water although in general $P_e$ is greater in the aqueous solution. The effective pressure is, therefore, a better criterion of ideality than the volume change on mixing.

As the chemical potential of a component in a phase must always be an increasing function of its concentration, it follows from well-known formulas[18] that the solubility of a solid in a liquid will be raised or lowered by pressure according as $(v_2 - v'_s)$ is negative or positive, where $v'_s$ is the specific volume of the solid phase whose solubility is under investigation (pure salt or addition compound). Thus for a given solute in different solvents we may expect an increase in solubility with pressure at low pressures in the more compressible solvents, particularly if $P_e$ is large, and that this increase with pressure will diminish as the pressure is raised. In the less compressible solvents increase of pressure may lower the solubility even at atmospheric pressure. At high pressures the change in solubility of a solid with pressure will have a sign which is independent of the solvent and will in general be negative as it depends only on the sign of the volume change on melting of the solid.

## Summary

The specific volumes and compressions of a number of solutions of salts in methanol, glycol and water have been determined, a new apparatus being used for the latter measurements. From these data apparent volumes and compressions and effective pressures have been computed. The apparent volumes of cadmium iodide in aqueous solution were found to vary with concentration in a manner different from that described in the literature.

The non-aqueous solutions behave under pressure in many ways like the aqueous solutions but they differ in three significant respects. The effective pressures of lithium bromide are greater than those of sodium bromide in glycol solutions, there is a marked correlation between the effective pressures and the apparent thermal expansibilities of glycol in different salt solutions, and up to 2 molal, methanol solutions of four salts whose aqueous solutions differ markedly all have the same effective pressures. The partial volumes of the salts in different solvents at different pressures have been examined and certain general conclusions about the course of pressure-solubility curves have been drawn.

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[18] L. H. Adams, THIS JOURNAL, 53, 3804 (1931).

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

# Calorimetric Investigations of Organic Reactions. I. Apparatus and Method. The Inversion of Sucrose and the Decomposition of Diacetone Alcohol[1]

BY JULIAN M. STURTEVANT

## Introduction

Physical methods have been used frequently for the measurement of the velocities of homogeneous chemical reactions in solution. Such methods for making this fundamental chemical measurement are chiefly of importance in those cases to which analytical methods are inapplicable; such cases arise frequently in the organic field where analytical procedures are relatively few in number and inferior in accuracy.

Physical methods which have received most attention are based on changes in such properties as density, optical rotatory power, refractive index and electrical conductivity. Most of these methods are rather restricted in applicability. A method based on following the evolution or absorption of heat during reaction should be much more widely applicable, since nearly all reactions proceed with an appreciable change in heat content. Aside from its general applicability, such a calorimetric method should have several advantages which will be discussed briefly.

Many physical methods require the use of relatively concentrated solutions in order that an appreciable change in the observed property be obtained. The great sensitivity attainable in calorimetric measurements would make it possible to work with dilute solutions even with reactions involving very small heat changes, and in many cases to obtain an accuracy not easily reached by other methods.

It is only necessary to determine the heat capac-

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[1] Presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

ity of the calorimeter and contents at the end of the reaction to obtain the heat of the reaction with approximately the same accuracy as the velocity of the reaction. This is of importance because there is at present very little reliable work on the heats of slow reactions. Such data have been restricted, with a few exceptions, to very inaccurate values obtained from heats of combustion, or to values calculated from equilibrium data in the case of reversible reactions. A few calorimetric[2] measurements of the heats of slow reactions have been made, though these measurements, with the exception of those Tschelinzew, have not been applied to the determination of reaction rates.

In all physical methods it is necessary to assume that the value of the observed property changes linearly with the extent of the reaction. In some cases[3] this is known to be not strictly true. One usually has no alternative but to judge the accuracy of this assumption by the freedom of the calculated velocity constants from trend during the reaction. In the calorimetric method one can obtain direct evidence of the validity of this fundamental assumption. Obviously if the heat capacity of the reacting solution remains constant during the reaction the heat evolved or absorbed will be strictly proportional to the extent of the reaction, providing no other reactions take place. A direct measure of the change in heat capacity is obtained by determining the heat of reaction as a function of the temperature, since $(\partial \Delta H/\partial T)_P = \Delta \bar{c}_P$, where $\Delta H$ is the heat of the reaction, and $\Delta \bar{c}_P$ is the difference between the sum of the partial molal heat capacities of the products and that of the reactants. In any case where $\Delta \bar{c}_P = 0$ the assumption of linearity will be strictly true. With dilute solutions a value of $(\partial \Delta H/\partial T)_P$ considerably different from zero will be tolerable since the heat capacity of the solvent remains constant.

A survey of the literature has revealed a few previous applications of this method for determining the velocities of reactions. Åkerlöf[4] showed incidentally to a dilatometric investigation of the decomposition of diacetone alcohol that even a simple experiment where the temperature changes were followed by a Beckmann thermometer gave fairly accurate results. Tian[2] has described a microcalorimeter and has mentioned the fact that it should be possible to measure reaction velocities with it. However, even in cases where velocity data were needed in the determination of the heats of certain slow reactions, Tian and his associates appear always to have relied on independent measurements using ordinary analytical methods.

An ingenious modification of the calorimetric method has been employed[5] in the observation of very fast reactions. The reaction mixture is streamed at high velocity through a tube fitted with thermocouples at regular intervals.

In view of the slight attention which has been given the calorimetric method, it seemed that a detailed experimental investigation would be worth while. The author has been interested particularly in its development as a means of opening up for quantitative study many organic reactions which can be measured by no other method at present available.

**Apparatus.**—The calorimetric method could be employed in two distinct ways, one involving direct measurement of the chemical heat effects by observation of the electrical energy necessary to duplicate them, and the other depending on thermometric observation of the reacting solution. The former method would be most accurately carried out with twin calorimeters; with exothermic reactions the tare calorimeter would be supplied with electrical energy sufficient to keep its temperature equal to that of the solution calorimeter, while with endothermic reactions the solution calorimeter would be electrically heated. While it seems probable that the most accurate measurements could be obtained with twin calorimeters, nevertheless the thermometric method was chosen for the present experiments since considerably simpler apparatus would be required.

The aim in the present design has been to secure an accuracy of 1–2% in the reaction velocity and the heat of reaction, and to keep the apparatus as simple as possible consistent with this accuracy. To this end several deviations from usual calorimeter design have been employed. It is evident that the extension of calorimetric observations over a period of several hours necessitates the use of the adiabatic method. The adiabatic jacket employed was a heavy copper cylinder electrically heated. This type of jacket allows rapid and accurate adjustment of its temperature and avoids the need of stirring. It obviously cannot be employed with a falling calorimeter temperature, so that in the case of endothermic reactions it was necessary to overcompensate the chemical heat effects by electrical heating.

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[2] See, for example, Brown and Pickering, *J. Chem. Soc.*, 756, 783 (1897); Tschelinzew, *Chem. Centr.*, **83**, II, 1899 (1912); Barry, THIS JOURNAL, **42**, 1911 (1920); Tian, *Bull. soc. chim.*, [4] **33**, 427 (1923); *J. chim. phys.*, **30**, 665 (1933); Berenger-Calvet, *ibid.*, **24**, 323 (1927); Calvet, *ibid.*, **30**, 1, 140, 198 (1933); Coon and Daniels, *J. Phys. Chem.*, **37**, 1 (1933); Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65–75 (1935).

[3] See, for example, the discussion of the sucrose inversion given by Pennycuick, *J. Chem. Soc.*, 2049 (1924); THIS JOURNAL, **48**, 6 (1926).

[4] Åkerlöf, *ibid.*, **49**, 2955 (1927).

[5] Hartridge and Roughton, *Proc. Cambridge Phil. Soc.*, **22**, 426 (1925); **23**, 450 (1926); La Mer and Read, THIS JOURNAL, **52**, 3098 (1930).

It was considered desirable, if possible, to avoid the use of a stirrer in the calorimeter. An investigation[6] of the lags to be expected in an unstirred cylindrical calorimeter under conditions approximating those of the actual velocity determinations showed that stirring could be safely dispensed with providing a calorimeter of sufficiently small diameter and having a low enough heat capacity were employed. Application of the results of this calculation to the calorimeter actually used indicated that the time lag should be constant and less than fifteen seconds.

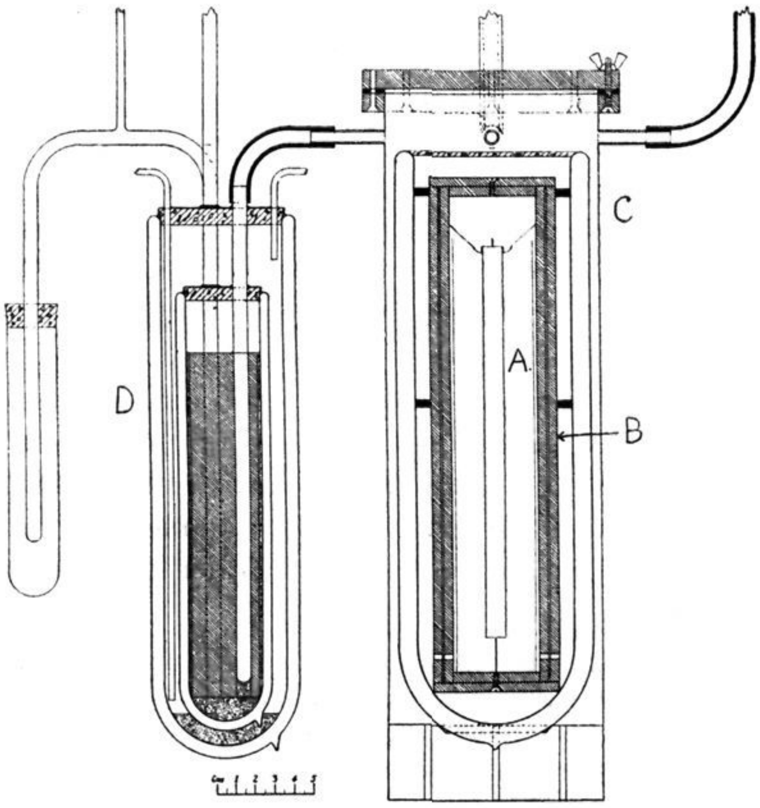

Fig. 1.—Calorimeter and cold calorimeter assembly: A, platinum calorimeter; B, adiabatic jacket; C, submarine can; D, cold calorimeter.

It would obviously be impossible to initiate the reaction within the calorimeter in the absence of any stirring device. In the present experiments two procedures were employed. In the experiments on the sucrose inversion and the glucose mutarotation the reactants were mixed in a thermostated flask and after thorough stirring a sample was transferred to the calorimeter with a vacuum-jacketed pipet. In the experiments on the decomposition of diacetone alcohol the sodium hydroxide solution was placed in the calorimeter and, after adjustment of the temperature, the diacetone alcohol dissolved in a small amount of water was added and the mixture stirred manually for thirty to forty-five seconds with a stirrer made of five thin platinum disks on a platinum wire. The stirrer was then left in the calorimeter during the measurements. These rather cumbersome procedures limit the apparatus to the study of reactions having half-times greater than about ten minutes. Attempts at present are being made to equip the calorimeter with a mechanical stirrer which need only be operated for a minute or so at the start of the reaction, so that the reaction can be initiated in the closed calorimeter. With this device it will then be possible to obtain three quantities from one experiment—the velocity of reaction, the heat of solution of one of the reactants, and the heat of the reaction.

The apparatus, excluding the electrical measuring instruments, is shown in Fig. 1. The calorimeter is a platinum cylinder 1 cm. in internal diameter, 20 cm. long, and weighing with the cover 21 g. There is a small platinum collar at the top to protect the thermocouples, etc., on the outside of the calorimeter in case of accidental overflow. The calorimeter is supported at the bottom on a short piece of constantan wire and is held in place at the top by a paper cone. The calorimeter heater is a bifilar winding of 0.0008 in. (0.02 mm.) thick Advance ribbon on the outside of the calorimeter, insulated from the latter by a thin layer of Cellophane, and having a resistance of 46 ohms. The heater is connected with current-carrying and potential leads of No. 34 copper wire in such a way that no lead corrections are necessary. The adiabatic jacket, composed of two concentric chromium-plated copper cylinders with a winding of Advance wire between them, weighs 3.7 kg., including the end-plates which are also electrically heated. The jacket is contained in a Dewar flask in a copper can with a water-tight cover.

Temperatures are measured with ten-junction copper-Advance thermels composed of two opposable sets of five junctions each. One thermel measures the calorimeter-jacket temperature difference, another the calorimeter–cold calorimeter difference, and a third the cold calorimeter–thermostat difference. The twenty junctions on the calorimeter are arranged in the form of a spiral of two turns from the top to the bottom, and are bound down over the heater with fine silk thread, being insulated from the heater with a spiral of thin lacquered paper. The reading with the two halves of the main (calorimeter to cold calorimeter) thermel connected in opposition gives a measure of the magnitude of the vertical thermel gradient in the calorimeter. Insulation and other non-metallic material on the calorimeter is kept to a minimum to avoid excessive lags. The ten thermocouple junctions on the jacket are also arranged in the form of a spiral. They are enclosed in thin glass capillaries cemented into 1-mm. copper cylinders soldered to a 0.005 in. (0.13 mm.) nickel-plated copper sheet. The copper sheet is pressed against the inside wall of the jacket with the tubes holding the junctions against the jacket. With the junctions arranged in this way, they measure the temperature of the face of the jacket controlling heat exchange with the calorimeter; since the lag of the junctions behind the jacket heater is very small, the control of the jacket heating current is easy. The thermocouple and heater connections with the calorimeter are exposed to the jacket temperature for a distance of about 35 cm. before emerging into the thermostat.

The cold calorimeter is of the "cascade" type described by White.[7] The inner Dewar contains a copper cylinder drilled with holes to accommodate a heater, the "cold" junctions of the main thermel, and the "hot" junctions of the cold calorimeter to thermostat thermel. Provision is made for circulation of thermostat water through the space between the Dewars during adjustment of the cold calorimeter temperature. The half-time of the heat exchange between the cold calorimeter and the thermostat is about ten hours. Since the thermostat temperature

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(6) Sturtevant, *Physics*, **7**, 232 (1936).

(7) White, *Rev. Sci. Instruments*, **5**, 269 (1934).

is held constant to better than 0.01° by a large grid-form mercury thermoregulator controlling a thyratron tube. the cold calorimeter gives an adequately constant reference temperature for experiments extending over several hours. The temperature of the bath is measured by thermometers checked against a platinum resistance thermometer calibrated by the Bureau of Standards. The temperatures are thus known with an accuracy of about 0.01°.

The calorimeter–cold calorimeter assembly is suspended from a wooden base so that it may be lowered readily under the water level in the thermostat or raised sufficiently to open the calorimeter can.

All insulation resistances were checked at the time of assembly of the apparatus and were found to be much greater than 500 megohms. except for that between the calorimeter and calorimeter heater (Cellophane) which was about 20,000 ohms. Since this resistance is so large compared to that of the heater it was considered that it could introduce no serious asymmetry into the heater.

It is easy to keep the reading of the calorimeter-to-jacket thermel less than ±0.0002° by manual control of the jacket heating current. With a temperature difference of 0.0002°. the temperature of the calorimeter filled with water changes by $1 \times 10^{-6}$ degree per minute. On the assumption that the thermel actually measures the effective temperature gradient between the calorimeter and the jacket even when the calorimeter temperature is rising as in a velocity determination. it would seem that the adiabatic control is quite sufficient. especially since the thermel readings fluctuate between positive and negative values during manual control. However. there is evidence that at constant calorimeter temperature the readings of the thermel are in error by small amounts that vary from day to day. This is presumably due to leakage from the relatively high potential heater circuits which the shielding system does not prevent. These slight variations in the adiabatic control would have very little effect on the reaction velocity. but if they were serious they would show up in the heat of reaction.

The thermocouple and heater leads are carried through shielded cables to the electrical measuring instruments. The potentials across the calorimeter heater and across a calibrated 30-ohm resistor in series with it are measured on a Leeds and Northrup student type potentiometer against an Eppley standard cell. The potentials of the thermels are observed with a Leeds and Northrup narrow-coil HS type galvanometer having a voltage sensitivity of 0.07 microvolt per mm. (scale at 3 meters). With a ten-junction thermel this corresponds to about 0.00018° per mm. In series with the main thermel is placed a special thermo-free potentiometer. manufactured by Leeds and Northrup. having a range of 550 microvolts in steps of 5 microvolts. Suitable resistors (bifilar manganin) and copper knife switches are included in the thermocouple circuits to allow connecting the two halves of each thermel in opposition and using the galvanometer at one-tenth and one-hundredth as well as full sensitivity. The zero deflections of the galvanometer are observed when it is connected to a neutral resistor immersed in the thermostat. the leads from which are carried in the same cable as the thermel leads. The switches. resistors and potentiometer in the thermel circuits are enclosed in a cabinet and are manipulated by external controls.

It is important to note that no accurate calibration of the main thermel is needed. A calibration of sufficient accuracy (for temperature corrections outlined later) is obtained by measuring the heat capacity (in joules per microvolt) of the calorimeter empty and filled with a known amount of water. The heat capacity of the empty calorimeter (*in vacuo*) is 0.0124 joule per microvolt. From measurements with the calorimeter filled with water the temperature sensitivity of the main thermel is found to be 0.00255° per microvolt. The heat capacity of the calorimeter is thus 4.87 joules (1.16 cal.) per degree. Since it holds about 16 cc., its empty heat capacity is about 0.07 of its heat capacity filled with water. It may be added that this calorimeter permits heat capacity determinations with an accuracy of about 0.5%.

**Method of Calculation.**—It is convenient to assume that the readings (microvolts) start from the moment of mixing the reagents. The hypothetical initial reading $\mu_0$ can be obtained with sufficient accuracy by analytical extrapolation. If $a_0$ is the concentration at mixing of the reactant present in smallest stoichiometric amount and if only one reaction takes place, then the concentration of this reactant at time $t$ is

$$a = a_0(\mu_\infty - \mu)/(\mu_\infty - \mu_0) \qquad (1)$$

where $\mu$, $\mu_\infty$ are the readings at $t = t$ and $t = \infty$. We assume here, of course, that the heat capacity of the system remains constant. The expression for $a$ is then substituted in the usual velocity equations.

Direct determinations of $\mu_0$, $\mu_\infty$ are impossible, the first because of the heat of mixing, the second because of calorimetric limitations. Roseveare[8] has shown how the initial and final readings can be eliminated in the cases of first-order reactions and second-order reactions in which the initial concentrations of the reactants are equal. Three readings (of concentration or of any quantity varying linearly with it) are taken at equal time intervals. In the present application the readings would be $\mu_1$ at $t_1$, $\mu_2$ at $t_1 + \Delta t$ and $\mu_3$ at $t_1 + 2\,\Delta t$. Then for an irreversible monomolecular reaction the velocity constant is given by

$$k = \frac{1}{\Delta t} \ln \frac{\mu_1 - \mu_2}{\mu_2 - \mu_3} \qquad (2)$$

Roseveare's method of calculation has been extended by Sturtevant[9] to include most of the other important types of reactions, so that no trouble arises from the fact that initial and final readings of the temperature cannot be obtained.

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[8] Roseveare, THIS JOURNAL, **53**, 1651 (1931).

[9] Sturtevant, *ibid.*, **59**, 699 (1937).

The heat (in joules per mole) of an irreversible reaction is obviously

$$-\Delta H = (\mu_\infty - \mu_0)\,(C/m_0) \qquad (3)$$

where $C$ is the heat capacity (in joules per microvolt) of the calorimeter and its contents, and $m_0$ is the initial number of moles of the reactant present in smallest stoichiometric amount. On the assumption that $C$ is constant, its value may be determined when the reaction is complete. It is shown easily that for a monomolecular irreversible reaction

$$\mu_\infty - \mu_0 = \frac{(\mu_1 - \mu_2)\,(\mu_2 - \mu_3)}{2\mu_2 - \mu_1 - \mu_3}\, e^{k(t_1 + \Delta t)} \qquad (4)$$

If the reaction under investigation has a large temperature coefficient of velocity, or if the readings cover a wide temperature range, correction should be made for the variation of the velocity with temperature. Since this correction will be small, its application with sufficient accuracy is not difficult. A description of the procedure for a monomolecular irreversible exothermic reaction will be given. Similar procedures may be applied to other types of reactions.

We may write with sufficient accuracy for the small temperature changes involved that

$$k = (1 + \beta T)k_0 \qquad (5)$$

where $T$ is the temperature of the calorimeter relative to the thermostat and $k_0$ is the velocity constant at $T = 0$. Denoting the temperature sensitivity (degrees per microvolt) of the measuring thermel by $\alpha$ and setting $\gamma = \alpha\beta$, we have

$$k = (1 + \gamma\mu)k_0 \qquad (6)$$

The kinetic equation is then

$$\mathrm{d}\mu/\mathrm{d}t = k_0(1 + \gamma\mu)\,(\mu_\infty - \mu) \qquad (7)$$

which gives on integration

$$k_\infty t = \ln \frac{1 + \gamma\mu}{1 + \gamma\mu_0} \cdot \frac{\mu_\infty - \mu_0}{\mu_\infty - \mu} \qquad (8)$$

where

$$k_\infty = (1 + \gamma\mu_\infty)k_0 \qquad (9)$$

Proceeding in a manner analogous to that recommended by Roseveare we obtain the relations

$$k_\infty\,\Delta t = \ln \frac{1 + \gamma\mu_2}{1 + \gamma\mu_1}\frac{\mu_\infty - \mu_1}{\mu_\infty - \mu_2} = \ln \frac{1 + \gamma\mu_3}{1 + \gamma\mu_2}\frac{\mu_\infty - \mu_2}{\mu_\infty - \mu_3} \qquad (10)$$

Solution of these equations for $\mu_\infty$ gives as a first approximation ($\gamma = 0$)

$$\mu_\infty^0 = \frac{\mu_2^2 - \mu_1\mu_3}{2\mu_2 - \mu_1 - \mu_3} \qquad (11)$$

or, more accurately

$$\mu_\infty = \mu_\infty^0 - \gamma(\mu_\infty^0 - \mu_2)^2 \qquad (12)$$

where powers of $\gamma$ above the first have been neglected. Substitution of this result in either of equations (10) gives

$$k_\infty\,\Delta t = \ln\,[1 + \gamma(\mu_3 - \mu_1)]\,\frac{\mu_1 - \mu_2}{\mu_2 - \mu_3} \qquad (13)$$

With sufficient accuracy

$$k_0 = (1 - \gamma\mu_\infty^0)\,k_\infty \qquad (14)$$

To the same approximation it is shown easily that

$$-\Delta H = \frac{C}{m_0}\,(\mu_\infty^0 - \mu_0^0)\,[1 - \gamma(\mu_\infty^0 - \mu_0^0)] \qquad (15)$$

where

$$(\mu_\infty^0 - \mu_0^0) = \frac{(\mu_1 - \mu_2)\,(\mu_2 - \mu_3)}{2\mu_2 - \mu_1 - \mu_3}\, e^{k_\infty(t_1 + \Delta t)} \qquad (16)$$

**The Inversion of Sucrose.**—In order to test the apparatus it was thought to be advisable to measure the velocities of some reactions for which accurate data can be found in the literature. Several attempts were made to measure the velocity of the rearrangement of N-chloroacetanilide to *p*-chloroacetanilide, a reaction which has been studied accurately by several investigators. However, very erratic results were obtained, and each run showed a large trend in the calculated first-order velocity constants. It was discovered that the solutions were always colored yellow on removal from the calorimeter, while they remain colorless for long periods in glass containers. Presumably the course of the reaction is different in the platinum than it is in glass. It is interesting that despite the limited solubility of the reactant more than sufficient heat is liberated in the reaction to enable it to be measured.

The next reaction tried was the inversion of sucrose catalyzed by hydrochloric acid, an exothermic reaction. Baker analyzed sucrose was dried in a vacuum desiccator and used without further purification. The stock hydrochloric acid solution was made up from Baker analyzed acid and was standardized gravimetrically. All runs were made at 25°. A known amount of sugar freshly dissolved in a known weight of water was added from a weight buret to the acid in a well-stirred glass vessel in the thermostat and after thorough mixing a sample was transferred with a vacuum-jacketed pipet to the calorimeter. Another sample was pipetted out for weighing. Calibration of the pipet with water permitted calculation of the normality of the acid as well as the molality.

A typical run is illustrated in Table I. The first column gives the time of the first reading in each set of three, measured from the time of starting the reaction. The next three columns give the readings in microvolts at $t_1$, $t_1 + 80$ and $t_1 + 160$ min., respectively. In the fifth column are the values of $k_\infty \Delta t$ calculated from equation (13) using common logarithms and times expressed in minutes, and in the sixth the values of $\mu_\infty - \mu_0$ calculated from equations (15) and (16). The last column gives the values of $\mu_\infty$ obtained by equation (12). The value of $\gamma$ was obtained from the temperature sensitivity of the main thermel and the quantity $\frac{1}{k}\frac{\mathrm{d}k}{\mathrm{d}T} = 0.147$ calculated from the observations of Lamble and Lewis.[10]

TABLE I

INVERSION OF SUCROSE AT 25.03°

0.5570 mole HCl per 1000 g. $H_2O$. 0.5310 mole HCl per 1000 cc. solution. 0.1082 mole sucrose per 1000 cc. solution. 0.001728 mole sucrose in calorimeter. Heat capacity of calorimeter and solution 0.1789 joule per microvolt. $\Delta t$, 80 min. $\gamma$, 0.000375.

| $t_1$, min. | (microvolts) $\mu_1$ | $\mu_2$ | $\mu_3$ | $k_\infty \Delta t$ | $-\Delta H\, m_0/C =$ $\mu_\infty - \mu_0$ | $\mu_\infty$ |
|---|---|---|---|---|---|---|
| 20 | 21.28 | 67.56 | 98.82 | 0.1968 | 145.6 | 152.1 |
| 30 | 28.09 | 72.11 | 100.77 | .1981 | 144.8 | |
| 40 | 34.61 | 76.39 | 103.56 | .1980 | 145.0 | 151.8 |
| 50 | 40.83 | 80.47 | 106.18 | .1986 | 144.6 | |
| 60 | 46.75 | 84.35 | 108.69 | .1989 | 144.4 | 151.6 |
| 70 | 52.37 | 88.00 | 111.05 | .1986 | 144.6 | |
| 80 | 57.72 | 91.44 | 113.32 | .1968 | 145.9 | 152.3 |
| 90 | 62.76 | 94.72 | 115.44 | .1967 | 146.1 | |
| | | | Mean | 0.1978 | 145.13 | 151.95 |

Maximum deviation from mean 0.5% 0.7%

$k_{25.03} = 0.002339$ $k_{25.00} = 0.002322$ $\Delta H = -15{,}020$ joules per mole

It is evident that the calculated values of the velocity constant are free from any significant trend. In some experiments a slight upward trend of about 1% was observed. Evidence was obtained that this trend was due mainly to slight errors in the first few observations resulting from a vertical thermel gradient in the calorimeter. It appeared that in the presence of such gradients the main thermel did not quite correctly measure the average temperature of the calorimeter.

In Table II are summarized all the determinations made, with the exception of two runs which were discarded because they gave values of the heat of reaction differing excessively from the others. The quantities in the sixth column are interpolated in the polarimetric data of Worley[11] by means of the empirical equation

$$k \times 10^3 = 0.044 + 2.889m + 2.069m^2$$

where $m$ is the molality of the catalyst. This expression fits Worley's data for his runs in which moles sucrose/moles HCl = 0.25 to within 0.3% in the range 0.3 to 1.4 $m$. It will be observed that the calorimetric values are higher than Worley's. Worley observed a considerable upward trend in his experiments, and his reported velocity constants were obtained by extrapolation of the calculated constants back to zero time.

The present results are 3 to 6% *lower* than those of Lamble and Lewis,[10] the deviations increasing regularly with increasing catalyst concentration. Part of this discrepancy is probably due to the fact that these authors mixed equal volumes of hydrochloric acid and sucrose solution and assumed the final normality was half that of the original acid.

There has been considerable discussion as to whether the sucrose inversion is strictly monomolecular. Many workers have noted a trend in the velocity constants. Pennycuick[3] showed that at lower catalyst concentrations the glucose mutarotation would have an observable effect on the polarimetric observations, and that the fructose rearrangement and mutarotation are rapid enough to be negligible. Exclusion of the mutarotational lag did not, however, remove all the trend from Pennycuick's experiments. Scatchard[12] recalculated Pennycuick's data and showed that the velocity constants varied as a function of the time rather than of the fraction of the sucrose converted, so that a process similar to a diffusion caused the trends. This indicated that Pennycuick did not obtain complete mixing of the reactants at the start of the reaction. Scatchard concluded that the sucrose inversion is very accurately monomolecular.

Before the explanation of faulty temperature measurement was found for the trends observed in some of the present work, three determinations of the heat of the mutarotation of $\alpha$-glucose were made. These runs were made in $5 \times 10^{-5}$ normal hydrochloric acid, in the range of $p$H at which the velocity has its minimum value. The results are summarized in Table III. The values in the third column are the sum of the velocities of the forward and reverse reactions. The accuracy of these data is below that for the other reactions studied because of the very small heat of reaction. However, the mean of the sum of the velocity constants agrees well with the data in the literature,[13] the most reliable value being 0.0104–0.0105.

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[10] Lamble and Lewis, *J. Chem. Soc.*, **107**, 233 (1915).

[11] Worley, *ibid.*, **99**, 349 (1911).

[12] Scatchard, THIS JOURNAL, **48**, 2259 (1926).

[13] See the summary of previous work on this reaction given by Hamill and La Mer, *J. Chem. Phys.*, **4**, 395 (1936).

TABLE II

INVERSION OF SUCROSE BY HYDROCHLORIC ACID AT 25.00°

| Moles HCl per 1000 g. $H_2O$ | Moles HCl per 1000 cc. Solution | Moles sucrose in calorimeter $\times 10^3$ | Moles sucrose per mole HCl | $k \times 10^3$ (min.$^{-1}$, common logarithms) Obsd. | Calcd. | Difference, % | $-\Delta H$, kilojoules per mole | $-\Delta H$, cal.$_{15°}$ per mole |
|---|---|---|---|---|---|---|---|---|
| 0.4102 | 0.3959 | 1.838 | 0.2906 | 1.659 | 1.577 | +5.6 | 14.86 | 3.551 |
| .5507 | .5310 | 1.728 | .2037 | 2.322 | 2.262 | +3.1 | 15.02 | 3.589 |
| .5650 | .5458 | 1.586 | .1819 | 2.396 | 2.337 | +3.0 | 14.94 | 3.570 |
| .5862 | .5633 | 1.982 | .2202 | 2.495 | 2.448 | +2.4 | 15.19 | 3.630 |
| .9182 | .8769 | 1.940 | .1385 | 4.483 | 4.441 | +1.4 | 14.91 | 3.563 |
| .9488 | .9059 | 1.840 | .1272 | 4.687 | 4.647 | +1.3 | 15.02 | 3.589 |
| 1.3003 | 1.2312 | 1.886 | .09713 | 7.471 | 7.298 | +2.8 | 14.72 | 3.517 |
| 1.3324 | 1.2689 | 1.476 | .07280 | 7.769 | 7.565 | +3.1 | 14.63 | 3.496 |
| | | | | | | Mean | 14.91 | 3.563 |

Maximum deviation from mean 1.9%

TABLE III

MUTAROTATION OF $\alpha$-GLUCOSE IN $5 \times 10^{-5}$ $N$ HCl AT 25.00°

| Glucose % by weight | Mole glucose in calorimeter | $k_1 + k_2$ (min.$^{-1}$, common logarithms) | $-\Delta H$, joules per mole | $-\Delta H$, cal.$_{15°}$ per mole |
|---|---|---|---|---|
| 12.96 | 0.01186 | 0.01011 | 694 | 166 |
| 13.17 | .01208 | .01033 | 670 | 160 |
| 18.17 | .01700 | .01055 | 664 | 159 |
| | Mean | 0.01033 | 676 | 162 |
| Maximum deviation from mean | | 2.1% | | 2.7% |

Calculation by the method outlined by Pennycuick indicates that the glucose mutarotation can introduce no trend in the calorimetrically determined velocity of the sucrose inversion except at very low acid concentrations. The mutarotational effect is smaller in the calorimetric than the polarimetric method because of the small heat of mutarotation. It is to be supposed that the fructose rearrangement and mutarotation are negligible in both methods because of their high velocities. It may be concluded that the present work supports Scatchard's conclusion that the sucrose inversion is strictly monomolecular.

It is interesting to compare the present heat data with previous values. Barry[2] has made a careful calorimetric determination of the heat of inversion of sucrose (including all mutarotational heats), using sucrose of about the same concentration as used here (about 4%). His work was done at 20°, but it is safe to assume that substantially the same value would be obtained at 25°. He found[14] for this reaction $\Delta H = -14.90 \pm 0.09$ kilojoules per mole, in excellent agreement with the value given in Table II. Brown and Pickering[2] found the value $\Delta H = -443$ joules per mole for the heat of mutarotation of $\alpha$-glucose to the equilibrium mixture of $\alpha$- and $\beta$-glucose, a value which is considerably lower than the value obtained in the present work. Nelson and Beegle[15] found that the specific rotations of $\alpha$- and $\beta$-glucose and of their equilibrium mixture are constant over the temperature range 0–37°, which would indicate that $\Delta H = 0$. However, recently Isbell and Pigman[16] obtained values for these quantities at 0.2 and 20° from which it can be calculated that $\Delta H = -260$ joules per mole. This value is subject to a large error since the observed changes in specific rotation are very small.

**The Decomposition of Diacetone Alcohol.**—This reaction was investigated for two reasons. It is strongly endothermic, and therefore offers an opportunity for testing the behavior of the calorimeter when heat is being absorbed by the solution and introduced at the wall of the calorimeter by the heater. Also there has arisen in the literature some disagreement as to the velocity of the reaction at low concentrations of the catalyst sodium hydroxide.

The diacetone alcohol was an Eastman product. It was redistilled at about 20 mm. pressure through a 60-cm. column no more than an hour or two before use. The sodium hydroxide stock solution was made up from Baker analyzed material with careful exclusion of carbon dioxide, and was analyzed by titration from weight burets against gravimetrically standardized hydrochloric acid. The solution was 0.00225 molal in $Ba^{++}$. Dilute solutions were prepared just before use with distilled water boiled and cooled under carbon dioxide-free air.

In some of the runs the heater current was decreased between sets of readings to keep the experiment more nearly isothermal. No correction for changing temperature was necessary; the mean velocity constant was calculated to the de-

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[14] Barry does not state the type of calories in which his results are expressed. The factor 4.185 has been employed to convert his results to joules.

[15] Nelson and Beegle, THIS JOURNAL, **41**, 559 (1919).

[16] Isbell and Pigman, *Bur. Standards J. Research*, **18**, 141 (1937).

sired temperature on the assumption that the experiment was isothermal at the temperature of the reading at the time of half completion.

In Table IV are given the data for a typical run. The figures in the second, third and fourth columns are the actually observed microvolt readings, and include the temperature changes due to the reaction and the electrical heat input. The fifth and sixth columns give the values of $k\Delta t$ and $\mu_0 - \mu_\infty$ calculated by equations (2) and (4) using common logarithms and times expressed in minutes, after deduction of the microvolt changes due to the calorimeter heater. The good constancy of the calculated velocity constants is satisfactory evidence of the absence of serious lags, since the heat input was varied twice during the reaction and only four minutes elapsed between the time of changing the heating current and the time of the next reading.

TABLE IV

DECOMPOSITION OF DIACETONE ALCOHOL AT 25.03°

0.03846 mole NaOH per 1000 g. $H_2O$. 0.03824 mole NaOH per 1000 g. solution. 0.4118% by weight diacetone alcohol. 0.0005575 mole diacetone alcohol in calorimeter. Heat capacity, 0.1785 joule per microvolt. $\Delta t$ = 30 min. Temp. rise due to heater: 0–38 min., 1.4774 microvolt per min. 38–67 min., 0.7014 microvolt per min. 67–96 min., 0.4782 microvolt per min.

| $t_1$, min. | Observed readings, microvolts at $t_1$ | at $t_2$ | at $t_3$ | $k\Delta t$ | $\mu_0 - \mu_\infty$ |
|---|---|---|---|---|---|
| 12 | 33.73 | 50.15 | 56.17 | 0.2514 | 71.08 |
| 15 | 35.09 | 50.51 | 56.60 | .2509 | 71.45 |
| 18 | 36.60 | 50.94 | 57.09 | .2525 | 71.15 |
| 21 | 38.21 | 51.46 | 57.63 | .2518 | 71.41 |
| 24 | 39.99 | 52.09 | 58.21 | .2502 | 72.02 |
| 27 | 41.93 | 52.76 | 58.85 | .2522 | 71.49 |
| 30 | 43.97 | 53.54 | 59.53 | .2510 | 71.91 |
| 33 | 46.17 | 54.39 | 60.25 | .2508 | 72.11 |
| 36 | 48.49 | 55.31 | 61.01 | .2499 | 72.45 |
| | | | Mean | 0.2512 | 71.67 |
| Maximum deviation from mean | | | | 0.5% | 1.1% |

$k_{25.00} = 0.008236$ $\Delta H = +22.950$ joules per mole

$\frac{k_{25.00}}{m} = 0.2141$

The results obtained for the decomposition of diacetone alcohol at 25 and 30° are summarized in Table V. As found by previous investigators the velocity constant is proportional to hydroxide concentration up to 0.1 molal.

TABLE V

DECOMPOSITION OF DIACETONE ALCOHOL AT 25.00 AND 30.00°

Velocity constants in min.$^{-1}$, common logarithms

| $m$ mole NaOH per 1000 g. $H_2O$ | $M$ mole NaOH per 1000 g. solution | Diacetone alcohol % by weight | $(k/m) \times 10^3$ | $(k/M) \times 10^3$ | $\Delta H$, kilo-joules per mole | $\Delta H$, cal.$_{15°}$ per mole |
|---|---|---|---|---|---|---|
| | | 25.00° | | | | |
| 0.03011 | 0.02996 | 0.3908 | 209.9 | 210.9 | 23.55 | 5.627 |
| .03846 | .03842 | .4118 | 214.1 | 215.4 | 22.95 | 5.484 |
| .05974 | .05922 | .6255 | 211.2 | 213.1 | 22.96 | 5.486 |
| .07842 | .07801 | .2262 | 207.5 | 208.6 | 22.71 | 5.427 |
| .09603 | .09535 | .3210 | 209.1 | 210.6 | 22.56 | 5.391 |
| | | Mean | 210.4 | 211.7 | 22.95 | 5.484 |
| Maximum deviation from mean | | | 1.8% | 1.7% | 2.6% | |
| | | 30.00° | | | | |
| 0.03043 | 0.03018 | 0.7006 | 342.8 | 345.6 | 22.87 | 5.465 |
| .04248 | .04224 | .3968 | 341.1 | 343.0 | 23.21 | 5.546 |
| .05072 | .05039 | .4519 | 341.2 | 343.5 | 23.53 | 5.622 |
| .06098 | .06057 | .4237 | 335.4 | 337.6 | 22.90 | 5.472 |
| | | Mean | 340.1 | 342.4 | 23.13 | 5.527 |
| Maximum deviation from mean | | | 1.4% | 1.4% | 1.7% | |

In Table VI the results obtained by the calorimetric method are compared with those obtained by dilatometric observation of the reaction. It is interesting to note that a much smaller concentration of diacetone alcohol suffices in the calorimetric method. It also appears that as good accuracy is obtained by the calorimetric as by the dilatometric method.

The results of French[17] and Murphy[18] agree well with each other, but are considerably below those of La Mer and Miller.[19] The results of French should be about 2% and those of Murphy about 2.5% lower than those obtained in the present work, since they used larger diacetone alcohol concentrations. The agreement between the present results and those of Murphy would be rendered perfect if the latter's results at 0.01 molal hydroxide were discarded. In any event, both French's and Murphy's results agree within stated experimental errors with those obtained by the calorimetric method.

The values of La Mer and Miller should be directly comparable with the present values, since their catalyst concentrations are expressed in normalities. Slight discrepancies should exist because of the deviation of the solutions from unit density, but no more than a few tenths of a per cent. difference could be accounted for on this basis. It is difficult to understand the differences actually found, since they should be well beyond the experimental error. The early results of Koelichen[20] are still higher than those of La Mer and Miller.

It has been suggested by one of the referees of this paper that some of the discrepancies in the values of the velocity of the diacetone alcohol decomposition reported by various authors may be

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[17] French, THIS JOURNAL, **51**, 3215 (1929).

[18] Murphy, *ibid.*, **53**, 977 (1931).

[19] La Mer and Miller, *ibid.*, **57**, 2674 (1935).

[20] Koelichen, *Z. physik. Chem.*, **33**, 159 (1900).

TABLE VI

DECOMPOSITION OF DIACETONE ALCOHOL AT 25.00 AND 30.00°. COMPARISON WITH PREVIOUS VALUES

Velocity constants in min.$^{-1}$, common logarithms

| Author | | Value | No. of detns. | Max. dev. from mean, % | Diacetone alcohol concn. | Deviation from Sturtevant's value of $k/M$, % |
|---|---|---|---|---|---|---|
| French | $k_{25}/m$ | 0.204 | 7 | 2.9 | 0.15 molal | $-3.9^c$ |
| Murphy | $k_{25}/m$ | .2048 | 8 | 4.3 | 2.5% by volume | $-3.2^c$ |
| | $k_{30}/m$ | .3335 | 8 | 2.5 | 2.5% by volume | $-2.6^c$ |
| La Mer and Miller | $k_{25}/N$ | .2219 | 7 | 1.1 | 2.0% by volume | +4.8 |
| | $k_{30}/N$ | .3604[a] | 3 | 1.4 | 2.0% by volume | +5.3 |
| Koelichen | $k_{25}/N$ | .2262[b] | 5 | 3.1 | 5.0% by volume | +6.9 |
| Sturtevant | $k_{25}/M$ | .2117 | 5 | 1.7 | 0.2–0.6% by weight | .. |
| | $k_{30}/M$ | .3424 | 4 | 1.4 | 0.4–0.7% by weight | .. |

[a] Calculated from the result at 29.90°, using their temperature coefficient.

[b] Obtained by reducing the value at 25.2° by 2%.

[c] These deviations are almost entirely due to the difference in concentration units employed. See the discussion in the text.

due to the presence of acid impurities in the diacetone alcohol used. Provided such impurities exert no specific catalytic effect, errors from this cause should not appear in the work of La Mer and Miller, since these authors determined their sodium hydroxide concentrations by direct analysis at the end of each velocity determination. While this procedure was not followed in the present work, and in the work of French and Murphy, nevertheless, errors from this cause would be of relatively small importance in the results obtained by the calorimetric method since such small concentrations of diacetone alcohol were employed.

A sample of the Eastman diacetone alcohol used, which had been standing for some months in a tight container, was found on titration with barium hydroxide to contain 0.00121 equivalent of acid per mole. Distillation *in vacuo* through a 60-cm. column lowered this figure to 0.00091 equivalent per mole. In the absence of specific catalytic effects, this concentration of acid introduces in the most unfavorable case (0.03 *m* sodium hydroxide at 30°) in the present work an error of 0.2% in the value of $k/M$.

An experiment was performed to determine if any acidic substance is formed as a result of side reactions during the diacetone alcohol decomposition. Eighteen grams of freshly distilled diacetone alcohol was made just neutral to phenolphthalein and was then mixed with a warm solution (about 150 cc.) containing 0.01558 mole of barium hydroxide. Titration at the end of an hour showed the presence of 0.01559 mole of barium hydroxide.

The heat of activation calculated from the results at 25 and 30°, 17,260 cal., agrees well with the values obtained by Murphy and by La Mer and Miller in this temperature range.

The values of $\Delta H$ at 25 and 30° agree within experimental error, so that probably no significance is to be attached to the apparent difference. It is nevertheless of interest to calculate roughly the change in heat capacity of the reacting solution. According to the relation $(\partial \Delta H/\partial T)_P = \Delta \bar{c}_P$, we find $\Delta \bar{c}_P \approx 8$ cal. per degree per mole. About 0.0013 mole of diacetone alcohol was used, so that the actual change in heat capacity would be of the order of 0.01 cal. per degree. This change is entirely negligible in a total heat capacity of about 20 cal. per degree.

There are no previous direct calorimetric data with which the value of $\Delta H$ may be compared. Koelichen[20] determined the equilibrium constant at 0 and 25.2°, obtaining the values 0.1176 and 0.0351, respectively. From these data one calculates that $\Delta H$ = 32.4 kilojoules per mole, about 40% higher than the result of the present investigation. These results are not directly comparable because the equilibrium measurements were necessarily made in very concentrated solutions. How much of the discrepancy would be removed by inclusion of the appropriate heats of dilution cannot be stated.

It is planned at some future time to explore the possibility of obtaining highly precise velocity and heat data by the use of a more elaborate calorimeter.

## Summary

An unstirred adiabatic calorimeter designed for the determination of the velocities and heats of slow reactions is described. Tests of this apparatus with exothermic and endothermic reactions having half-times of fifteen minutes to three hours

indicate that an accuracy of about 2% in the velocity and heat of reaction is obtained.

Investigation by means of this calorimeter of the sucrose inversion supports the conclusion that this reaction is quite strictly monomolecular.

Measurements of the velocity of decomposition of diacetone alcohol check the results of French and Murphy rather than those of La Mer and Miller and Koelichen.

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[CONTRIBUTION FROM M. W. KELLOGG COMPANY RESEARCH LABORATORY]

# The Thermal Decomposition of Azomethane

BY E. W. RIBLETT AND L. C. RUBIN

The thermal decompositions of aliphatic azo compounds, particularly that of azomethane, have been considered as examples of simple unimolecular reactions. Ramsperger and Rice[1,2] and Kassel[3] have presented theories of unimolecular reactions and have found that azomethane decomposition furnished the best test of the theories.

The comparison of the theory with the experimental data has been made upon the supposition that the pressure increase in the decomposition was directly proportional to the extent of the decomposition. This was in line with Ramsperger's statement[4] that the decomposition of azomethane is almost entirely represented by the equation $CH_3NNCH_3 = C_2H_6 + N_2$.

In the course of some work upon azomethane in this Laboratory, evidence was obtained that the above equation of Ramsperger did not represent the true course of the reaction. The importance that has been attached to the decomposition of azomethane was thought to warrant a description of the results obtained from analyses of the gaseous products from the decomposition.

## Experimental

Azomethane was prepared by Thiele's[5] method as modified by Allen and Rice.[6] It was purified by five distillations, each distillation being followed by a thorough evacuation at liquid nitrogen temperatures. Combustion analyses showed the product to be pure azomethane.

The decomposition apparatus consisted of a 200-cc. Pyrex reaction vessel connected to a large storage vessel through an auxiliary, calibrated filling vessel of 200-cc. capacity. The purpose of the filling vessel was (1) to prevent an explosion spreading to the storage vessel, and (2) to enable a more accurate determination of the initial pressure in the reaction flask. The reaction vessel was also connected to a Toepler pump and to the usual pumping system.

The reaction bulb was placed in an electrically heated air-bath provided with a temperature controller. The temperature was determined from millivolt readings of an iron–constantan thermocouple located in a glass thermowell near the center of the reaction vessel.

Each experiment was conducted by admitting azomethane from the storage bulb to the filling vessel, noting the pressure in the filling vessel, opening the filling vessel to the reaction bulb for two seconds, and closing the stopcock which isolated the reaction chamber. The reaction was followed by means of a manometer until the desired decomposition was obtained, whereupon the contents of the reaction vessel were removed quickly by expansion into a previously evacuated flask at room temperature. The gas was subsequently forced out of this flask by means of mercury into a graduated gas buret, where the quantity was measured. The gas quantities used for an analysis varied from 100 to 175 cc.

The gas was then passed into a small fractionating column, the bottom of which was cooled with carbon dioxide–acetone mixture to about −78°. The top of the column was cooled with liquid nitrogen. A portion of the sample passed through the two condensing media and consisted largely of nitrogen. The remainder of the sample was then fractionated into four portions, the last portion being obtained by opening the column (about 4 cc. total capacity) to an evacuated 400-cc. flask.

Each of the five fractions was then analyzed by combustion with oxygen over a heated platinum spiral. The first fraction was mostly nitrogen with small amounts of methane. The second fraction contained methane with small quantities of nitrogen. The third fraction was ethane with small amounts of methane and possibly traces of ethylene. The fourth fraction contained the remainder of the ethane and, in experiments involving partial decomposition, azomethane. The last fraction, in the case of complete decomposition, showed the same analysis as the fourth fraction. Where azomethane was present, the last fraction was largely azomethane.

At the end of each distillation a small amount of liquid was observed on the walls near the bottom of the column. This was not volatilized by boiling water at a pressure of about 20 mm. In this connection, a pronounced fog was observed when the sample from the reaction vessel was brought to atmospheric pressure. This fog usually disappeared during the transfer to the gas buret.

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(1) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

(2) Rice and Ramsperger, *ibid.*, **50**, 617 (1928).

(3) Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

(4) Ramsperger, THIS JOURNAL, **49**, 1495 (1927).

(5) Thiele, *Ber.*, **42**, 2575 (1909).

(6) Allen and Rice, THIS JOURNAL, **57**, 310 (1935).