Baxter. During an early part of the work Dr. L. B. Arnold and Mr. R. E. Leary participated in the construction of the apparatus.

As already pointed out, this investigation would have been impossible without a grant from the Rockefeller Foundation.

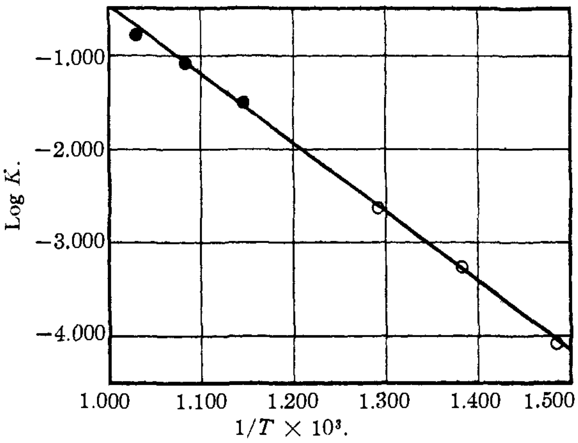

Fig. 6.—A plot of recalculated data of Frey and Huppke ○ and of data of Pease and Durgan ●.

Summary

1. A calorimeter is described which is designed to measure the heats of catalytic hydrogenations and other reactions in the gas phase at temperatures not in excess of 150° with a precision of the order of one-tenth of one per cent.

2. A sensitive quantitative method for detecting small amounts of ethylene in saturated hydrocarbon–hydrogen mixtures is described.

3. A still head for fractionating columns designed to operate at constant pressure with partial return while distilling low-boiling compounds is described.

4. The heat of hydrogenation of ethylene has been determined at 82° as $\Delta H = -32{,}824 \pm 50$ cal. From this the following values have been calculated with the aid of available heat capacity data: $\Delta H_{298} = -32{,}575 \pm 50$ cal.; $\Delta H_{273} = -32{,}460 \pm 50$ cal.; $\Delta H_0 = -31{,}000 \pm 150$ cal.

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[25] Parks and Huffman, "Free Energies, etc.," Chemical Catalog Co., N. Y., 1932.

[26] Frey and Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

[27] Dr. Frey informs us that he sees no grave objections to this procedure.