HEATS OF COMBUSTION AND FORMATION OF SOME SIMPLE ALIPHATIC AMINES

by

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I. INTRODUCTION

The heat of formation ($_{\Delta}H_f$) of a molecule is defined as the change in enthalpy for the isothermal reaction in which a mole of the substance in a defined state is formed from the elements, each in its standard state, as for example;

$$C \text{ (graphite)} + O_2 \text{ (gas)} = CO_2 \text{ (gas)}$$

The standard states customarily used are the ideal gas at a pressure of one atmosphere and the solid or liquid under a pressure of one atmosphere (or under its own vapor pressure), all at the temperature specified.

It is possible to analyse a chemical reaction thermochemically into two steps. The first step involves the decomposition of each of the reactants in the given state into its elements in the defined states. The heat of this process is the negative of the sum of the heats of formation of the reactants. The second step is the recombination of the elements to form the products in the given state with a heat equal to the sum of the heats of formation of the products.

$$\text{Reactants} = \text{elements} \qquad (1)$$
$$\Delta H_1 = -\Sigma \Delta Hf_R$$

$$\text{elements} = \text{Products} \qquad (2)$$
$$\Delta H_2 = \Sigma \Delta Hf_P$$

adding reactions 1 and 2 gives

$$\text{Reactants} = \text{Products} \qquad (3)$$
$$\Delta H_3 = \Delta H_2 + \Delta H_1 = \Sigma \Delta Hf_P - \Sigma \Delta Hf_R$$

The heat of reaction (3) can be computed if the heat of formation of each substance in the state involved in the reaction is known. This follows as a consequence of the definition of the internal energy (U) and the enthalpy (H) as functions of the state of a system and, for a particular mass, defined by the variables temperature and pressure[1]. The change in energy for a reaction is thus a function only of the initial and final states; thermodynamically speaking, the path by which the reaction takes place is of no consequence. This was first shown to be true experimentally by Hess[2] (Hess' law) in 1840 and has been verified by countless experiments since then. This law is the basis of thermochemistry.

The heat of formation of a compound may be measured calorimetrically either by direct synthesis from the elements, as in the case of carbon dioxide or water,

$$H_2 \text{ (gas)} + 1/2\ O_2 \text{ (gas)} = H_2O \text{ (gas)}$$

or indirectly by a reaction in which the heats of formation of all the substances involved, with the exception of the molecule in question, and the heat of the reaction are known. For the majority of the organic compounds the indirect method is the more practical one. The heat of combustion of these compounds, where the substance is burned in oxygen to form well defined products (CO_2, H_2O, N_2) is especially useful because of the high precision with which it can be carried out experimentally. In addition, the heats of formation of the products have been determined to a high degree of accuracy.

If the heat of formation of every compound were known it would be possible to compute the heat for any reaction involving any of the compounds. To obtain this information it would be necessary to measure at least one chemical reaction for each compound. However, it is possible to reduce the number of reactions that must be measured through correlations of internal energy with molecular structure. This has been done with great success for the hydrocarbons, in which the method of energy increments for specific normal alkyl radicals has been adopted.

In the hydrocarbons, it is possible to break the molecule into two portions. The first part is the functional group. This may be simply a methyl group, or a more complex

unit such as CH_2=CH-, CH≡C-, phenyl, cyclohexyl, or cyclopentyl. The second portion is the n-alkyl chain, $-(CH_2)_nCH_3$. From the heats of combustion of the simple normal paraffin hydrocarbons, the alkyl benzenes, 1-alkenes, alkylcyclopentanes, and alkylcyclohexanes, it is possible to arrive at values for the changes in the heat of combustion and the heat of formation, in both the liquid and gaseous states, as $-CH_2-$ groups are inserted in the alkyl chain[3]. These increments are constant, beginning with the third member of the series, propane. The addition of further $-CH_2-$ groups increases the heat of combustion by a constant amount, independent of the functional group or the length of the chain. To a lesser degree, this works with branched side chains, provided the point of branching is at least two or three carbons removed from the functional group. In this case the paraffin hydrocarbon with the same branched structure is used as a reference, rather than the straight chained compound. The difference between the heats of combustion of the two paraffin compounds (normal and branched hydrocarbon) is used as a correction term to the value calculated by the simple increment method. Where the branching is close to the functional group, as in tert-butylbenzene, the steric strains created by the $-CH_3$ groups and the benzene ring prevent an accurate estimate of the heat of combustion. This situation does not exist in a compound such as 1-phenyl-4, 4-dimethylpentane, and its heats of combustion and formation may be estimated with reasonable accuracy.

Thus, with the energy increment for the $-CH_2-$ group and a dozen or so experimental values, it is now possible to calculate the heat of combustion and formation, in both the liquid and gaseous states, for any number of hydrocarbons.

A still more fundamental picture of the energy content of a molecule may be obtained when one relates the energy content directly to the molecular structure. The positions of the atoms, the relationship of one atom to another, the valence bonds between atoms as they form a molecule, represent an interplay of forces. When the atoms are rearranged or the bonds are ruptured, a change of energy content is involved. The formation of new molecule gives rise to a new energy content and the difference between the energy contents of the old and the new molecules is the heat of reaction. Unfortunately, it is impossible to measure the actual total energy of a molecule. All that can be determined is the energy relative to some reference state. What one measures or calculates is the difference in energy between two states and not the actual bond energies.

In the comparatively simple molecule methane (CH_4), the energy of the C-H bond (the "average" bond energy) is considered to be one fourth of the energy of atomization. The reaction involved is

$$CH_4 \text{ (gas)} = C \text{ (gas)} + 4H \text{ (gas)} \qquad (4)$$

From the heats of formation of both carbon gas and hydrogen gas and the heat of formation of methane gas it is possible to calculate the heat of reaction (4). In this reaction four C-H bonds have been ruptured, therefore the average C-H bond strength is given by one fourth of the total heat of reaction (4). Using the bond energy for the C-H bond and a measured heat of formation for ethane (CH_3-CH_3) it is possible to calculate a C-C bond energy. By propitious choice of compounds it is possible to obtain a series of bond energies which can be used to estimate the energy content of a substance to a fair degree of accuracy without experimental measurements. In a homologous series such as the hydrocarbons, it has been possible to evaluate energies for the various types of bonds, taking into account the neighboring bonds, so that the energy of more complex compounds may be calculated[4].

With a mass spectrometer it is possible to determine the energy involved in breaking individual bonds. Thus the energy involved in breaking the first N-H bond in ammonia is 104 kcal/mole[5] although the average bond energy of a N-H bond is 93.4 kcal/mole. In computing the heat of combustion the average bond energy is in general sufficient.

With this in mind, the heats of combustion of the simplest alkylamines, the primary, secondary, and tertiary methyl and ethylamines, were measured to provide a basis for the increment method of computing the heats of combustion and formation of homologous compounds, and to obtain values for the C-N bond energies.

II. MATERIALS, PURITY AND PURIFICATION

A. Sources

Methylamine, dimethylamine and trimethylamine are gases at room temperature and pressure. These were obtained as liquids under pressure in steel cylinders from the Olin Matheson Co. Ethylamine, diethylamine and triethylamine were Eastman Grade White Label reagent. Two or more fifty-ml. samples of each compound were transferred to break-off-tip ampoules[6]. In the case of methyl-, dimethyl- and trimethylamine, the original cylinder was attached to a manifold containing a number of fifty-ml. break-off-tip ampoules. The cylinder was cooled with a bath of solid CO_2 in a mixture of CCl_4 and $CHCl_3$ before it was opened to the manifold which had been evacuated to about 10^{-5} mm. of Hg. The material was allowed to distill under its own vapor pressure from the cylinder into an ampoule. When the ampoule was filled, the cylinder valve was closed and the material in the ampoule was frozen by placing a liquid nitrogen bath around it. The ampoule was sealed off from the manifold and stored in a freezer for future use. This procedure was repeated until the desired number of samples was obtained.

The ethyl-, diethyl- and triethylamines were received in glass containers. Each compound was poured into a pyrex vessel which was in turn sealed on to a manifold containing break-off-tip ampoules. The compounds were transferred to the break-off-tip ampoules as described above and stored.

The purity of these compounds, with the exception of dimethylamine and triethylamine, was determined from the measurement of the time-temperature freezing point curve[7,8]. The purity of the dimethylamine was obtained from infrared spectral data. The purity of the triethylamine was determined from the ratio of the weight of carbon dioxide obtained as a product of the combustion to the stoichiometric weight of carbon dioxide calculated from the weight of sample used.

B. Purity

1. Methylamine, Trimethylamine, Ethylamine, and Diethylamine

The purity of these compounds was determined from time-temperature freezing curves. The procedure for determining the purity by this method and the principles involved have been discussed in detail[7,8,9,10,11]. The procedure was followed with some modifications as described below, to permit the use of smaller test samples.

Figure I shows a cross-section of the Pyrex freezing tube. This consists of a center tube A, enclosed by a silvered jacket B which can be evacuated. The center tube contains a platinum resistance thermometer C which fits snuggly into a slotted brass core D. The entire system has been constructed so that it may be completely evacuated, to permit the measurement of a freezing curve of a sample under its own vapor pressure.

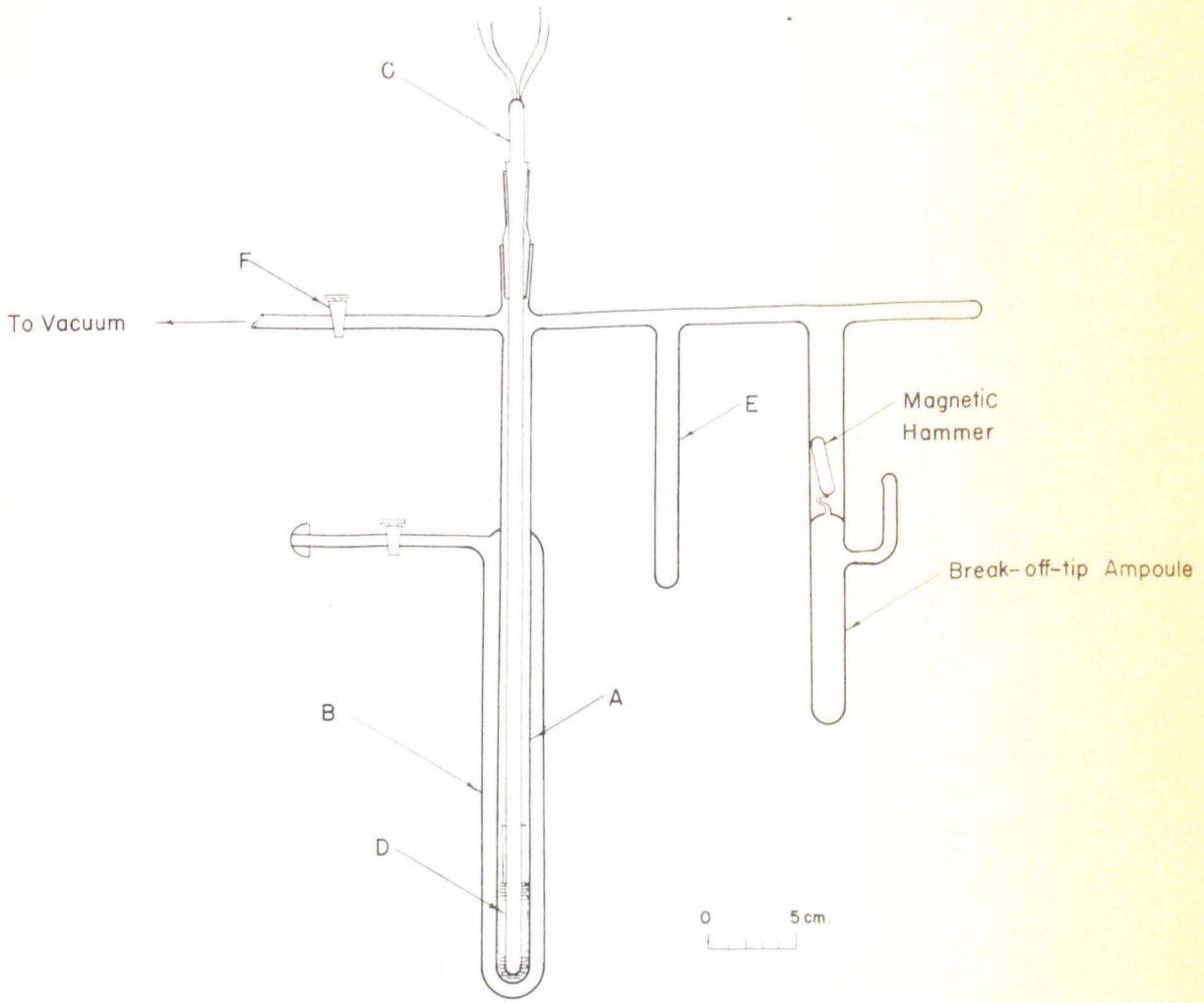

FIGURE I. Freezing Point Apparatus

The liquid when introduced into the tube A will cover the brass core. The purpose of this core is to distribute the heat uniformly throughout the body of the liquid sample. This core permits the elimination of the stirring mechanism, thereby reducing the over-all volume of the vessel. It is now possible to obtain the necessary data with a five-ml. sample instead of the usual fifty-ml. sample. Moreover, no correction term is necessary to account for energy due to stirring[11].

Approximately five ml. of a sample is transferred by vacuum distillation to the tube E. After this sample has been frozen in a liquid nitrogen bath, the stopcock F is opened and the entire system is evacuated. When the pressure is reduced to about 10^{-5} mm. of Hg, this stopcock is closed and the sample is allowed to melt. On melting, the liquid will give up any gases which are dissolved in it. The sample is once again frozen and the system is opened to the vacuum pump and evacuated. This procedure is repeated until the liquid shows no evolution of gases on melting. The liquid nitrogen bath is then placed around the tube B and the sample is transferred from tube E to tube A by vacuum distillation.

After this silvered jacket B has been evacuated, the apparatus is removed from the vacuum line. Figure II is a schematic drawing showing the arrangement of the various components used in obtaining the time-temperature curve. The thermometer is a Meyers and Knapp glass-envelope twenty-five ohm platinum resistance thermometer #S-109. The

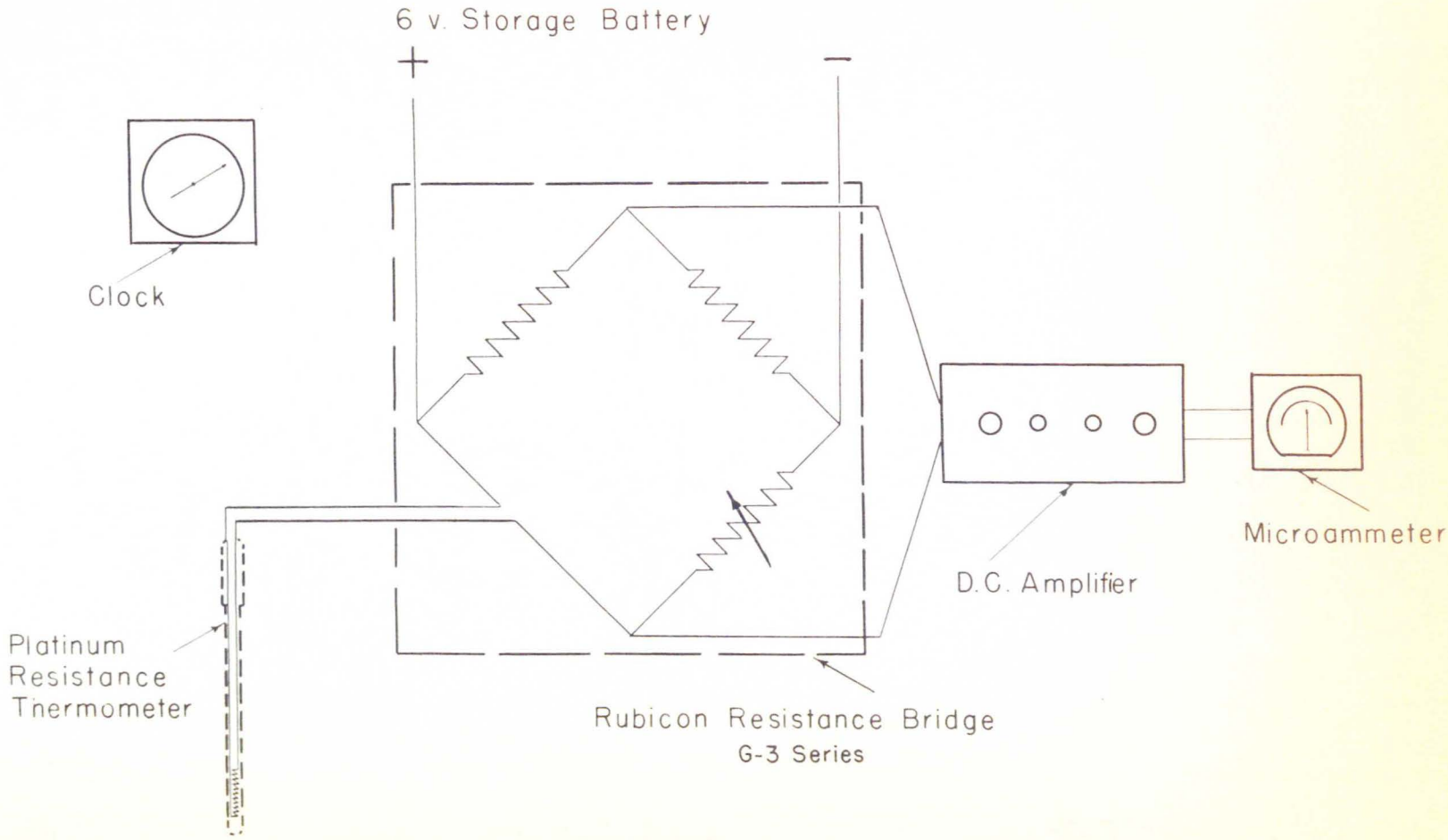

FIGURE II. Schematic drawing of the components used to measure Time-Temperature Curves

Wheatstone bridge is a Rubicon Model G-3, and the amplifier is a Liston-Becker direct current amplifier Model No. 14, which is connected to a Triplett microammeter whose scale reads 50-0-50. A six-volt storage battery is used to supply the thermometer current. The advantages of this system over the one used previously[11], which uses a suspension galvanometer and an optical system to increase the sensitivity of the galvanometer, are its compactness and its greater sensitivity. It is possible to increase the sensitivity of this system to be able to read a change of $1X10^{-6}$ ohms. The platinum resistance thermometer has been calibrated by the Heat Division of the National Bureau of Standards and the resistance bridge has been calibrated by the Electricity Division of the National Bureau of Standards.

After the thermometer has been connected to the bridge, the freezing bath is removed and the sample is allowed to melt completely, as indicated by a sharp rise in the rate of change of the temperature. The freezing bath is replaced around tube B and the temperature of the sample followed and recorded as it begins to freeze.

The bridge is set at an appropriate value of the resistance and the time is recorded when the microammeter indicates zero current. The rate of temperature change is estimated so as to give a reading at approximately every two minutes before the liquid freezes. While the liquid is being frozen the intevals are taken closer together to give a more defined curve.

The purity of the compound was calculated by the methods previously described with the basic equation

$$N_2 = \frac{1-r}{r} \; A \; (T_o - T_f)^{8,9}$$

N_2 is the mole fraction of impurity in the original substance, r the fraction of the sample frozen, A the cryoscopic constant $(\Delta H/RT_o^2)$, T_o the temperature at which crystallization would begin if no supercooling occurred, and T_f the temperature at which the crystallization is complete. This method does not require highly accurate measurement of absolute values of temperature since it is the difference between $T_o - T_f$ which is required.

Figure III shows a typical time-temperature freezing curve. Where the purity was found to be less than 99 mole percent, the material was further purified as described below.

Methylamine, dimethylamine, trimethylamine, and ethylamine were purified by fractional crystallization. The technique of fractional crystallization has been discussed in detail[12]. In essence the separation of a single component from its impurities by fractional crystallization depends upon the slow growth of crystals. If the rate of crystallization is very slow it becomes possible for the crystal to select preferentially the pure component and reject the impurites. Moreover the slow rate of growth will produce large crystals which have the advantage of small surface area. This will reduce the amount of liquid retained on the surface of the

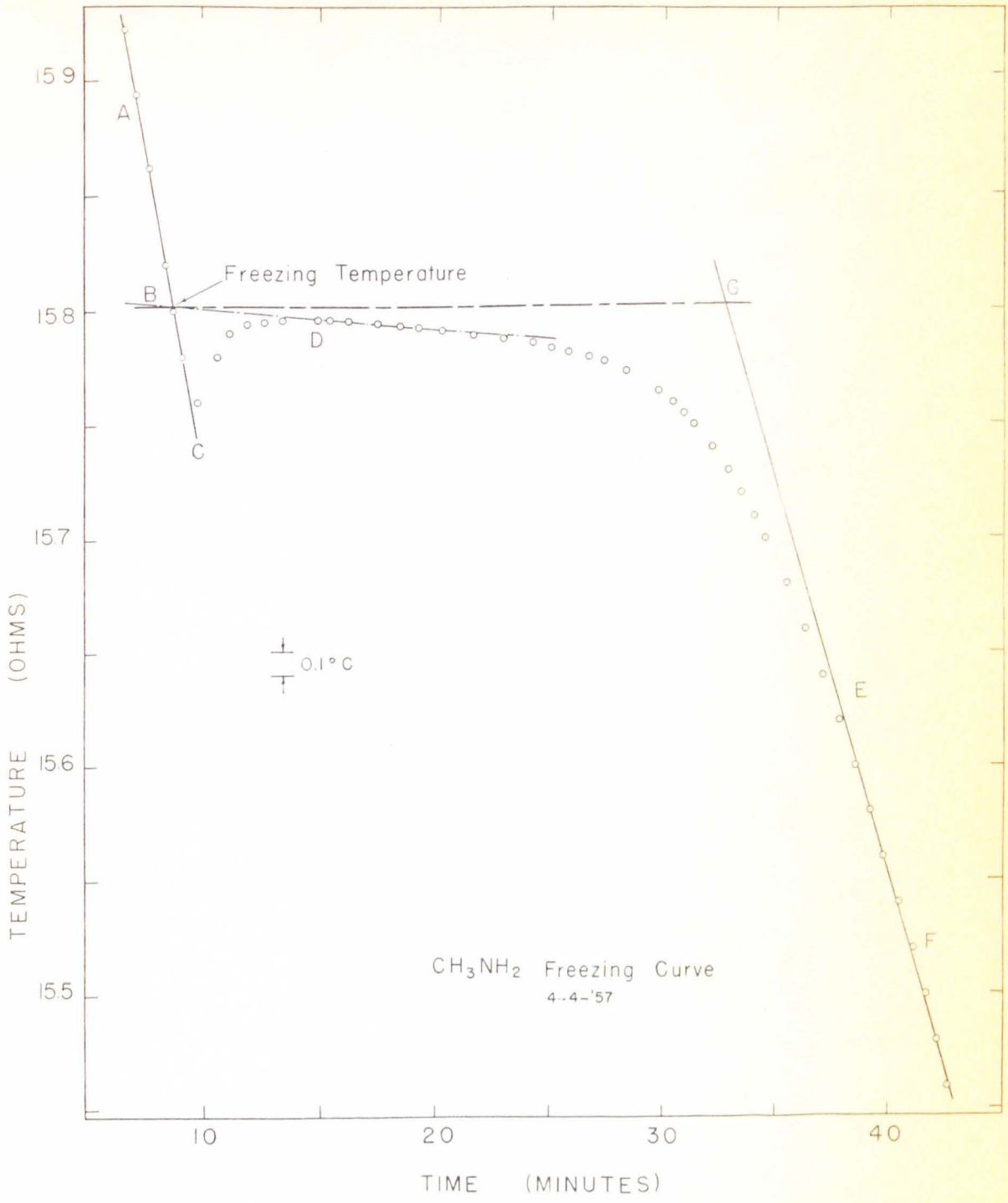

FIGURE III. TIME - TEMPERATURE CURVE

A-B, the liquid phase is cooled; B-C, the liquid phase is supercooled; C-D-E, the liquid phase is frozen; B-G, total time to complete freezing.

crystal. As the crystals grow, the liquid phase becomes more and more concentrated with respect to the impurity, and may be separated from the main body of material by decanting. In the present work the boiling points of the materials used range from -6° to +17°C. This makes it necessary to carry out the fractional crystallization in a closed system.

The apparatus developed for the fractional crystallization, Figure IV, consists of a large "U" tube A. Around one end is a vacuum jacket B, while on the other end is a series of tubes C, each capable of holding approximately twenty-five ml. of liquid. These tubes are attached in such a manner that they may be easily sealed off and removed. In addition to these tubes, a twenty-five ml. break-off-tip ampoule D is sealed on at the base of the "U" tube. The entire apparatus is made of pyrex glass.

This crystallization cell is sealed on to a vacuum line. A break-off-tip ampoule containing approximately fifty ml. of the impure sample E, is also sealed on the vacuum line. The entire system is pumped down to approximately 10^{-5} mm. of mercury. When this point is reached a liquid nitrogen bath is placed around tube B and the break-off-tip in ampoule E is broken. When nearly all the sample has been transferred by vacuum distillation from E to A, a liquid nitrogen bath is placed around the ampoule E, and any excess sample remaining in E is frozen solid. The crystallization cell is removed from the vacuum line by sealing it off with a hot flame at F. A vacuum 10^{-5} mm. of Hg or better is established

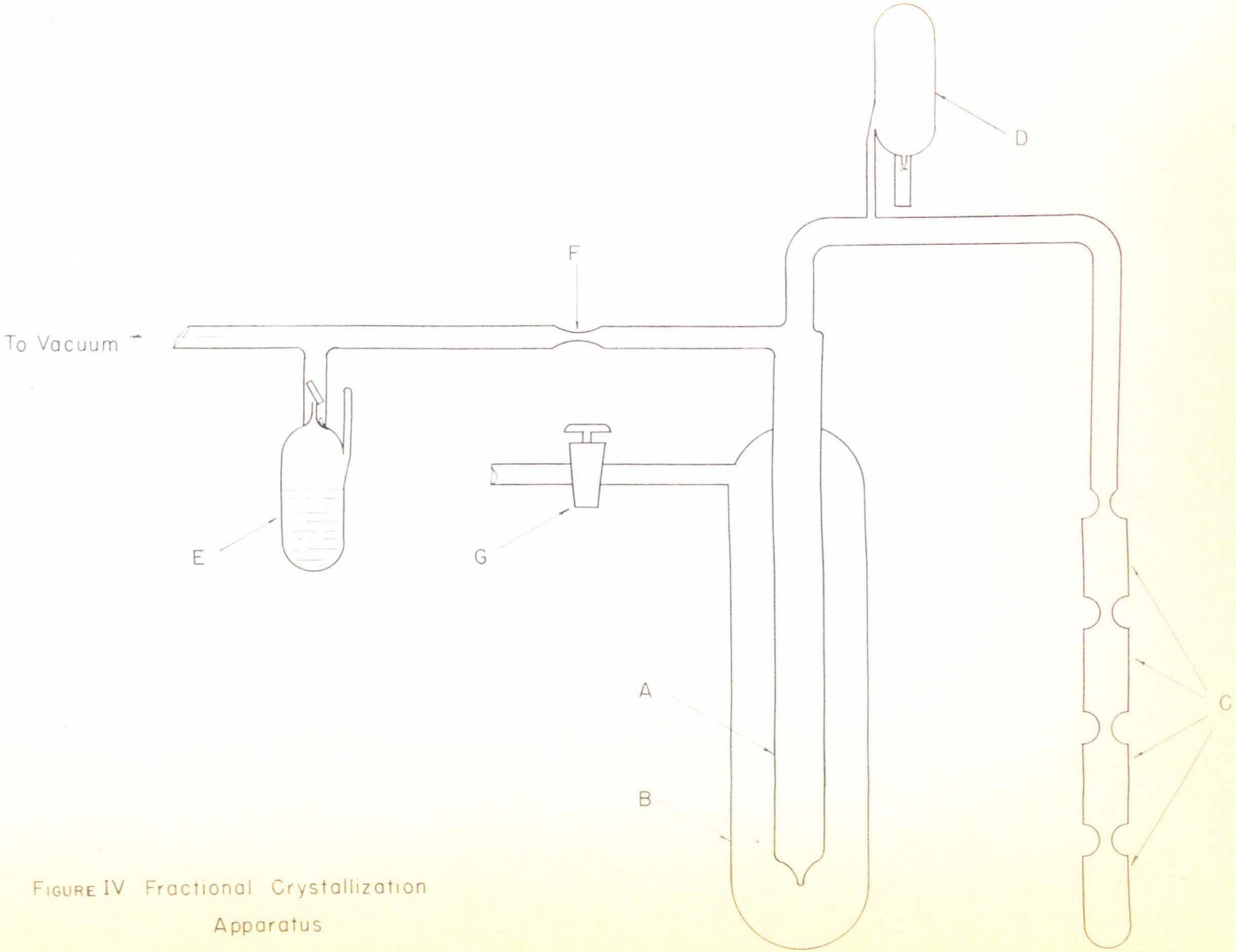

FIGURE IV Fractional Crystallization Apparatus

between A and B and the material is ready to be purified.

The crystallization cell is clamped securely to a sturdy ring stand with the vacuum jacketed arm in a large Dewar flask. Liquid nitrogen is poured into the Dewar flask until the level of the liquid nitrogen is even with the bottom of tube A containing the sample. The top of the Dewar flask is covered by a lid cut to fit around the cell. The level of the liquid nitrogen is maintained constant until crystals begin to appear in the liquid at the base of the tube A. When these crystals appear, the level of the liquid nitrogen is raised slowly causing more crystals to grow. This process is continued for a period of twenty to twenty-four hours until all but approximately five ml. has crystallized. The cell is removed from the ring stand and quickly inverted, pouring the liquid phase of the sample in A to the bottom tube at C. The cell is then replaced on the ring stand with both arms of the tube now submerged in liquid nitrogen baths. The liquid in C is frozen and the tube containing the impure material sealed off and removed. The crystallized material is allowed to melt completely whereupon the procedure as described above is repeated. When this has been repeated three times, the cell is inverted and the purified liquid is transferred to the break-off-tip ampoule D where the liquid is frozen and the ampoule is sealed off and removed.

2. Triethylamine

It was not possible to obtain a time-temperature freezing curve on triethylamine. This compound when cooled

solidified into amorphous glass. As is characteristic of this type of substance, there is no sharply defined freezing point. To obtain an estimate of its purity the ratio of the mass of carbon dioxide obtained as a product of the combustion to the stoichiometric mass of carbon dioxide calculated from the original mass of sample used was examined. The average ratio for five experiments is 0.99515±0.00254. This would indicate that the purity of triethylamine is better than 99 mole percent. Table I gives a summary of the data including the freezing points of the pure compounds, T_{fo}, the purities of the original sample and that of the purified sample and finally the average ratios obtained in the manner described above.

3. Dimethylamine

An infrared analysis was made on a sample of dimethylamine by J. Stewart of the Gas Chemistry Section of the National Bureau of Standards. This analysis was made to determine the purity and the identity of any amines other than dimethylamine. The results showed the presence of less than 0.07 mole percent of ammonia and less than 0.03 mole percent of methylamine. The spectral data showed no indication of ethylamine or trimethylamine within the limits of the determination, which were considered to be less than 1% of the values reported. The purity of dimethylamine was estimated from these data to be better than 99.8 mole percent. The mean carbon dioxide ratio obtained for this compound was 1.00116±0.00031.

Table I. Physical Properties of the Amines

Amine	Tf° °K	Purity (original) mole percent	Purity (purified) mole percent	Ratio*
methyl-	179.3	99.1	99.7	1.00133 ±0.00076
dimethyl-	180.7	98.7	99.8	1.00116 ±0.00031
trimethyl-	155.2	98.9	99.1	0.99565 ±0.00272
ethyl-	256.0	99.2	99.9	0.99345 ±0.00300
diethyl-	224.3	99.7		0.99814 ±0.00305
triethyl-		99+		0.99515 ±0.00254

*Ratio of mass of CO_2 determined experimentally to stoichiometric mass of CO_2 calculated from mass of sample burned.

III. HEATS OF COMBUSTION

The energy content of an organic compound, relative to that of the constituent elements at the same temperature, is most easily determined from measurements of its heat of combustion. These data may then be combined with the appropriate auxiliary data, such as the heats of formation of the products, to obtain the heat of formation of the compound. In this method the heat of formation is obtained as the relatively small difference between the sum of the heats of formation of the combustion products and the heat of combustion. For this reason a high degree of precision is necessary in the measurement of the heats of combustion.

The determination of a heat of combustion may be considered to consist of two parts, the calorimetric and chemical. The calorimetric part is the measurement of the heat evolved during a particular reaction, in this case the combustion of an amine; the chemical part is a determination of the precise reaction which took place, or characterizes the initial and final states of the reaction.

A. Method and Apparatus

The method, apparatus, and procedure used have been described in detail in previous publications[13,14,15,16,17,18]. The calorimetric apparatus consists of an isothermal-jacketed calorimeter which houses a calorimeter can containing a weighed amount of water, a bomb, a platinum resistance thermometer, a heater, and the electrical connections for igniting the sample.

The jacket of the calorimeter contains approximately eleven liters of water which is kept near 28°C. The temperature of the jacket is controlled by a photo-electric regulator which maintains the temperature of the bath to within ±0.001°C[18].

The calorimeter can has been modified slightly from that described previously. The three ivory pegs which supported the can have been replaced by three insulated brass supports (120° apart, one inch below the rim of the calorimeter well), which serve as contacts for the heater, the ignition lead, and the ground lead. The calorimeter can has three insulated brass rods approximately 5/8 of an inch long projecting horizontally from the top of the can. These rods on the can fit into brass supports in the calorimeter well. When the calorimeter can is set in position, it is suspended from the brass supports with an air gap approximately 1/2 inch wide on all sides. The insulated brass rods on the can serve as terminal posts on the inside of the can. One post is used for the heater which is used to supply heat to the water and bomb in the can to raise them to the proper temperature. This heater is mounted permanently below the stirrer and replaces the coiled heater which formerly fitted snugly around the bomb[18]. The second post is used for the ignition wire and the third post is used as a ground. The can, heater, and ignition leads have become a single unit. This facilitates the assembly of the apparatus and reduces considerably the heat leak by conduction through the leads.

The thermometer used is a Leeds and Northrup blade-type,

metal-encased platinum resistance thermometer No. NBS-616. The resistance of this thermometer is measured with a Mueller-type resistance bridge of the G-2 series made by the Eppley Laboratories and a Leeds and Northrup suspension galvanometer. Both the platinum resistance thermometer and the resistance bridge were calibrated at the National Bureau of Standards. The bomb employed is a double valve Parr bomb similar to those previously used[13,19], except that it has a Teflon (polytetrafluoro-ethylene) washer in place of the large gold washer, Teflon valve packings, and a Teflon electrode insulator.

The amines were burned in the liquid state. Because of the high vapor pressure of the amines the samples were sealed in weighed glass ampoules filled by vacuum distillation at low temperature. The ampoules were thin-walled soft-glass spherical bulbs, which were made to withstand a pressure of thirty atmospheres. The soft-glass spherical bulb was chosen since its shape gives the greatest strength while the soft glass is easily broken by the ignition wire.

To test the spherical bulbs before filling they were sealed as shown in Figure V-A and placed in the empty bomb. The bomb was sealed and filled slowly with oxygen to a pressure of thirty atmosphere. The pressure was then slowly lowered to one atmosphere and the bomb was opened. Those ampoules which survived the test were opened. The open stem and bulb was weighed and sealed onto a pyrex manifold, Figure V-C, with Apiezon Wax W*. Eight bulbs and a break-

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* Manufactured by the Metropolitan-Vickers Electrical Co., Ltd., England

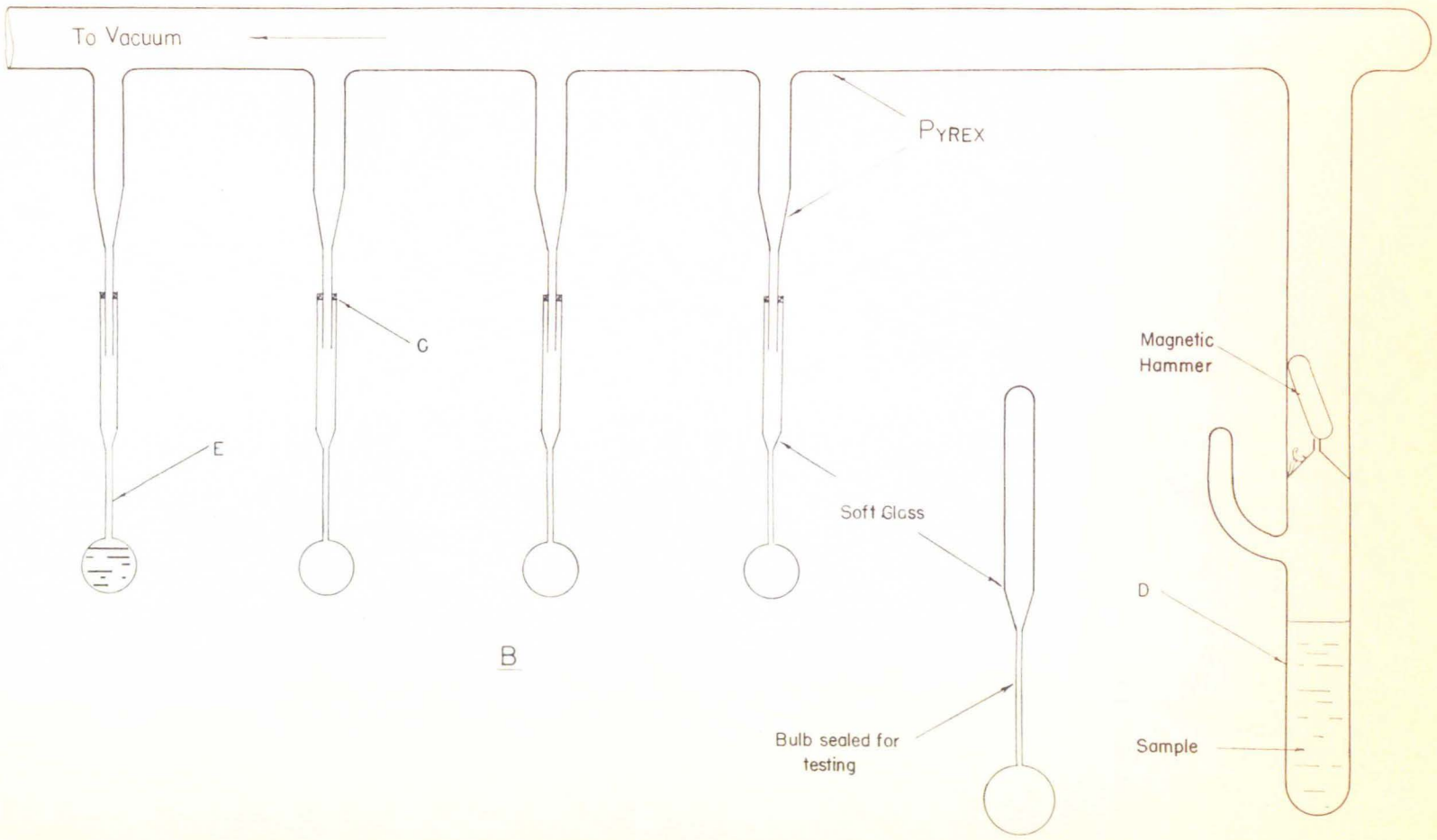

FIGURE V. Assembly for filling soft-glass bulbs

off-tip ampoule which contained the pure sample were attached to the pyrex manifold. The entire system was evacuated and tested for leaks with a Tesla Spark coil. After the system was proven to be vacuum tight it was evacuated to 10^{-5} mm. Hg and isolated from the vacuum pump by a stop-cock. A liquid nitrogen bath was placed at the bottom of the first soft-glass ampoule, the tip in the ampoule containing the sample was broken, and the sample transferred under its own vapor pressure to the ampoule. Because these substances have low freezing points and the liquids have high coefficients of expansion, the bulbs could not be filled entirely, as the expanding liquid on warming to room temperature would break the ampoule. When it was estimated that sufficient liquid had been transferred (approximately 1.5 ml.), a liquid nitrogen bath was placed around the ampoule D and the liquid was frozen solid. The soft-glass ampoule was sealed off with a hot flame and removed. The stop-cock was opened and the manifold was tested again for leaks. The liquid nitrogen bath was removed from around D and the compound was allowed to warm up to room temperature. The entire procedure as described above was then repeated for the second bulb.

When all the ampoules were filled, the manifold was opened to the atmosphere and all the stems were marked corresponding to their bulbs and removed from the systems. These stems were cleaned throughly with carbon tetrachloride and then weighed with their respective filled bulbs to obtain the mass of sample contained in each bulb. The samples were stored in the constant temperature calorimetric laboratory

until they were burned. After it was weighed a bulb was placed in a platinum crucible and the crucible was then placed in a 330-ml. bomb to which 1 ml. of water had been added. The bomb was flushed with oxygen and then filled to 30 atm. The oxygen had been passed through a copper oxide furnace to oxidize any hydrogen and carbon monoxide present to water and carbon dioxide. From the furnace the oxygen passed through a tube containing Ascarite to remove the CO_2 and then through a second tube filled with magnesium perchlorate and phosphorous pentoxide to remove any water. The bomb and its contents were placed in the calorimeter can which contained 3615 gms. of distilled water. The entire system was then allowed to reach thermal equilibrium.

The thermometric portion of an experiment consists of a twenty minute 'fore' period, a sixteen minute 'reaction' period, and finally a twenty minute 'after' period. With the temperature of the jacket held constant at approximately 28°C, the combustion experiment was started at an initial temperature near 25°C. During the 'fore' period the temperature was recorded every two minutes. At the twentieth minute the sample was ignited by placing a potential of 32 volts across the iron fuse wire 5 cm. long and 0.012 cm. in diameter which was coiled above the ampoule in the bomb. The ignition current flows for a period of approximately two to three seconds, stopping automatically when the iron wire burns through. In the first five minutes of the 'reaction' period, observations were made of the time, to the nearest tenth of a

second, at which the resistance of the thermometer attained certain preselected values. This was accomplished with the aid of a tape chronograph which has two needles recording tracks parallel to one another. One needle traces standard second impules which it receives from the Time Section of the National Bureau of Standards. The second needle is activated by a telegraph key which is tapped at the instant the temperature reaches the preset resistance. During the remaining eleven minutes of the 'reaction' period, during which time the calorimeter reestablishes thermal equilibrium, the temperature change was very small and observations were made every minute. The 'after' period followed,during which the temperature was recorded every two minutes. At the end of the 'after' period, the temperature of the jacket was measured. Five combustion experiments were made of each of the amines, and five combustion experiments were made on benzoic acid which was used to calibrate the calorimeter system. The same procedure was followed in all the experiments. In the case of ethylamine the addition of an auxiliary substance, n-hexadecane, was required to obtain complete combustion of the ethylamine.

B. Chemical Procedure

In all cases the amount of sample burned was determined from an analysis of the CO_2 formed as a result of the combustion. To measure the amount of CO_2 formed, the bomb was removed from the calorimeter can at the end of the 'after'

period and connected to an analytical train. This train consists of an absorption tube containing magnesium perchlorate and phosphorous pentoxide and a weighed absorption tube containing Ascarite* (sodium hydroxide deposited on asbestos), to absorb carbon dioxide, and magnesium perchlorate and phosphorous pentoxide to absorb the water formed as a result of the reaction of the carbon dioxide with the sodium hydroxide. The bomb was emptied through these tubes at a rate of approximately 200 ml. of gas per minute to insure absorption of all the carbon dioxide. When the bomb reached room pressure it was flushed with purified oxygen at the same rate for a period of ninety minutes. The Ascarite tube was removed, cleaned, and weighed to obtain the weight of the carbon dioxide formed as a result of the combustion reaction. The bomb was removed from the train, opened and washed out with distilled water. The washings were collected and titrated with a 0.1 N solution of sodium hydroxide to determine the amount of nitric acid formed. Methyl red was used as the indicator.

It is unlikely that any of the lower oxides of carbon and nitrogen would be present in this oxygen-rich atmosphere. To confirm this, spot checks for carbon monoxide were made on some of the experiments with carbon monoxide indicating tubes[20]. These tubes were placed in the analytical train and the gases from the bomb were passed thru. In all cases

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* Distributed by A. H. Thomas Co., Philadelphia, Pa.

the amount of carbon monoxide present was extremely small, less than 0.001%. To determine the presence and amount of any other oxides of nitrogen in addition to nitrogen pentoxide (nitric acid) a mass-spectrometric analysis was made on samples of the gases obtained as products from separate combustions of methylamine and diethylamine. Two samples were obtained from each substance by collecting the gases as they flowed from the bomb. Samples marked one were taken before the gases passed into the absorption tube containing the Ascarite. The samples marked two were collected as the gases left the Ascarite tube. Thus one contained all the gases and two contained the same gases with the exception of the carbon dioxide, giving a check on the analysis. The mass-spectrometric analysis were made by the Section on Molecular Structure and Properties of Gases of the National Bureau of Standards. The results reported are given in Table II. The high percentage of carbon monoxide found in the mass-spectrometric analysis is inherent in the spectrometer as a consequence of the carbon filament used.

In the first combustion experiments on ethylamine the ratios obtained from the mass of carbon dioxide collected and the mass calculated from the weight of sample used were discordant and unusually low, due to incomplete combustion. To insure complete combustion an auxiliary compound was added to increase the intensity of the heat applied to the bulb and to maintain a flame of longer duration; n-hexadecane, NBS Standard Sample No. 568-55, which has a purity of

Table II. Mass Spectrometric Analysis

Sample No.	Components (mole percent)						
	CO_2	A	O_2	N_2	CO	N_2O	NO_2
CH_3NH_2 No.1	4.4	0.25	90.4	1.2	3.7	0.03	0.01
CH_3NH_2 No.2	0.07	0.22	93.2	2.6	3.9	0.03	
$(CH_3CH_2)_2NH$ No.1	12.2	0.20	81.4	1.2	4.9	0.02	0.00
$(CH_3CH_2)_2NH$ No.2	0.14	0.27	95.3	1.3	3.0	0.02	

99.94 ± 0.04 mole percent, was used. In this case, as in those above, the total reaction was based upon the weight of CO_2 collected.

To calibrate the calorimeter benzoic acid (NBS Standard Sample 39-G) was used. In these calibration experiments the amount of reaction was determined from the mass of sample burned[21]. However, in many cases, both the mass of sample introduced and the mass of carbon dioxide produced were determined. The average ratio of the amount of carbon dioxide formed to that calculated stoichiometrically from the mass of sample (benzoic acid) used was 0.99999 ± 0.00007 (standard deviation of the mean). This ratio of near unity for benzoic acid indicates that the carbon dioxide analyses are correct. By using the carbon dioxide analysis to determine the extent of reaction and not the sample weight, small amounts of water or any inert impurities in the amine samples will not affect the calorimetric results. The atomic weights of carbon, oxygen, hydrogen, and nitrogen were taken as 12.010, 16, 1.0080 and 14.008[22]. The unit of energy is the absolute joule (j). To convert to thermochemical calories, the relation 1 cal = 4.1840j was used.

IV. RESULTS

The calculations involved have been discussed in detail in previous publications[13,17]. A sample calculation for a combustion experiment is given in Appendix A. The data obtained in the calibration of the calorimeter and the combustion experiments on the amines are summarized in Tables III-VI. Table III contains the data for the six calibration experiments with benzoic acid. Listed are the mass of benzoic acid used (all weights are corrected to vacuum); e_1, the deviation of the experimental system from the standard calorimetric system, including the heat capacity of benzoic acid and of the parts of the system changed since the selection of the standard system; $^{*}\Delta R_c$, the corrected change in temperature in ohms; q_i, the ignition energy (7.5 j/mg iron)[25]; q_n, the heat evolved by the formation of nitric acid (57.8 kj/mole HNO_3(aq)[25]; and E_s, the energy equivalent of the standard calorimetric system. The quantity E_s is computed from the relation $E_s = (Q/\Delta R_c) - e_1$, where Q designates the total amount of heat evolved in the bomb process for the experiment at the constant temperature of 28°C (final temperature of the experiment), 26432.2 j/g of benzoic acid. The

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* The system used for the first calibration experiment is taken as the standard system. This system is used throughout the calibration and combustion experiments; corrections are applied to take into account any small changes to the apparatus or conditions of the experiments.

Table III. Calibration experiments with standard benzoic acid

(NBS Standard Sample 39g.)

Expt. No.	Mass of benzoic acid g	Δe_1 j/ohm	ΔR_c ohm	q_i j	q_n j	E_s j/ohm
1	1.57522	16.7	0.295850	37.5	3.2	140856.9
2	1.56719	16.6	0.294309	35.6	2.9	140866.0
3	1.57688	16.8	0.296053	35.2	2.5	140898.2
4	1.57519	17.0	0.295863	35.6	2.8	140839.6
5	1.57660	16.8	0.295982	36.4	2.0	140909.4
6	1.57408	16.8	0.295575	38.0	2.9	140885.4
mean						140875.9
Standard deviation of the mean						±10.8

heat of combustion of the standard benzoic acid under standard bomb conditions and at 25°C was taken as 26433.8 j/g[15,23,24].

In Table IV-VI, the data are listed for the combustion experiments on methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, and triethylamine. The mass of carbon dioxide given is that collected as a result of the combustion of the sample. In the case of ethylamine, where n-hexadecane is used as an auxiliary compound to insure complete combustion, the value given is the total mass of carbon dioxide collected minus the mass of carbon dioxide calculated stoichiometrically from the mass of n-hexadecane used. It is assumed that in all cases the combustion of the n-hexadecane was complete. The remaining quantities have the following significance; e_2 is the deviation of the actual calorimetric system from the standard calorimetric system and includes the heat capacity of the sample, of n-hexadecane where applicable, and those parts of the system which have been changed since the selection of the standard system; ΔR_c, the corrected temperature rise; Q, the total amount of heat evolved in the bomb during the experiment, is computed with relation $Q = (E_s + e_2)\,\Delta R_c$. ΔU^o is computed from the relation $-\Delta U^o = Q - (q_i + q_n) - W_c$, where q_i and q_n are the corrections for the ignition energy and the heat of formation of nitric acid and W_c is the "Washburn correction"[17,26], calculated for the over-all reaction in the bomb. It is the purpose of the Washburn correction to reduce the heat of combustion in the bomb process to the standard heat of com-

Table IV. Calorimetric combustion experiments for monoalkylamines

Expt. No.	Total mass of CO_2 g.	Δe_2 j/ohms	ΔR_c ohms	Q (28°C) j	q_i j	q_n j	w_c j	Q (n-hexadecane) j	$-\Delta U°$ (28°C) j/g CO_2
				Methylamine					
1	1.14411	24.2	0.196071	27626.4	36.9	96.0	0.65		24030.4
2	1.03538	21.1	0.177852	25058.8	36.9	112.4	0.41		24058.5
3	1.24997	27.9	0.214225	30185.1	35.8	58.4	0.87		24073.0
4	1.48032	33.1	0.253712	35750.3	36.2	112.1	1.32		24049.6
5	1.02748	20.9	0.176383	24851.8	35.8	85.5	0.41		24069.2
mean									24056.1
Standard deviation of the mean									±7.6
				Ethylamine					
4	1.56378	23.08	0.216401	30490.7	36.8	103.7	7.0		19403.9
7	0.73799	8.97	0.102266	14407.7	37.1	41.0	1.6		19419.6
9	1.11948	14.12	0.159804	22514.8	34.0	36.8	2.6	706.0	19416.9
10	1.16938	15.97	0.160255	22578.6	37.2	37.4	2.6	804.5	19435.6
11	1.14966	14.42	0.163446	23028.0	40.8	77.7	2.8	571.6	19428.6
mean									19420.9
Standard deviation of the mean									±5.4

Table V. Calorimetric combustion experiments for the dialkylamines

Expt. No.	Total Mass of CO_2 g.	Δe_2 j/ohm	ΔR_c ohm	Q (28°C) j	q_i j	q_n j	w_c j	$-\Delta U°$ (28°C) j/g CO_2
			Dimethylamine					
1	1.03421	12.3	0.146108	20570.4	37.1	77.1	7.3	19775.4
2	1.27876	18.9	0.180515	25415.7	37.1	89.5	8.9	19769.8
3	1.20238	17.6	0.169748	23899.5	37.6	92.8	8.4	19762.0
4	1.63192	25.9	0.230152	32406.0	37.0	94.2	11.3	19770.4
5	0.69374	11.2	0.098086	13809.3	37.1	53.0	5.4	19768.8
mean								19769.3
Standard deviation of the mean								±2.2
			Diethylamine					
1	1.82278	16.3	0.224212	31589.7	36.8	60.4	16.4	17260.9
2	2.20678	21.3	0.270661	38135.4	37.1	31.2	11.9	17238.0
3	1.90041	16.8	0.233730	32880.6	37.0	73.0	15.7	17228.4
4	1.95680	19.0	0.240440	33876.8	35.8	70.7	14.7	17243.3
5	2.50178	26.3	0.306933	43247.5	37.8	36.4	8.5	17248.5
mean								17243.8
Standard deviation of the mean								±5.4

Table VI. Calorimetric combustion experiments for trialkylamines

Expt. No.	Total Mass of CO_2 g.	Δe_2 j/ohm	ΔR_c ohm	Q (28°C) j	q_i j	q_n j	w_e j	$-\Delta U°$ (28°C) j/g CO_2
			Trimethylamine					
1	1.42013	11.9	0.185157	26086.4	36.3	38.7	3.9	18291.2
2	0.92595	5.5	0.120955	17040.3	36.2	48.5	4.2	18307.4
3	2.28447	23.1	0.297663	41940.4	37.0	98.0	3.2	18296.6
4	2.31427	24.4	0.301545	42487.8	36.7	99.7	3.2	18296.9
5	1.12783	8.4	0.147100	20724.1	37.0	37.0	4.1	18305.5
mean								18299.8
Standard deviation of the mean								±3.0
			Triethylamine					
1	2.22825	15.7	0.261943	36905.6	46.8	35.7	23.3	16515.1
2	2.27407	16.0	0.267478	37685.5	48.1	35.8	23.6	16524.5
3	2.28822	16.1	0.269229	37932.2	55.7	35.8	23.8	16526.8
4	2.21951	16.2	0.261270	36810.9	49.0	36.7	23.3	16536.4
5	2.31690	16.0	0.272515	38395.2	55.6	38.4	24.2	16520.8
mean								16524.4
Standard deviation of the mean								±3.6

bustion with each substance in its thermodynamic standard state. The thermodynamic standard state for the gases (oxygen, carbon dioxide, and nitrogen) is defined as unit fugacity, while for liquids (water) the standard state is the pure liquid under a pressure of one atmosphere. Where n-hexadecane was used as an auxiliary compound, $\triangle U^{\circ}$, the heat of combustion of the sample at 28°C, was calculated from the equation,

$$\triangle U^{\circ}(28°C)\ (\text{sample}) = \triangle U^{\circ}(28°C)\ (\text{over-all-reaction})$$

$$-\triangle U^{\circ}(28°C)\ (\text{n-hexadecane}).$$

The heat of combustion of n-hexadecane, $\triangle U^{\circ}(28°C)$, was taken as -10675.5 kj/mole[27].

V. DISCUSSION

A. Conversion to Standard Conditions

The values of $\Delta U^{\circ}(28°C)$ were reduced to $\Delta H^{\circ}C(28°C)$ using the relation

$$\Delta H^{\circ}(28°C) = \Delta(PV) = \Delta U^{\circ} + \Delta nRT$$

where PV is the pressure-volume correction applied in converting the reaction from constant voluum to constant pressure; Δn, is the number of moles of gaseous product formed minus the number of moles of gaseous reactants used; R, is the gas constant (8.3149 j/deg. mole), and T is the absolute temperature (301.16°K). The values of $\Delta H^{\circ}(28°C)$ so obtained were corrected to 25°C. The heat capacities needed for the methylamines were obtained from short extrapolations of published low-temperature heat data (methylamine[28], dimethylamine[29], trimethylamine[30]). The heat capacities for the ethylamines were estimated from the above data and from data available for the analogous paraffin hydrocarbon[31]. Values for CO_2(gas), N_2(gas), and H_2O(liq.) were taken from NBS Circular 500.

The heat of combustion and the heat of formation reported for the liquid are for the general reactions:

$$C_aH_bN\ (liq.) + (a+b/4)\ O_2\ (gas) = aCO_2\ (gas) + b/2\ H_2O\ (liq.) + 1/2\ N_2\ (gas), \qquad (1)$$

and

$$aC\ (c,\ graphite) + b/2\ H_2\ (gas) + 1/2\ N_2\ (gas) = C_aH_bN\ (liq.) \qquad (2)$$

The values used for the heats of vaporization for these compounds are summarized in Table VII. The heats of vaporization for methyl-[28], dimethyl-[29], trimethyl-[30], and diethylamine[32,33] were obtained from direct calorimetric measurements. These heats of vaporization for ethyl-[34], and triethylamine[34,35,36] were calculated with the approximate Clausis-Clapyeron equation from vapor pressure data.

With the exception of trimethylamine and triethylamine, the entropy of vaporization of these compounds at their boiling points is approximately 23 e.u. Trimethylamine has an entropy of vaporization of 19.9 e.u. and triethylamine 20.5 e.u. In addition, the boiling point of trimethylamine is somewhat lower than dimethylamine. This type of behavior may be accounted for on the basis of association of the molecules with one another in the liquid phase. Arbuzov and Katseva[37], thru the measurement of the parachor, have found that all primary aliphatic amines are associated in the liquid phase. The degree of association decreases with increasing molecular weight. Of the secondary amines only the dimethylamine and diethylamine are appreciably associated. Tertiary amines are not appreciably associated. The entropy of vaporization of trimethyl- and triethylamine

Table VII. Heats of vaporization of the amines

	Boiling Point °K	ΔH_v kcal/mole	ΔS_v e.u.	ΔH_v (25°C) kcal/mole
ammonia	239.73	5.6	23.3	5.1
methylamine	266.84	6.2	23.2	5.8
dimethylamine	280.04	6.3	22.5	6.0
trimethylamine	276.03	5.5	19.9	5.1
ethylamine	289.7	6.8	23.5	6.7
diethylamine	328.66	7.3	22.2	7.6
triethylamine	361.66	7.4	20.5	8.1

is close to that to be expected for a non-associated liquid, in contrast to the other amines which have the higher value characteristic of associated liquids such as NH_3(23.28e.u.)[25] and H_2O(26.04e.u.)[25]. Trimethyl- and triethylamine cannot easily form a hydrogen bond between the nitrogen atoms of two adjacent molecules in the liquid, as there is no hydrogen atom directly attached to a nitrogen atom to serve as a ready bonding atom. In addition, three aliphatic groups tend to shield the nitrogen atom obstructing any bonding. The other amines have a readily available hydrogen atom to form this bond. Higher primary and secondary amines should be less associated because of the steric shielding effects of the larger alkyl groups.

Using the heats of vaporization for the amines (Table VII), it is possible to obtain the heats for the general reactions similar to (1) and (2) involving the gaseous amines. The heats of combustion and the heats of formation for both the liquid and the gas are summarized in Table VIII. To calculate the heats of formation from the heats of combustion, the values for the standard enthalpy of formation at 25°C of water (liq.) and carbon dioxide (gas) of -68.317 and -94.054 kcal/mole[25] respectively, were used.

B. Errors

In determining the uncertainty to be applied to the heat of combustion the following have been taken into account: the statistical uncertainty in the calibration experiments,

Table VIII. Heat of combustion and formation of the amines

Amine	$-\Delta U°(28°C)$ (liquid) j/g CO_2	$-\Delta H_c°(25°C)$ (liquid) kj/mole	$-\Delta H_c°(25°C)$ (liquid) kcal/mole	$-\Delta H_c°(25°C)$ (gas) kcal/mole	$-\Delta H°f(25°C)$ (liquid) kcal/mole	$-\Delta H°f(25°C)$ (gas) kcal/mole
methyl-	24056.1 ±7.2	1060.83 ±0.36	253.54 ±0.09	259.3 ±0.3	11.30 ±0.09	5.5 ±0.3
dimethyl-	19769.3 ±2.2	1743.55 ±0.40	416.71 ±0.10	422.7 ±0.3	10.51 ±0.10	4.5 ±0.3
trimethyl-	18299.8 ±3.7	2421.04 ±0.63	578.64 ±0.15	583.7 ±0.4	10.95 ±0.15	5.9 ±0.4
ethyl-	19420.9 ±5.0	1713.37 ±0.52	409.50 ±0.12	416.2 ±0.5	17.72 ±0.12	11.0 ±0.5
diethyl-	17243.8 ±5.9	3042.42 ±1.14	727.16 ±0.27	734.8 ±0.6	24.80 ±0.27	17.2 ±0.6
triethyl-	16524.4 ±3.6	4370.69 ±1.14	1044.62 ±0.27	1052.7 ±0.6	32.02 ±0.27	23.9 ±0.6

statistical uncertainty in the combustion experiments, an uncertainty of 0.01% assigned to the value for the sample of benzoic acid used, and an additional systematic error of 0.01%.

Because the samples used were reasonably pure and the amount of reaction was determined by the weight of carbon dioxide evolved as a result of the combustion, traces of water have no measureable effect on the final result. Similarly traces of impurities such as the isomeric and homologous amines which have heats of combustion of the same order of magnitude per gram of carbon dioxide have only a second order effect on the final heat of combustion.

In determining the heat of formation of the gases, an error of ±0.3 kcal/mole was assigned to those heats of vaporization which had been determined calorimetrically. Heats of vaporization calculated from vapor pressure data were assigned an uncertainty of ±0.5 kcal/mole.

C. Comparison of Results with Previous Investigations

The heats of combustion of the simple aliphatic amines were measured during the period from 1881 to 1910 by J. Thomsen[38], M. Berthelot[39,40], J. A. Muller[41,42], and P. Lemoult[43]. These results in general are not self-consistent and the results from the various investigations differ rather markedly. The experimental details are not reported fully, except in the case of Thomsen; temperatures of the experiments are not given, nor are calibration details

reported. The purities of the compounds used, completeness of the reaction, and the nature of the reaction products are not known. Thomsen measured the heats of combustion of the amines in his "Universal Burner". The amine was introduced as a gas and burned in an oxygen-rich atmosphere. The amount of reaction was determined from the carbon dioxide absorbed in a standard base. Berthelot used a bomb in which the liquid amine was introduced in a weighed ampoule. The bomb was filled with oxygen at one atmosphere; the ampoule was broken, and the amine vaporized and burned as the gas. Lemoult and Muller used some modification of the method and apparatus as described by Berthelot. In all of these experiments it is highly improbable that the combustion reactions were complete. It may be suspected that carbon monoxide and various oxides of nitrogen were formed. No check was made for these compounds.

The data reported by Thomsen were corrected using the best present data for the molecular weight of carbon dioxide, specific heat of water, and for the temperature of the reaction (all data were converted to 25°C). Lemoult had calibrated his apparatus with naphthalene, using a value for the heat of combustion of ΔH_c = -1238.6 kcal/mole. The data were recalculated using -1231.5 kcal/mole at 25°C[44]. Similar corrections were applied to these results given by Berthelot and Muller. The corrected values are summarized and compared with the results of the present investigation in Table IX.

Table IX. Heats of formation at 25°C for the amines in the gaseous state

Amine	Thomsen[1] kcal/mole	Berthelot[2,3] kcal/mole	Muller[4,5] kcal/mole		Lemoult[6*] kcal/mole	This Investigation* kcal/mole
methyl-	-6.7		-3.6[4]	-7.9	-3.0	-5.5 ±0.3
dimethyl-	-6.9		+0.9[4]	-1.4	-3.2	-4.5 ±0.3
trimethyl-	-7.4	+1.7	+4.1[4]	-12.0	-3.9	-5.9 ±0.4
ethyl-	-10.9	-18.1			-16.9	-11.0 ±0.5
diethyl-	-18.0			-27.6	-23.0	-17.2 ±0.6
triethyl-	-25.0			-29.6	-33.1	-23.9 ±0.6

*Calculated from data on the heat of combustion of the liquid.

D. The Average Bond Energy for the C-N Bond

The heats of formation of the amines may be used to calculate values for the bond energy of the C-N bond, as methyl and ethyl groups are substituted for the first, second, and third hydrogen atoms on the nitrogen atom in ammonia. The reaction

$$5H(gas) + C(gas) + N(gas) = CH_3NH_2(gas) \qquad (3)$$

involves the formation of three C-H bonds, two N-H bonds, and one C-N bond. Similarly dimethylamine has six C-H bonds, one N-H bond, and two C-N bonds, and trimethylamine nine C-H bonds and three C-N bonds. For the ethylamines a similar situation exists with the addition of the C-C bond. The heat of reaction (3), and the corresponding reactions for the other amines, may be calculated using the values 52.089 kcal/mole[25], 171.300 kcal/mole[45,46], and 112.95 kcal/mole[45,46] for the heat of formation at 25°C(ΔH°_f) of H(gas), C(gas), and N(gas), respectively, and the heat of formation for the gaseous amine. The value for the (C-H) bond was calculated from methane[25] to be 99.5 kcal/mole, with the assumption that all the C-H bonds in methane are the same. The value of the N-H bond is known to differ, depending upon whether it is the first, second or third N-H bond on ammonia which is broken. The dissociation energy (ΔH_D) of the H_2N-H bond is 104 kcal/mole[5]; that of N-H is 87.6 kcal/mole[47]. From these and the heat of formation of NH_3 gas the dissociation energy -NH-H is calculated as

88.2 kcal/mole. With these and the value 79.2 kcal/mole for the C-C bond, calculated from ethane[25], it is possible to obtain values for the C-N bond, first as methyl groups are substituted for the hydrogens on the ammonia, and then as ethyl groups are substituted. The results are given in Table X. An example of this type of calculation is given in Appendix B.

It is observed that the first C-N bond is 5 kcal. stronger than the second or third. Moreover, the heat of formation of the second and the third bonds is essentially the same, differing by approximately one kilocalorie. The first C-N bond formed is the most stable bond; the stability of the C-N bond decreases as two and three are formed on the same nitrogen atom.

In comparing the methylamines with the ethylamines the dissociation energies for similar C-N bonds differ by about 3.7 kcal/mole. This difference may be attributed to the difference between the formation of the C-N bond with a primary carbon atom as in the methylamines and a secondary carbon atom as in the ethylamines.

E. Energy Increment for $-CH_2-$ Radical

In the reactions

$$CH_3NH_2(gas) + \frac{9}{4} O_2(gas) = CO_2(gas) + \frac{5}{2} H_2O$$

$$(liq.) + \frac{1}{2} N_2(gas) \qquad (4)$$

Table X. The energy of dissociation for the C-N bond in the methyl- and ethylamines at 25°C.

Amine	D(C-N) kcal/mole	Amine	D(C-N) kcal/mole	ΔD(C-N) kcal/mole
methyl-	75.3	ethyl-	79.0	3.7
dimethyl-	70.4	diethyl-	74.4	4.0
trimethyl-	69.0	triethyl-	72.4	3.4

and

$$CH_3CH_2NH_2(gas) + \frac{15}{4}O_2(gas) = 2CO_2(gas) +$$

$$\frac{7}{2}H_2O(liq.) + \frac{1}{2}N_2(gas) \qquad (5)$$

it is evident that the reactions are the same with the exception of the presence in reaction (5) of an additional methylene group, $-CH_2-$. If the heats of the above reactions are compared, and likewise the heats for the analogous reactions between dimethylamine and diethylamine, in which two $-CH_2-$ groups are involved, and trimethylamine and triethylamine, in which three $-CH_2-$ groups must be considered it is possible to obtain a mean energy increment in the heat of combustion, $\Delta(\Delta H_c)$, -155.5 kcal/mole per $-CH_2-$ group in the liquid state at 25°C and -156.5 kcal/mole for the gas state under the same conditions.

Using the heat of combustion of methylamine (ΔH°_c = -253.5 kcal/mole (liq.)) and adding the energy increment equivalent to three $-CH_2-$ groups ($\Delta(\Delta H)$ = -466.5 kcal), the estimated heat of combustion for butylamine in the liquid state is -720.5 kcal/mole at 25°C. Fairbrother and Evans[48] have reported a calorimetrically measured value of ΔH_c = -721.4 kcal/mole for the heat of combustion of liquid n-butylamine. Thus the heat of combustion of n-butylamine maybe estimated to about 0.1%. Conversely, the value for n-butylamine may be used to obtain another value for the

increment, -155.9 kcal/mole, which is close to the value reported for the hydrocarbons, -156.24 kcal/mole[28]. However, not too much weight can be given, at present, to this value, as the experimental details of the determination have not been reported. If the heat of combustion of a still higher amine, in which the energy of addition of a $-CH_2-$ group is no longer affected by adjacent CH_3- and NH_2- groups, becomes available it should be possible to make a final adjustment in the value for the energy increment for the $-CH_2-$ group, which will make estimates for other amines more exact. In all probability, as the chains become longer, the energy increment will become equal to that found for the hydrocarbons[27]. With the data obtained in this investigation and with the data compiled for the paraffin hydrocarbons, it is possible to estimate the heats of combustion and formation for primary, secondary, and tertiary amines, for mixed amines, and for amines having side chain hydrocarbon groups.

To obtain reliable estimates of heats of combustion for amines with one or more secondary or tertiary alkyl groups attached to the amine group, it will be necessary to measure the heat of combustion of compounds such as isopropylamine, bis(isopropyl)amine, and tertiary-butylamine to determine the effect of the branched carbon chain on the C-N bond. Tertiary amines with highly branched alkyl groups, such as tris(tert-butyl)amine, should have considerably steric strain, and the C-N bond should be much weaker. The data reported here, however, should give reliable estimates for the simpler amines.

VI. SUMMARY

The heats of combustion of the following amines were measured in the liquid state with a bomb in an isothermal jacketed calorimeter; methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine. The purities of these compounds were determined from measurements of time-temperature freezing curves. Those compounds which indicated an initial purity of less than 99.0% were further purified by fractional crystallization. The results obtained for the standard heat of combustion ($_{\Delta}H^{o}_{c}$), in the liquid state at 25°C and constant pressure are: methylamine, -253.54±0.09; dimethylamine, -416.71±0.10; trimethylamine, -578.64±0.15; ethylamine, -409.50±0.12; diethylamine, -727.16±0.27; triethylamine, -1044.62±0.27 kcal/mole. From these data and the heats of vaporization obtained from other sources it was possible to calculate the heat of formation of both the liquid and the gas state.

Using the above data it was possible to calculate an energy increment in the heat of combustion ($-_{\Delta}(\Delta H_{c})$) of 155.5 kcal/mole per $-CH_2-$ group for the liquid state at 25°C and 156.5 kcal/mole for the gas state under the same conditions. This compares favorably with the value 156.24 kcal/mole for the liquid state which has been obtained from a more extensive study of the paraffin hydrocarbons. Comparison of values obtained by calculation with experimental measurements for n-butylamine in the liquid state leads to results which

agree to within 0.1%.

Values calculated for the C-N bond indicate that the stability of the C-N bond decreases as the number of carbon bonds on the nitrogen atom increase. In addition the C-N bond becomes stronger by approximately 3.7 kcal when the carbon in the C-N bond is changed from a primary to a secondary carbon.

APPENDIX A.

CALCULATION OF A TYPICAL COMBUSTION EXPERIMENT
(Ethylamine Experiment No. 4)

1. Calculation of Corrected Temperature Rise

R_{20}	0.096388 Ω	Temperature at the twentieth minute.
R_0	0.084714 Ω	Temperature at the zero minute.
$S_{10} = \frac{(R_{20}-R_0)}{20}$	0.0005837 Ω/min.	Rate of temperature rise, 0-20 minutes.
R_{60}	0.317412 Ω	Temperature at the sixtieth minute.
R_{40}	0.315169 Ω	Temperature at the fortieth minute.
$S_{50} = \frac{(R_{60}-R_{40})}{20}$	0.0001122 Ω/min.	Rate of temperature rise, 40-60 minutes.
$\frac{S_{10}-S_{50}}{R_{50}-R_{10}} = k$	0.002089 min.	Radiation Factor
R_j	0.366972 Ω	Temperature of calorimeter jacket.
$u = S_{50}-k(R_j-R_{50})$	0.0000063 Ω/min.	Energy rate due to stirring.
$16u = U$	0.000101 Ω	Temperature rise due to stirring for the reaction period.
A = Area	1.090952 Ω/min.	Area bounded by T_{20}, T_{36}, temperature of the jacket, and reaction curve. Obtained by numerical integration of R-t curve during the reaction period.

$k(\text{Area}) = K$	0.002279 Ω	Energy due to radition during the reaction period.
$R_{36}-R_{20}-U-K = R_c$	0.216401 Ω	Corrected temperature rise.

2. Calculation of Ratio and Correction Factors for Nitric Acid and the Iron Wire.

Weight of bulb and sample	9.92812 g
Weight of bulb	9.12898 g
Weight of sample = S	0.79914 g
(Vacuum factor) x (S) = S'	0.80042 g
(CO_2 factor) x (S') = Theoretical CO_2	1.56267 g

Weight of carbon dioxide absorption tube before the experiment	6.33367 g
Weight of carbon dioxide absorption tube after the experiment	4.76973 g
Weight of CO_2 absorbed = CO_2'	1.56394 g
(Vacuum factor) x (CO_2') = experimental CO_2(A)	1.56378 g
Ratio = CO_2(A)/CO_2	1.00071 g

Weight of iron wire before combustion	0.00490 g
Weight of iron wire after combustion	0.00000 g
Weight of iron wire used = W_{Fe}	0.00490 g
W_{Fe}-0.00460 = Iron wire in excess of calibration bomb conditions (W'_{Fe})	0.00030 g

$(7500)(W'_{Fe})$ = heat due to excess iron wire (q'i)	2.25 j
$q'_i + 34.5$ = heat due to combustion of iron wire (qi)	36.75 j
57.8 j/meq. dilute HNO_3 x N_{NaOH} x ml(NaOH) = heat due to formation of nitric acid as a result of the combustion of $N_2(q_n)$	103.71 j

3. Calculation of heat of Combustion (28°C) per gram of Carbon Dioxide.

$1/2(R_{20}+R_{36}) = Rm$	0.2058 Ω	Mean temperature of the calorimeter experiment.
$R_m - 0.2179 =$	-0.0121 Ω	Correction to calibration mean temperature.
$0.3693 - R_{36} =$	0.0541 Ω	Correction to calibration final temperature.
Deviation	0.67 j/Ω	Correction due to any changes in the system.
$44.6(R_m - 0.2179)$	-0.54 j/Ω	Correction to adjust mean temperature of the combustion experiment to the calibration mean temperature.
(C_v) x (Mass of glass)	0.38 j/Ω	Correction for the glass used in excess of the calibration bomb conditions.
(C_v) x (Mass of sample)	22.57 j/Ω	Correction due to the specific heat of the sample.

e_2 (joules)	23.08 j/Ω	Summation of correction.
E_s	140875.92 j/Ω	Energy equivalent of standard system in joules per ohm.
$E_s + e_2 = E'_s$	140899.00 j/Ω	Corrected energy equivalent.
$(R_c)(E'_s) = Q$	30,490.68 j	Total energy due to combustion.
q_n	-103.71 j	Correction for formation of nitric acid.
q_i	-36.75 j	Correction for combustion of iron wire.
W_c	-7.01 j	Washburn correction.
Q_i	30343.21 j	Corrected energy due to combustion.
Q_i/CO_2A	19403.76 j/gCO_2	Heat of combustion per gram of CO_2.
$C_v(0.3693-R_{36})$	0.11 j/gCO_2	Correction to calibration final temperature.
$U^{\circ}28^{\circ}C/gCO_2$	19403.87 j/gCO_2	Heat of combustion at 28°C at constant volume.

APPENDIX B.

CALCULATION OF THE ENERGY FOR THE C-N BOND FOR CH_3NH_2 AT 25°C

The heat of atomization of NH_3 is given by:

$$NH_3(gas) = N(gas) + 3H(gas) \qquad (1)$$

$$\Delta H_1 = \Delta Hf(N,gas)^{45,46} + 3\Delta Hf(H,gas)^{25} - \Delta Hf(NH_3,gas)^{25}$$

$$\Delta H_1 = 280.25 \text{ kcal/mole.}$$

Successive dissociation energies for the N-H bonds are:

$$NH_3(gas) = NH_2(gas) + H(gas) \qquad (2)$$

$$\Delta H_2 = 104 \text{ kcal/mole}^5$$

$$NH(gas) = N(gas) + H(gas) \qquad (3)$$

$$\Delta H_3 = 87.6 \text{ kcal/mole}^{47}$$

$$NH_2(gas) = NH(gas) + H(gas) \qquad (4)$$

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

$$\Delta H_4 = 88.6 \text{ kcal/mole}$$

For the reaction:

$$CH_4(gas) = C(gas) + 4H(gas) \qquad (5)$$

$$\Delta H_5 = \Delta Hf(C,gas)^{25} + 4\Delta Hf(H,gas)^{25} - \Delta Hf(CH_4,gas)^{25}$$

$$\Delta H_5 = 397.54 \text{ kcal/mole}$$

From this the average dissociation energy for the C-H bond is:

$$\Delta H_{(C-H)} = 99.39 \text{ kcal/mole.}$$

For the reaction in which CH_3NH_2(gas) is formed from its elements:

$$5H(gas) + C(gas) + N(gas) = CH_3NH_2(gas) \qquad (6)$$

$$\Delta H_6 = \Delta Hf(CH_3NH_2,gas) - 5\Delta Hf(H,gas)^{25} - \Delta Hf(C,gas)^{25} - \Delta Hf(N,gas)^{25}$$

$$\Delta H_6 = -549.74 \text{ kcal/mole.}$$

Methylamine contains three C-H bonds, two N-H bonds, and a single C-N bond.

$$\Delta H_{(C-N)} = -\Delta H_6 + 3\Delta H_{(C-H)} + \Delta H_3 + \Delta H_4$$

$$\Delta H_{(C-N)} = 75.33 \text{ kcal/mole.}$$

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