THERMOCHEMICAL AND KINETIC STUDIES OF POLYMERIZATION AND OTHER PROPERTIES

by

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PREFACE

This thesis is divided into four parts. Parts 1 and 2 deal with experimental studies of the thermochemistry and kinetics of polymerization. Polymers arising from polymerization of 1,1-disubstituted ethylenes are known to exist in a state of strain if polymerization proceeds in a "head to tail" arrangement. The strain in a polymer, if sufficiently great, causes the substituent groups to be compressed. Information regarding the energy required for compression can be obtained from heat of polymerization studies. In the present work the heats of polymerization of monomeric acrylates and methacrylates were studied to determine if there was any dependence of heat of polymerization on small structural changes in the ester group.

While this thermochemical work was in progress, it became apparent that relative rate constants for the propagation steps of the polymerization of the different monomers could be determined. Determination of these rates could be obtained from the available thermochemical data with no further experimental work necessary.

The results of the thermochemical and kinetic studies are reported in Parts 1 and 2. The results are interpreted in terms of steric hindrance and inductive effects in the monomers and polymers.

Part 3 deals with the experimental determination of heats of vaporization. In view of the lack of literature data on this property, it was decided to adapt the Calvet microcalorimeter to the measurement of heats of vaporization at 25°C. The heats of vaporization data obtained, on the homologous series of aliphatic alcohols studied, were fitted to an additivity scheme previously devised by Laidler. This work has been published in the Canadian Journal of Chemistry 41, 1867 (1963).

Part 4 of the thesis is concerned with the development of an empirical bond-energy scheme for the calculation of several physico-chemical properties of different families of compounds. The properties treated are molar volume, molar refraction, entropy of formation heat of atomization, magnetic susceptibilities and molar sound velocities.

ACKNOWLEDGEMENTS

It was a great priviledge for the author to work under the supervision of Dr. K.J. Laidler on the research described in this thesis. Dr. Laidler's valuable suggestions, keen interest and infinite patience proved to be an inspiration, and made studying of the problems involved in this research a pleasant task. The author is

also indebted to Mr. Othman bin M. Nor for an extensive literature survey on molar sound velocities and diamagnetic susceptibilities, and also to Mr. Andre Ladouceur for the least square determinations on the computor for the additivity schemes. Thanks are also due to Rohn and Haas Company for supplying the monomers used in the polymerization studies. The assistance of the National Research Council in the form of two studentships is hereby gratefully acknowledged. Finally, the author takes special pleasure in acknowledging the assistance and understanding offered by his wife and daughter throughout the duration of these studies.

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ABSTRACTS

Heat of Polymerization

With the use of a Tian-Calvet microcalorimeter, the heats of polymerization of a number of monomers have been measured in aqueous emulsion systems; the emulsifying agent was cetyltrimethylammonium bromide, and initiation was by Fenton's reagent (Fe^{++} + H_2O_2). The monomers employed were acrylic acid, methyl, ethyl and butyl acrylates, hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, methacrylic acid, and methyl, ethyl, butyl and hexyl methacrylates. The heats of polymerization lie in the range from 13 to 19 kcal per mole, the experimental standard deviation being 40 to 110 cal per mole. A steady increase was observed for acrylic acid and its CH_3, C_2H_5 and C_4H_9 esters, and for methacrylic acid and its CH_3, C_2H_5, C_4H_9 C_6H_{13} esters. This change is attributed to a steady increase in the proportion of head to head, tail to tail polymers, leading to a decrease in steric hindrance in the polymer. Abnormally low heats observed with hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate are attributed to the solvation of the monomer, less solvation being possible in the polymer as a result of shielding.

Kinetics of Polymerization

The microcalorimeter has been used to obtain rates of polymerization of a number of monomers in emulsion

systems. The rates with the acrylates are consistently higher than those with the methacrylates, and this is attributed to there being less steric hindrance in the acrylate polymerization. Low rates found with the monomers containing a hydroxyl groups are explained as due to solvation in the initial monomer state. In both the acrylates and methacrylates the rates go through a maximum as one goes up the series methyl : ethyl : butyl : hexyl. This is discussed in terms of inductive and steric effects.

Heats of Vaporization

Heats of vaporization of fourteen alcohols, having from one to five carbon atoms, have been determined in a Calvet microcalorimeter, using a special technique. The method consisted of allowing the alcohol to vaporize into a vacuum, the heat required for the vaporization being provided by passing a current through a resistance wire which was immersed in oil in a U-tube surrounded by the alcohol. The additivity scheme previously devised by Laidler for heats of formation and related properties was applied to the results, and the agreement with experiment was within a few tenth of a percent.

Additivity

An empirical bond energy scheme has been

derived and applied to several physico-chemical properties of several families of compounds. The scheme proposed is a modification of Tatevskii's scheme. It defines three types of C-H bonds and several types of C-C bonds depending on their multiplicity and their environment. Other functional groups (e.g. -CHO, -COH) have been considered as a group and have been treated as such. They are assigned group symbols and their contribution to the physico-chemical property is a group contribution.

The scheme has been applied to alkanes, alkenes, dienes and cylic hydrocarbons for the following properties; molar volume, molar refraction, entropy of formation and heat of atomization, all at 25°C. Molar sound velocities and diamagnetic susceptibilities are two other properties treated for several families of compounds.

PART I

HEATS OF POLYMERIZATION

INTRODUCTION

Considerable interest in the last twenty years has been focussed on the heats of polymerization of monosubstituted (CH_2=CHX) and 1,1-disubstituted (CH_2=CXY) ethylenes. Heats ($-\Delta H$) of polymerization calculated from heats of formation of monomeric anologues of the structural units of the polymers are close to 20 kcal. per mole (1a). While the heats of polymerization of the monosubstituted ethylenes are in agreement with this value, the disubstituted ethylenes have heats of polymerization that are smaller by from 3 to 9 kcal. per mole.

The discrepancy between the calculated heats of polymerization, from heats of formation, and the experimental heats of polymerization of disubstituted ethylenes has been attributed to the energy of repulsion between the neighboring units (2,3) in the polymer formed. Prevalence of the head-to-tail arrangement in vinyl polymers has been abundantly confirmed by determinations of polymer structures (4).

These polymers, especially in the 1,1-disubstituted ethylenes, exist in a state of strain. Steric hindrance in polymers arising from 1,1- disubstituted monomers arises from substituent groups on the same carbon atom interfering with those on adjacent monomer residues. If steric hindrance is severe the substituent groups are compressed, and this is reflected in the values of the heats of polymerization. This has been shown convincingly by Baxendale (5) in studies on the heats of copolymerization of a disubstituted ethylene and a monosubstituted ethylene, $CH_2=C(CH_3)COOCH_3$ and ($CH_2=CHCN$). It seems apparent that steric hindrance in a polymer composed entirely of a 1,1- disubstituted monomer might be reduced by the incorporation of a monosubstituted monomer into the growing chain, thereby separating the mutually interfering substituents of adjacent monomer units. As the mole fraction of acrylonitrile in the copolymer increases above 0.4, the heat of polymerization increases, confirming the existence of strain in the polymer and its relief by separating the interfering groups.

The present studies were carried out to measure some heats of polymerization of acrylate and methacrylate monomers, under constant experimental conditions. The literature data available to date on heats of polymerization show only that the heats evolved in the polymerization of methacrylates

are lower than those of the acrylates. In neither case has any systematic attempt been made to study the effect of changes of the ester group on the heats of polymerization. The observed heats of polymerization of t-butyl and cyclohexyl methacrylates are lower than the heat of polymerization of methyl methacrylate, a result that has been attributed to steric hindrance caused by these bulky groups. (6).

General Characteristics of Polymerization

The process by which unsaturated monomers are converted to polymers of high molecular weight exhibits the characteristics of typical chain reactions. They are readily susceptible to catalysts, photoactivation and inhibition. The quantum yield in a photoactivated polymerization in the liquid phase, expressed as the number of monomer molecules polymerized per quantum absorbed, may be of the order of 10^3 or more (7). The efficiency of certain inhibitors is of a similar magnitude, thousands of monomer molecules being prevented from polymerizing by a single molecule of the inhibitor (8).

Another common feature of the so called vinyl polymerizations suggests that the active center of the kinetic chain is retained by a single polymer molecule throughout the course of its growth. At any instant during the polymerization process the reaction mixture consists almost entirely of unchanged monomer and high polymer; material at intervening

stages of growth is virtually absent. The proportion of active growing chains is so small as to be immeasurable by ordinary chemical methods (9). If the active centers responsible for execution of the conversion of monomer to polymer were transferred indiscriminately at almost every step from one molecule to another, all molecular species would participate in the process of chemical combination with other species at all stages of the process. All polymer particles would thus grow more or less simultaneously; lower species, such as dimers, trimers and tetramers would be prevalent at early stages of polymerization and these would advance in size as the process is continued; these intermediates are generally undetectable. Such considerations, together with the fact of extremely high molecular weight of the polymer molecules produced, leads inescapably to the conclusion that a given molecule is formed by consecutive steps of a single chain process set off by the creation of an active center. Evidently the active center is in some way retained by a growing polymer chain from each addition of a monomer molecule to the next. The following free radical chain mechanism, first suggested by Bates (10) for liquid-phase polymerization, offers an explanation for the general characteristics of vinyl polymerizations:

$$R\cdot \xrightarrow{CH_2=CHX} R\text{-}CH_2\text{-}\dot{C}H\cdot \xrightarrow{CH_2=CHX} R\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}\dot{C}H\cdot \xrightarrow{\text{etc.}}$$

where X is a substituent C_6H_5, Cl, Br, $OCOCH_3$ or H. Disubstituted monomers such as vinylidene chloride and methyl methacrylate are to be included. The chain-propagation step consists essentially of free-radical attack at one of the doubly-bonded carbon atoms of the monomer. One electron of the double bond pairs with the odd electron of the free radical to form a bond between this free radical and this carbon atom; the remaining electron of the double bond shifts to the other carbon atom, which then becomes a free radical. In this way, the active center shifts uniquely to the newly added monomer, which is thereby rendered capable of adding another monomer.

Final and conclusive evidence for the free radical mechanism is afforded by detection in the polymer of radical fragments from the initiator. Polystyrene and (polymethylmethacrylate) prepared with bromobenzoyl peroxide, contain bromine which cannot be removed by repeated precipitation of the polymers (11). Poly(methylmethacrylate) (12, 13) and polystyrene (14) prepared in an aqueous medium using hydrogen peroxide and ferrous ion contain hydroxyl end groups, as expected on the basis of mechanism of free-radical generation.

Initiation of Polymerization

Polymerizations are readily initiated by free radicals. In the present study the free radicals were generated by means of Fenton's reagent (15). The chemical formation of free radicals necessarily involves electron transfer, and therefore a reduction of one component and an oxidation of the other, i.e. a redox reaction between the components of a redox system.

The detailed mechanisms of the reaction between ferrous ion and hydrogen peroxide has been elucidated (16), and the principal steps are known to be:

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- - OH\cdot \qquad (a)$$

$$Fe^{++} + OH\cdot \longrightarrow Fe^{+++} + OH^- \qquad (b)$$

$$OH\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot \qquad (c)$$

$$Fe^{++} + HO_2\cdot \longrightarrow Fe^{+++} + HO_2^- \qquad (d)$$

$$Fe^{+++} + HO_2\cdot \longrightarrow Fe^{++} + H + O_2 \qquad (e)$$

In the presence of sufficient monomer only step (a) will be operative since all OH· radicals liberated in this process will initiate polymerization. This mechanism accounts for the fact that if the ferrous ion is initially present in excess over the hydrogen peroxide, the reaction is stoichiometric, while if the hydrogen peroxide is initially present in large excess, some of it decomposes to oxygen and water (17).

Initiation of the polymerization of several monomers in aqueous solutions by the redox couple hydrogen peroxide-ferrous ion has been reported by Baxendale et al. (12).

That the active initiating agent is the same as that involved in the induced decomposition of hydrogen peroxide or in the Fenton reaction was demonstrated by showing that : (i) oxidation of glycolic acid by the redox couple was suppressed by addition of the monomer, (ii) oxygen evolution, which normally takes place if the peroxide is in large excess over the ferrous ion, was likewise suppressed by the addition of monomer. However, if the hydrogen peroxide was in extremely large excess over the ferrous ion (1M vs 10^{-4}M), so that all of the HO• radicals were replaced with $HO_2^{\bullet}$ radicals according to step (c), no polymerization of acrylonitrile took place (16); thus $HO_2^{\bullet}$ radicals cannot be initiating species. The mechanism of the initiation and propagation was therefore postulated as:

$$HO\bullet + CH_2=CHX \longrightarrow HOCH_2\dot{C}HX \qquad (f)$$

$$HOCH_2\dot{C}HX + CH_2=CHX \longrightarrow HOCH_2CHXCH_2\dot{C}HX \qquad (g)$$

If the growing polymer chain reacts only with monomer molecules or with another growing chain, the hydroxyl radical is in effect removed from the system by reaction with the monomer.

Considering now the stoichiometry of the primary (H_2O_2-Fe^{++}) reaction, with both reactants initially present in comparable concentrations, we see that in the absence of monomer one mole of peroxide oxidizes two gram-ions of ferrous iron, by reactions (a) and (b); whereas on the addition of increasing amounts of monomer, reaction (b) is increasingly replaced by (f), so that in the limit one mole of hydrogen peroxide should oxidize only one gram-ion of ferrous iron by

reaction (a). This behavior was actually observed (12) for each of the four monomers studied (ethylene, acrylonitrile, methyl acrylate and methacrylic acid). From aquantitative study of the competition between steps (b) and (f), it was shown that the hydroxyl radical attacks methyl acrylate about five times as fast as it attacks ferrous ion.

A great number of polymerization reactions have been studied using $Fe^{++} - H_2O_2$ initiation. (13, 18, 19, 20, 21)

Emulsion Polymerization

The polymerizations of the monomers in this study were carried out in emulsified systems. In emulsion reactions, the rates and degrees of polymerization are very much higher than those found in bulk polymerization. Another important advantage of the emulsion polymerizations over those in bulk or suspension is that the products are obtained as aqueous dispersions rather than single polymer masses.

The emulsifying agent used in this study was cetyltrimethylammonium bromide. It was selected initially as an emulsifying agent in polymerizations by Baxendale (18), because of its stability in acid solutions, and because it did not give an unstable iron compound, was not oxidized by the hydrogen peroxide-ferrous system and was not attacked by bromine during estimation of the monomer.

Mention should be made of a possible complication arising from the use of cetyltrimethylammonium bromide.

Baxendale (18) used this emulsifier because it was "not oxidizable by the ferrous iron system." Subsequent work (22,23) has shown that the bromide ion is attacked by the hydroxyl radical approximately 22 times as fast as is the ferrous ion. Kolthoff (24) has more recently stated that this value may possibly be inaccurate. It seems most probable that the reaction

$$HO\cdot + CH_2{=}CHX \longrightarrow HOCH_2\dot{C}HX$$

would be largely replaced by

$$HO\cdot + Br^- \longrightarrow Br\cdot + OH^-$$

in the presence of 0.03M bromide ion (25). Unfortunately no attempt to identify bromine in the polymer has been made.

The precise course of emulsion polymerization has been established by McBain (26) and Harkins (27,28,29), and their evidence and conclusions about the mechanism are presented in Part 2. Conclusive proof of Harkins's theory is found in the quantitative considerations evoked by his hypothesis, which has been treated by Smith and Ewart (30) and is presented in Part 2.

Heats of Polymerization

For a polymerization reaction which may be represented exactly by the chemical equation

$$nM_1 \longrightarrow M_n$$

the heat of polymerization is usually equated to $-\Delta H$, where the overall enthalpy increase is $n\Delta H$.

Numerous approaches and methods are available for obtaining heats of polymerization. Some of the more important are outlined below.

1) Combustion Methods

Heats of polymerization have been obtained indirectly by measuring the heat of combustion of the monomer and that of the polymer, the difference between the two being the heat of polymerization. Since heats of combustion are many times greater than heats of polymerization (10 to 100 times), this method requires high precision combustion measurements if reasonably accurate heats of polymerization are to be obtained (31, 32, 33). Purity of monomers and polymers is very important if reliable heats of polymerization are to be obtained. Vinyl monomers, as supplied, usually contain traces of inhibitors to stabilize them against premature polymerization. This must be completely removed before combustion or left in the monomer and a correction applied for the inhibitors contribution to the heat of combustion. Polymers must be carefully purified to remove traces of catalysts used in their preparation (34). Some polymers tend to be slightly hygroscopic and must be carefully dried if the result is to be based on the weight of polymer (35). The polymer should also be characterized by molecular-weight measurements before combustion.

2) Direct Calorimetry

a) Non-isothermal methods

i) Integral Method

This method involves the measurement of the amount of heat corresponding to the formation of a certain weight of polymer. Evans and Tyrrall (18) have employed this method for the measurement of heats of polymerization. They used a calorimeter of the Dewar-vessel type with moderate success. The amount of polymer formed was determined by bromination of the initial monomer solution and of the monomer remaining in the solution after polymerization.

ii) Differential Method

This method involves the measurement of heat evolved, q, and of a physical property related to the extent of reaction, measured at convenient time intervals. Often the physical property measured is the volume, V; in this case dq/dV, corrected for the effect of the temperature (36), need only be combined with the yield-contraction ratio dw/dV to give dq/dw. This method has the advantage that a less rapid rate of reaction is required than in method (i). The yield-contraction ratio must be known at a series of temperatures and may be found by three methods: (a) by recovering and weighing the polymer after different extents of contraction; (b) by measurement of the density of appropriate polymer-

monomer-solvent solutions; (c) when no solvent is used it is fairly reliable to calculate the yield-contraction ratio from the densities of pure monomer and polymer, assuming no volume change on mixing.

The change of volume which accompanies polymerization is observed through a transparent strip in the Dewar vessel, which serves as the calorimeter (6).

iii) Self-heating Method:

Originally devised by Bengough (37) this method depends on the fact that when a reaction is initiated photochemically the conditions at the center of the illuminated volume may remain adiabatic sufficiently long after irradiation has begun for the central volume element to be used as its own adiabatic calorimeter. Thus, a polymerization reaction occurring at the center of a dilatometer constructed from 25- mm. diameter soda-glass tubing is adiabatic for at least 10 sec. from commencement, and often for periods of 30 sec. Hence the heat of reaction may be obtained by equating the rate of temperature rise under adiabatic conditions (i.e. over the first 20 sec. following the onset of polymerization) to the rate of reaction measured dilatometrically.

b) Vaporization Calorimetric Method:

Tong and Kenyon (38,39,40,41) have used this method for the measurement of heat of polymerization. Tong and Kenyon's calorimeter is in effect an all-glass refluxing

apparatus, in which the heat of a given polymerization reaction is used to evaporate a liquid in equilibrium with its vapor at the boiling point. One measures the weight of liquid evaporated, to which the heat is directly proportional.

c) Fusion Calormetric Method

Dainton et al. (42) have used the isothermal calorimeter, with diphenyl ether as the working substance. There are virtually no heat losses, and the calorimeter is capable or recording small rates of heat evolution over long periods of time.

3) Other Methods

a) Thermodynamic Method

A long-chain polymer can be in thermodynamic equilibrium with monomer only at a certain activity, similar to the fact that a solid or liquid has a definite equilibrium vapor pressure at a given temperature. Measurement of this activity at different temperatures permits the evaluation of the heat of polymerization by application of the isochore (43). This method has been applied to methyl methacrylate (44,45) and ethyl methacrylate (46) as well as other monomers. Where calorimetric and thermodynamic methods are both available, the agreement is usually within experimental error.

b) Semi-Empirical Methods

When experimental heats of polymerization are not available it is sometimes possible to make estimates by means of a semi-empirical group method such as that of Anderson (47).

Janz (48) has outlined the methods. They depend on the experimental fact that heats of formation are approximately additive, the introduction of a given group into different compounds having about the same effect on the heat of formation of each compound so long as the substitution is at a structurally similar point. The additivity methods make no allowance for interaction between substituents on alternate carbon atoms in a molecule such as polyisobutene. Considerable difference exists between the calculated 17.1 kcal/mole (42) and the observed 12.6 kcal/mole (49) values of the heat of polymerization of isobutene and this is attributed to steric strain in the polymer arising from the repulsive interactions of the methyl side groups.

Semi-empirical methods were first applied to polymerization reactions by Flory (50) who calculated ΔH_{gg} values for various alkenes. Roberts (32) revised these values on the basis of improved thermochemical data, and Dainton (51) extended the calculations to vinyl and vinylidene monomers.

Values of heats of polymerization ($-\Delta H$) have been recorded of between 9 and 22 kcal. $mole^{-1}$, appreciably less heat being evolved with most monomers than in the case of ethylene. The structure factors influencing heats of polymerization are: (52)

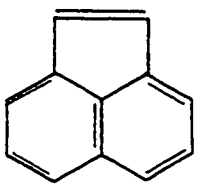
1) Change of bond type, e.g. the formation of single bonds from double bonds.

2) Change of energy of stabilization by conjugation or hyperconjugation.

3) Steric strain in the polymer.

4) Steric strain in the monomer.

In the case of ethylene derivatives all four effects are exhibited. The heat of polymerization of ethylene $-\Delta Hgg = 22.35$ kcal mole^{-1} (53) may be taken as due to the change of bond type. Here $-\Delta Hgg$ is the heat of polymerization of monomer to polymer, both being in the gaseous state. Substitution of a hydrogen atom by a methyl group in ethylene lowers $-\Delta Hgg$ to 20.7 (42) kcal mole^{-1} or by 2 kcal.mole^{-1} as a result of hyperconjugation. A second methyl group produces a further lowering by approximately 2 kcal mole^{-1} (42). For isobutene a further decrease of about 3-4 kcal. mole^{-1} is attributed to strain in the polymer caused by interaction of the pendant methyl groups. The loss of conjugation energy($\simeq$ 5 kcal. mole^{-1}) causes the $-\Delta H$ for styrene to be lower than that for vinyl acetate. A combination of the effects of conjugation and hyperconjugation in the monomer and strain in the polymer causes a low heat of polymerization of 8.4 kcal. mole^{-1} for α-methylstyrene. A case of strained ethylenic monomer appears to be that of acenaphthylene (5) where polymerization through the



double bond must relieve some of the strain in the five membered ring, giving it a high heat of polymerization of 24 kcal/mole. Strain in the polymer has been attributed as the cause of low heats of polymerization of the methacrylates (52).

EXPERIMENTAL

The Calorimeter

The heats of reaction were measured with a differential microcalorimeter of the Tian-Calvet type (54). It consists essentially of a large block of metal, held at constant temperature, in which are mounted two metal reaction vessels, (Figure I). Each reaction cell is surrounded by a thermopile which has one set of junctions in thermal contact with the reaction cell, and the other set in contact with the isothermal heat sink, common to both cells. In operation, the reaction to be measured is carried out in one reaction vessel, and a suitable blank reaction in the other, the reagents first being allowed to reach thermal equilibrium with the block. The thermopiles are connected in electrical opposition (see Figure 2) to each other, and a voltage will therefore appear in the thermopile circuit only if there is a temperature difference between the reaction cells.

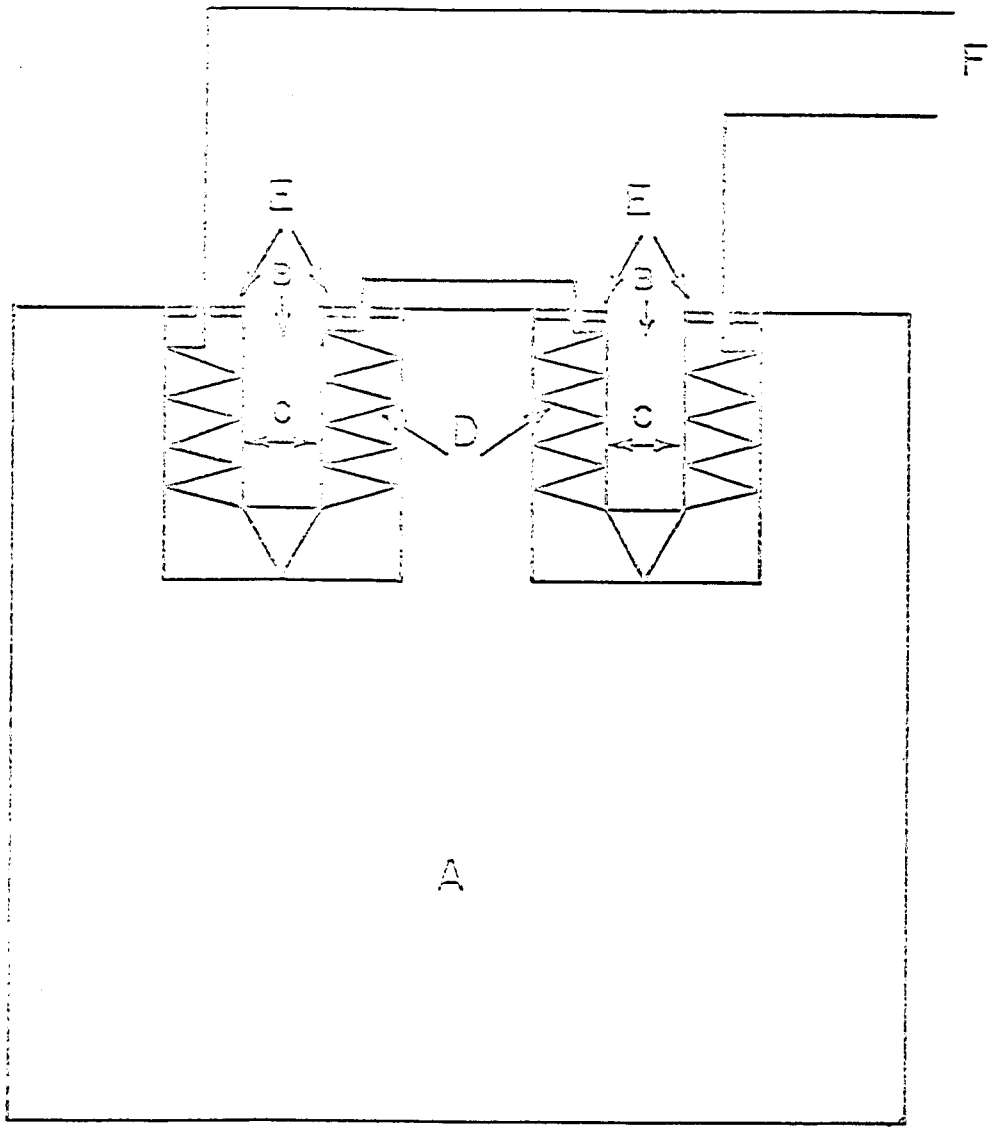
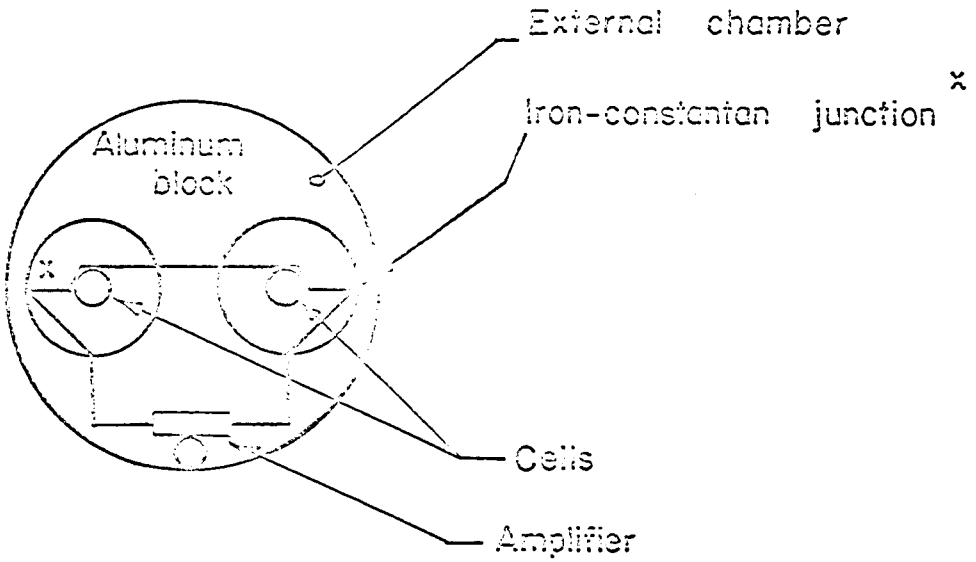


Fig. 2 Schematic view of the electrodes


External chamber
Iron-constanten junction
Aluminum block
Cells
Amplifier

In Figure I, A represents the heat sink which consists of a cylindrical sixty-pound block of aluminum. There are two holes, B, in the top of the block, the centres of which lie on a diameter of the block, and at an equal distance from its centre. A silver thimble, C, is suspended in each hole by means of a plastic support ring, E. The thermopiles, D, are installed in the space between the aluminum block and the silver thimbles. Each thermopile is composed of sixteen iron-constantan junctions. The junctions are attached to the thimbles and the block by Glyptal cement. This insulates the junctions electrically from the block and the thimble, but gives reasonably good thermal contact. The reaction vessels, to be described later, fit snugly into the silver thimbles.

The central aluminum block is surrounded by five concentric aluminum cans. The innermost can is made of two-inch thick aluminum, the remaining four cans of one-quarter-inch aluminum. The four innermost cans are insulated by dead air spaces, there being an increase in radius of about fifteen centimeters for each succeeding can. The space between the outermost two cans is packed with cotton. The second outermost can carries an adiabatic shield made up of several heating resistors distributed evenly around it. Control of the temperature is accomplished by a temperature-controlling unit manufactured by Polyelectronics Company of

Canada. Access to the silver thimbles is provided through long bakelite tubes which lead from the outside of the apparatus through the insulating cans to the silver thimbles.

The output from the thermopiles is fed to an electronic amplifier, which in turn is connected to a recording potentiometer. This arrangement gives a record of the amplified thermopile E.M.F. as a function of time. An electronic integrator is also connected to the amplifier, so that a direct measure of the area under the voltage-time curve is obtained.

The amplification and integration circuits have been described by Attree et al. (55). A schematic drawing of the amplification and integration circuits is shown in Figure 3a and Figure 3b respectively.

The output from the thermopiles is fed into a modified commercial unit, the Liston-Becker breaker amplifier, Model 14. Overall feedback has been incorporated in the circuit to improve stability of gain and to increase the input impedance. Output from the low pass filter, after passing through a calibrated resistor, is used to drive a Leeds and Northrup recording potentiometer.

The integrating circuit used is conventional in its basic arrangement. A resistance-capacitance network is connected to a high-gain, high-impedance, direct-current amplifier as shown in Figure 3b. The amplifier used is a

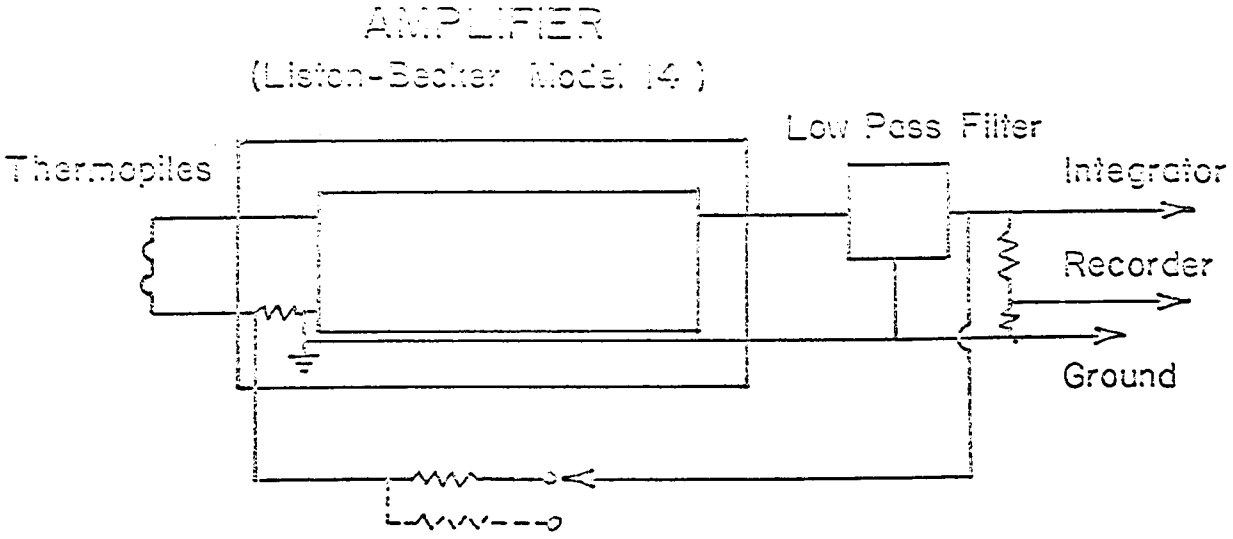


Figure 3. Schematic diagram of the high gain amplifier circuit

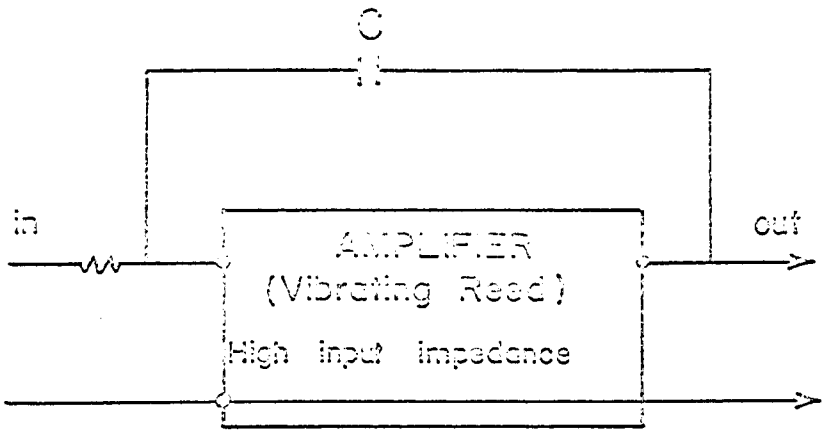


Figure 4. Schematic diagram of the high input impedance circuit

Cary Model 31 vibrating-reed electrometer, manufactured by Applied Physics Corporation. It can be shown (56) that for a circuit of this type:

$$e_o = \frac{1}{RC} \int_o^\tau e_i \, dt$$

where e_i is the input voltage and e_o is the output voltage, R is the value of the resistance, C is the capacitance, and t is the time. The input voltage is the amplified thermopile voltage. The output voltage, e_o, is used to drive a Leeds and Northrup recording potentiometer, so that a curve of area versus time is obtained.

The calorimeter was located in a small cabin, the temperature of which is controlled at 25± 0.2 ° C. This protects the calorimeter from large temperature fluctuations, aiding in the thermostating of the calorimeter at 25 °C. The cabin temperature is controlled by bimetallic strip thermo-regulators, acting through mercury relays. The relays activate either a heating element in the cabin or a pump which circulates cold anti-freeze through a coil in the cabin, depending on whether the cabin is to be heated or cooled.

The Reaction Cell Assembly.

The reaction cell is capable of keeping the reactants and initiator separated until thermal equilibrium with the calorimeter has been attained. It provides a convenient method of adding the initiator to the reactants and a method of effective gentle stirring. A schematic drawing of the reaction cell assembly is given in Figure 4. Two reaction cells of the type shown in Figure 4 and described below were built.

The reaction cell (A) is completely made of glass; it is equipped with a female $\frac{19}{38}$ ground glass joint (C) which unites it to the upper part of the assembly (B). One of the reactants is put directly into cell (A). The initiator is held in a one-cubic-centimeter syringe (D) in the upper part of the assembly.

The syringe needle (E) passes through the ground glass joint, as does a small diameter glass tube (F) and a glass tube (G) carrying insulated electrical leads; these are sealed in with epoxy resin. The glass tubing, with the electrical leads, ends in a bulb (H) containing a calibrated resistor immersed in oil. The height of this bulb is such that it is submerged in the middle of the liquid in the reaction cell. The other glass tube (F) is used to stir the reactants in the following manner. Regular alternations in the pressure, between small limits, are imposed on the tube. The liquid in the reaction cell is thus caused to oscillate a short distance

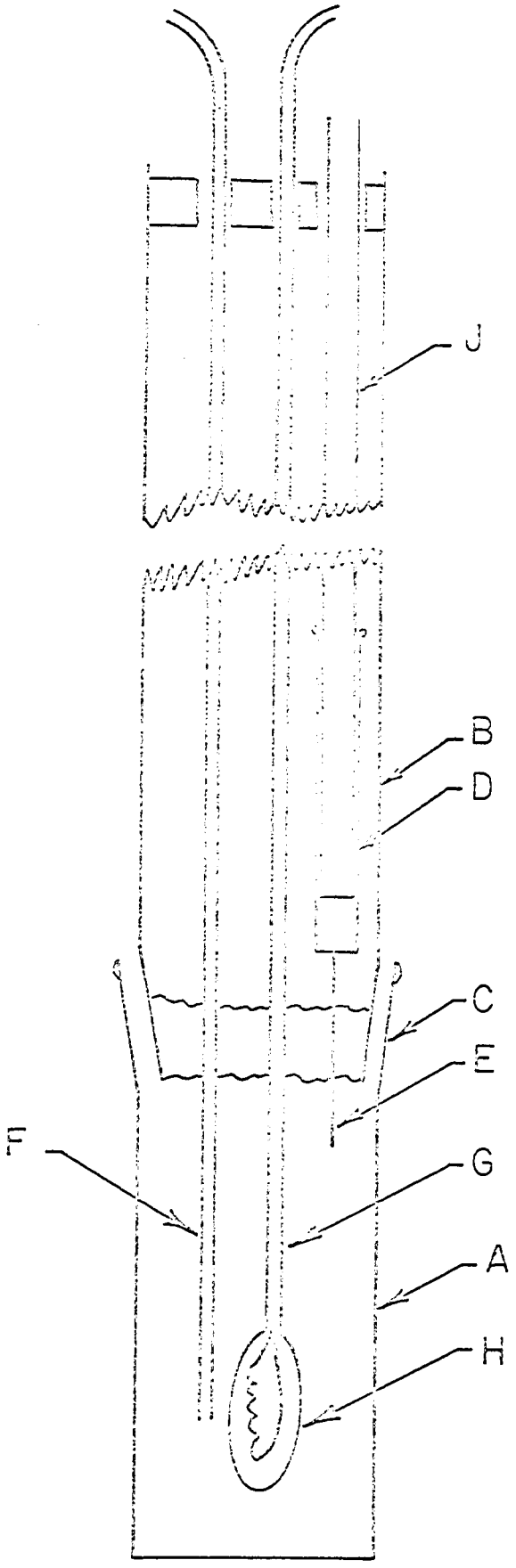


Figure 1 The [illegible] assembly

in the tube, giving smooth effective stirring. The regular alternations in the pressure were caused in the following manner. A glass U-tube was partially filled with vacuum-pump oil. One side of the U-tube was connected to the glass tubing in the reaction cell by means of a short length of tygon tubing. A small piston was snugly fitted into the other end of the U-tube. The piston was driven by a geared-down electric motor at about 60 cycles per minute. Stirring by this method was gentle and reproducible. The syringe (D) is used to contain the initiator; its plunger was extended by a glass rod (J) out of the top of the assembly so that the initiator could be injected into the reaction cell by merely depressing the plunger.

The Relationship Between the Heat Liberated in the Calorimeter and the Integral of the Voltage-Time Curve.

The treatment given here is a modification of that due to Calvet and Prat (54).

A reaction occurring in one cell of the calorimeter increases the temperature of that cell from T_o, its initial temperature, to the temperature T, at time t. Let

$$\Delta T = (T - T_o) \qquad (h)$$

The rate of heat loss from the reaction chamber to the heat sink, $\frac{dq}{dt}$ is proportional to T. Newton's law of cooling for the reaction cell is

$$\frac{dq}{dt} = h \Delta T \qquad (i)$$

where h is a constant.

The thermopile circuit E.M.F. is also directly proportional to the temperature increase ΔT, so that

$$E = k\Delta T \qquad (j)$$

where k is another constant. Substituting equation (j) into equation (i) yields:

$$\frac{dq}{dt} = \frac{h}{k} \quad E$$

Integration over all time yields

$$Q = \frac{h}{k} \int_0^\infty E \quad dt$$

where Q is the total heat liberated in the reaction cell. In practice $\frac{h}{k}$ is determined by calibration of the apparatus.

Calibration of the Calorimeter

Calibration of the calorimeter was carried out by generating different quantities of electrical heat in the reaction cell and measuring the area of the voltage-time curve for each of these heatings. The electrical heat was generated by passing a known current (I) through a measured resistance (R) for a definite period of time (t). The heat produced (J) was then calculated from $J = I^2Rt$ joules. The calories used are defined calories, the conversion factor for joules to defined calories being division by 4.1840. The area of the voltage-time chart was read directly from the integrating circuit chart.

The current flowing through the calibrating resistor in each calibration was determined by measuring the voltage across a known resistance in series with the calibrating resistor. The voltage across this known series resistor was measured by a Tinsley potentiometer, Type 3589-R. The series resistor and the calibrating resistor were both precision resistors, the values of which did not change over long periods of time or with small fluctuations in temperature. These resistances were checked periodically on a Tinsley Wheatstone Bridge, Type 4970. The current of about 0.1 amperes was drawn from a six-volt battery, and it remained essentially constant during the calibration.

It has been shown (57) that equal quantities of heat generated in each reaction cell gives a net area of zero under the voltage-time curve. As a check on the calibration, the heat of a known reaction was redetermined (57). The reaction chosen was the solution of anhydrous lithium sulphate crystals in water. The reaction is:

$$Li_2SO_4\ (c) + 220\ H_2O\ (l) \rightarrow Li_2SO_4.220\ H_2O$$

The measured value for the heat of reaction was 6.54 ± 0.10 kcal per mole, compared with the literature value (58,59) of 6.61 kcal per mole. The agreement was within experimental error, and the electrical calibration considered satisfactory.

Purity of Materials

Chemicals used in the polymerizations consisted of monomer, emulsifier (cetyltrimethylammonium bromide), initiator (H_2O_2, $FeSO_4.7H_2O$) and catalyst (H_2SO_4). The monomers used in this study were supplied by the Rohm and Haas Company. Table I lists the assay of each monomer as reported by Rohm and Haas Company.

When received, all monomers contained a few parts per million of hydroquinone as inhibitor. Just prior to polymerization of a monomer, the inhibitor was removed by distillation under a reduced pressure of nitrogen. The middle fraction of the distillate was collected and kept under refrigeration except for short intervals when monomer was removed from this stock for polymerization studies.

The water used in making up all the solutions was distilled water. It was boiled, and then cooled in a stoppered bottle just before use.

The emulsifying agent was cetyltrimethylammonium bromide, technical grade, manufactured by Eastman Kodak. It was purified by recrystallizing it twice from acetone.

The hydrogen peroxide and the ferrous sulphate were reagent-grade chemicals.

For the volumetric determination of the monomers the following reagents were used: bromine, chloroform, potassium bromide, potassium iodide and sodium thiosulphate.

TABLE I

Specifications and Typical Properties of the Monomers

	Specifications	Typical Properties Purity
Methacrylic acid	98.5%	99.0%
Methyl methacrylate	99.5%	99.8%
Ethyl methacrylate	98.0%	99.1%
Butyl methacrylate	98.5%	98.8%
Hexyl methacrylate	98.0%	99.8%
2-Hydroxyethyl methacrylate		96.5%
2-Hydroxypropyl methacrylate		96.5%
Acrylic acid	99.0%	99.3%
Methyl acrylate	98.5%	98.8%
Ethyl acrylate	98.5%	99.0%
Butyl acrylate	99.5%	99.6%

The potassium iodide was shown to be iodate free. The sulphuric acid, potassium bromide, bromine, potassium iodide, and sodium thiosulphate were Fisher certified reagent chemicals.

The bromine solution was made up by dissolving 30 grams of potassium bromide in 400 ml. of water, and then adding approximately 5.5 ml. of bromine.

The sodium thiosulphate solution was made up to approximately 0.15N using proportional quantities to those given in Kolthoff (60), and standardized against potassium iodate according to the procedure in Kolthoff (60).

Experimental Procedure

A similar procedure was used to measure the heat of reaction in every case and this may be described generally as follows. The syringes in the reaction assemblies were loaded with the appropriate amount of dilute H_2O_2 to give a 10^{-3}M solution when injected into 10 ml of solution in the reaction cell. Thirty-five ml. of distilled water was placed in a 100 ml. glass stopper volumetric flask. A stream of nitrogen was passed through the water for fifteen minutes to reduce the oxygen content. The appropriate amount of cetyltrimethylammonium bromide was weighed to give a 1% solution of emulsifier and this placed in the water, followed by enough dilute sulphuric acid to give a 10^{-2}N solution. A carefully weighed quantity of ferrous sulphate, to give a

10^{-3} M solution, was then dissolved in the solution. Into one cell ten ml. of this solution was placed and this cell joined to the rest of the reaction assembly and placed in the calorimeter. This is the blank experiment. To the remaining twenty-five mls. of the emulsion solution was added the appropriate amount of monomer and stirred vigorously. Ten ml. of this solution were then placed in the other reaction cell, joined to the assembly and placed in the calorimeter. Both cells were allowed to remain in the calorimeter for sufficient time to reach thermal equilibrium with the heat sink. When thermal equilibrium had been attained, the charts on the amplifier and integrator were started, and the amplifier and integrator controls set. The plungers on the syringes were depressed, the reaction being in this way initiated, and the stirring motor turned on. The stirring motor was allowed to run for the duration of the experiment. When the reaction had essentially stopped, as indicated by a zero voltage on the thermopile circuit, the heat evolved in the reaction was estimated, and approximately the same quantity of electrical heat was introduced into the reaction cell in the manner previously described. At the conclusion of this calibration the exact heat evolved in the reaction was calculated from the ratio of the two curve heights on the integrator and the electrical input.

Immediately following the completion of the calibration the amount of monomer in the initial solution and in the final partially polymerized solution was determined by titration. The blank cell in the calorimeter was used to determine the concentration of the bromine when no monomer was present. These determinations were carried out in the following manner. The procedure is a modification of that described in (61). Ten ml. of the bromine solution had been placed in each of three stoppered iodine-number flasks and had all been cooled in ice water to prevent volatilization of the bromine. Into one flask was pipetted five milliliters of the initial monomer solution and 5 ml. of $CHCl_3$ were added. Into one of the remaining flasks the partially polymerized monomer solution was poured, the reaction cell being rinsed twice with 2 ml. of water and twice with 2.5 ml. of $CHCl_3$. In the remaining iodine flask the contents of the other reaction cell was poured with similar washings as above. Immediately following the completion of additions of reagents to each iodine-number flask it was placed on an oscillating shaker. After the iodine flasks were shaken for one-hour periods each was removed in turn and subjected to the following procedure. The iodine-number flask was again chilled in ice-water and then 25 ml. of a 10% KI solution added by allowing the reduced pressure inside the flask to draw the

solution into it. The flasks were shaken by hand for two minutes and then titrated with standardized $Na_2S_2O_3$ solution, from a graduated 50 ml. burette, to a clear layer of $CHCl_3$.

The amount of monomer polymerized was then calculated by the following method. The amount of bromine added to the 5 ml. of initial monomer was calculated by subtracting the titer of this solution from the titer of the blank, $V_B - V_{mi}$: this is the amount of bromine reacting with 5 ml. of monomer solution. The amount of bromine which would add to 10 ml. is therefore $2(V_B - V_{mi})$. The amount of monomer adding to the partially polymerized solution was obtained by subtracting the volume used in its titer from the volume used in the blank, $(V_B - V_{mp})$. The volume of $Na_2S_2O_3$ corresponding to the amount of monomer polymerized is therefore $2(V_B - V_{mi}) - (V_B - V_{mp})$ or $V_B - 2V_{mi} + V_{mp}$. Multiplication of this volume by the normality of the $Na_2S_2O_3$, and the equivalent weight of the monomer, divided by the molecular weight of the monomer, gives the number of moles of monomer polymerized in the reaction for which the heat was measured:

$$(V_B - 2V_{mi} + V_{mp}) \times \frac{N_{Na_2S_2O_3}}{1000} \times \frac{\text{Eq. wt. monomer}}{\text{M.W. Monomer}} = \text{Number of moles polymerized}$$

Since $\text{Eq. Wt. Monomer} = \frac{\text{M.W. Monomer}}{2}$

the expression has the form

$$(V_B - 2V_{mi} + V_{mp}) \times \frac{N_{Na_2S_2O_3}}{2000} = \text{Number of moles polymerized}$$

Division of this quantity into the heat observed during the calorimetric measurement gives the heat of polymerization.

Duplicate titrations of monomer solutions were in agreement to better than 1% with one another. Titrations on weighed quantities of monomer showed that the gravimetric and volumetric determination agreed to better than 1%.

To confirm that the reaction of the ferrous ion and the hydrogen peroxide were effectively cancelled by the use of the differential calorimeter, the following arrangement was used. Both syringes were loaded with the same quantity of H_2O_2. Emulsifier, ferrous sulphate and sulphuric acid were added to degassed water and 10 ml. of this placed in each reaction cell. When thermal equilibrium had been attained the amplifier, integrator and recording charts were started. The plungers on the syringes were then depressed and the stirring motor was started. That any heat effects were cancelled by the differential nature of the calorimeter was exhibited by the fact that no area appeared on the E.M.F. vs time chart and hence no area on the integrator chart. This shows that neither the initiator reaction nor the stirring contributed to the heat measured by the calorimeter.

EXPERIMENTAL RESULTS

The experimental results are presented in Tables II to XII. For each reaction studied several results are given.

The average heat of reaction is given for every monomer along with the standard deviation of the measurements. For the sake of convenience the results are summarized in Table XIII.

All polymerizations were carried out at 25.0 degrees centigrade.

Except where noted one per cent of cetyltrimethylammonium bromide (emulsifier) and 10^{-3} molar ferrous sulphate and hydrogen peroxide (initiator) were used.

TABLE II

Heats of Polymerization of Methyl Methacrylate

Experiment Number	Initial Monomer Concentration m.moles per 10c.c. C_o	Final Monomer Concentration m.moles per 10c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per Mole
1	1.633	0.476	1.157	70.9	15.71	13,580
2	1.948	0.478	1.470	75.5	19.94	13,560
3	1.752	0.736	1.016	58.0	13.80	13,580
4	1.913	0.546	1.367	71.5	18.54	13,560
5	1.839	0.660	1.179	64.1	15.98	13,550
6 *	1.913	1.091	0.822	43.0	11.17	13,590
7	1.737	0.736	1.001	57.6	13.61	13,590
8	1.810	0.857	0.953	52.7	12.99	13,630
9 *	2.051	0.980	1.071	52.2	14.44	13,480
10 *	2.002	1.253	0.749	37.4	10.13	13,530
11 *	1.775	0.901	0.874	49.2	11.79	13,490
12	2.408	1.140	1.268	52.7	17.32	13,660
13	2.125	0.758	1.367	64.3	18.61	13,620
14	1.779	1.057	0.722	40.6	9.73	13,480

TABLE II - (Continued)

Heats of Polymerization of Methyl Methacrylate

Experiment Number	C_o	C_f	$C_o - C_f$	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per Mole
15	2.103	0.717	1.386	65.9	18.85	13,600
16 *	2.090	0.666	1.424	68.1	19.25	13,520
17 *	2.095	0.755	1.340	64.9	18.30	13,660
18.*	2.028	1.181	0.847	41.8	11.48	13,550
19.	2.140	1.079	1.061	49.6	14.27	13,450
20	1.915	0.996	0.919	48.0	12.59	13,700
21	2.230	0.903	1.327	89.5	17.96	13.540
					Mean	13,570 ± 60

* Experiment Number 6 — 0.5% emulsifier

Experiment Number 9 and 10 — 1.5% emulsifier

Experiment Number 11 — 2% emulsifier

Experiment Number 16 — 2×10^{-3} M initiator

Experiment Number 17 — 0.5×10^{-3} M initiator

Experiment Number 18 — 4×10^{-3} M initiator

TABLE III

Heats of Polymerization of Ethyl Methacrylate

Experiment Number	Initial Monomer Concentration m.moles per 10 c.c. C_o	Final Monomer Concentration m.moles per 10 c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per Mole
1	1.976	0.946	1.030	52.1	14.21	13,800
2	2.297	0.689	1.608	70.0	22.15	13,780
3	2.327	0.543	1.784	76.7	24.68	13,830
4	2.266	0.743	1.523	67.2	20.95	13,750
5	1.803	0.402	1.401	77.7	19.32	13,790
6	1.768	0.479	1.289	72.9	17.75	13,770
7	1.839	0.501	1.338	72.8	18.43	13,780
8	1.920	0.480	1.440	75.0	19.95	13,860
9	1.601	0.506	1.095	68.4	14.99	13,690
					Mean	13,780 ± 50

TABLE LV

Heats of Polymerization of n-Butyl Methacrylate

Experiment Number	Initial Monomer Concentration m.moles per 10c.c. C_o	Final Monomer Concentration m.moles per 10c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per Mole
1	1.946	1.003	0.943	48.5	12.90	13,680
2	1.961	0.721	1.240	63.2	17.20	13,870
3	2.087	0.717	1.370	65.6	18.90	13,790
4	1.857	0.965	0.892	48.0	12.48	13,990
5	2.069	0.756	1.313	63.5	18.11	13,790
6	1.976	1.084	0.892	45.1	12.37	13,870
7	1.985	0.645	1.340	67.5	18.70	13,960
8	2.015	0.666	1.349	67.0	18.83	13,960
9	2.065	0.569	1.496	72.5	20.51	13,710
10	1.812	0.474	1.338	73.8	18.57	13,880
11	1.804	0.377	1.427	79.1	20.00	14,020
12	2.015	0.461	1.554	78.1	21.37	13,750
					Mean	13,860 ± 110

TABLE V

Heats of Polymerization of n-Hexyl Methacrylate

Experiment Number	Initial Monomer Concentration m.moles per 10c.c. C_o	Final Monomer Concentration m.moles per 10c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per Mole
1	2.126	0.911	1.215	57.1	17.04	14,020
2	1.975	0.987	1.018	51.5	14.18	13,930
3	2.219	1.053	1.166	52.5	16.49	14,140
4	2.028	0.660	1.368	67.5	19.12	13,970
5	1.976	0.643	1.333	67.5	18.54	13,910
6	2.174	0.529	1.645	75.7	23.05	14,010

Mean $14,000 \pm 80$

TABLE VI

Heats of Polymerization of Hydroxylethyl Methacrylate

Experiment Number	Initial Monomer Concentration m.moles per 10c.c. C_o	Final Monomer Concentration m.moles per 10c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per Mole
1	2.231	1.216	1.015	45.5	12.09	11,910
2	1.959	1.515	0.444	22.7	5.31	11,950
3	2.476	1.854	0.622	25.1	7.52	12,080
4	2.566	1.699	0.867	33.8	10.28	11,850
5	2.327	1.734	0.593	25.5	7.07	11,910

Mean 11,940 ± 80

TABLE VII

Heats of Polymerization of 2-Hydroxylpropyl Methacrylate

Experiment Number	Initial Monomer Concentration m.moles per 10 c.c. C_o	Final Monomer Concentration m.moles per 10 c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per mole
1	2.310	0.555	1.755	76.0	21.06	12,000
2	2.453	0.839	1.614	65.8	19.53	12,100
3	2.516	0.573	1.943	77.2	23.41	12,050
4	2.060	0.427	1.633	79.3	19.66	12,040
5	2.002	0.490	1.512	75.5	18.42	12,180
6	2.486	0.338	2.148	86.4	26.15	12,180
7	2.424	0.295	2.129	87.7	25.90	12,160

Mean 12,100 ± 70

TABLE VIII

Heats of Polymerization of Methacrylic Acid

Experiment Number	Initial Monomer Concentration m.moles per 10 c.c. C_o	Final Monomer Concentration m.moles per 10 c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per mole
1	2.140	1.176	0.964	45.1	12.93	13,410
2	2.792	1.134	1.658	59.4	22.45	13,540
3	2.704	1.382	1.322	48.9	17.89	13,530
4	2.842	1.157	1.685	59.3	22.48	13,340
5	2.697	1.240	1.457	54.0	19.62	13,470
6.	2.789	1.347	1.442	51.7	19.42	13,470

Mean 13,460 ± 70

TABLE IX

Heats of Polymerization of Acrylic Acid

Experiment Number	Initial Monomer Concentration m.moles per 10 c.c. C_o	Final Monomer Concentration m.moles per 10 c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per mole
1	2.019	1.098	0.921	45.6	16.90	18,350
2	2.377	1.131	1.246	52.4	22.97	18,430
3	2.544	1.128	1.416	55.7	26.05	18,400
4	2.653	1.205	1.448	54.6	26.56	18,340
5	2.712	1.487	1.225	45.2	22.57	18,430
6	2.594	1.329	1.265	48.8	23.30	18,420

Mean 18,400 ± 40

TABLE X

Heats of Polymerization of Methyl Acrylate

Experiment Number	Initial Monomer Concentration m.moles per 10 c.c. C_o	Final Monomer Concentration m.moles per 10 c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per mole
1	2.271	0.270	2.001	88.1	37.20	18,590
2	1.666	0.319	1.347	80.9	24.98	18,540
3	1.367	0.259	1.108	80.8	20.63	18,620
4	1.557	0.333	1.224	78.7	22.66	18,510
5	1.531	0.307	1.224	80.0	22.83	18,650

Mean 18,580 ± 50

TABLE XI

Heats of Polymerization of Ethyl Acrylate

Experiment Number	Initial Monomer Concentration m.moles per 10c.c. C_o	Final Monomer Concentration m.moles per 10c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per Mole
1	1.495	0.175	1.320	88.3	24.78	18,780
2	1.708	0.181	1.527	89.4	28.70	18,800
3	1.314	0.194	1.120	85.4	21.03	18,780
4	1.324	0.169	1.155	87.1	21.77	18,840
5	1.429	0.198	1.231	86.1	23.06	18,730

Mean 18,790 ± 40

TABLE XII

Heats of Polymerization of n-Butyl Acrylate

Experiment Number	Initial Monomer Concentration m.moles per 10 c.c. C_o	Final Monomer Concentration m.moles per 10 c.c. C_f	Amount Polymerized m.moles per 10 c.c.	Percent Polymerization	Heat Evolved Calories	Heat of Polymerization Calories per mole
1	1.296	0.247	1.049	80.9	20.05	19,110
2	1.554	0.239	1.315	84.6	24.96	18,980
3	1.599	0.240	1.359	85.0	25.92	19,070
4.	1.477	0.240	1.237	83.8	23.60	19,080
5	1.729	0.520	1.209	69.9	23.08	19,090

Mean 19,070 ± 50

TABLE XIII

Summary of Heats of Polymerization

Temperature 25°C.

Monomer	Number of Experiments	Table Number	Heat of Polymerization Calories per mole	Standard Deviation Calories per mole
Acrylic acid	6	IX	18,400	40
Methyl acrylate	5	X	18,580	50
Ethyl acrylate	5	XI	18,790	40
n-Butyl acrylate	5	XII	19,070	50
Hydroxyethyl methacrylate	5	VI	11,940	80
2-Hydroxypropyl methacrylate	7	VII	12,100	70
Methyl acrylic acid	6	VIII	13,460	70
Methyl methacrylate	21	II	13,570	60
Ethyl methacrylate	9	III	13,780	50
n-Butyl methacrylate	12	IV	13,860	110
n-Hexyl methacrylate	6	V	14,000	80

DISCUSSION

Comparison with Previous Results

Heats of polymerization reported in the literature have a number of different standard states. Frequently, there are insufficient data to convert a measured heat of polymerization to the value for some arbitrarily chosen standard state common to all systems. Dainton and Ivin (43) used the following subscripts to define the value of ΔH to which reference is being made:

Subscript	Monomer State	Polymer State
gg	gas	gas (usually hypothetical)
gc	gas	condensed (liquid or amorphous solid)
lc	liquid	condensed (liquid or amorphous solid)
ls	liquid	solution in monomer
ss	solution	solution
sc	solution	condensed (liquid or amorphous solid)

Our values as best compared to those of ΔH_{ss} where available. A considerable number of investigators have measured the heats of polymerization of some of the monomers studied in this work. Table XIV presents the experimental data available to date on the heats of polymerization of these monomers.

TABLE XIV

Summary of Heats of Polymerization Available in the Literature

Monomer	Standard States	Heat of Polymerization kilocalories per mole	Temperature of Polymerization	Reference
Acrylic acid	ss	18.5 ± 0.3	20°C	(18)
Methyl acrylate	lc	18.7 ± 0.2	76.8°C	(62)
	ss	20.2 ± 1.0	20°C	(18)
Methyl acrylic acid	ss	15.3 ± 0.2	20°C	(18)
Methyl methacrylate	lc	13.0 ± 0.2	76.8°C	(39)*
	lc	13.9 ± 0.3	76.8°C	(63)
	ls	13.8 ± 0.2	26.9°C	(5)
	lc	13.4 ± 0.5	130°C	(44)(45)
	lc	12.9 ± 1.1	20°C	(18)
Ethyl methacrylate	lc	14.4 ± 0.6	120°C	(46)
	ls	13.8 ± 0.2	26.9°C	(5)
n-butyl methacrylate	lc	13.5 ± 0.2	76.8°C	(39)*
	ls	14.3 ± 0.3	26.9°C	(5)
n-hexyl methacrylate	ls	14.4 ± 0.3	26.9°C	(5)

*Not corrected for unreacted monomer

The standard deviations in the present studies on the heats of polymerization are all within 0.8% and nine of them are in the range of 0-0.6% of the average heat of polymerization. The technique employed therfore seems to provide a very reliable method of measuring heats of polymerization.

Agreement between the heats of polymerization of acrylic acid and of the acrylates with available experimental data is fair. Certainly the value of 18.5 ± 3 (18) is in excellent agreement with our value of 18.40 ± .04 for acrylic acid. The value of the heat of polymerization of methyl acrylate of Tong and Kenyon (62) is in good agreement with our value, but that of Evans and Tyrrall (18) is considerably higher. However, their estimated error of 1 kcal.per mole is approximately a 5% error and indicates a large degree of uncertainty in their result.

The value of methylacrylic acid given by Evans and Tyrrall (18) is considerably higher than that reported here. For methyl methacrylate the value we have obtained is in good agreement with the results of most investigators. The value of Tong and Kenyon (39) may be too low because they assumed complete polymerization.

The heats of polymerization of ethyl methacrylate are within the limits of the estimated experimental errors. The value we obtained for butyl methacrylate, 13.86 kcal/mole, is intermediate in value between the values in the literature and outside their estimated experimental error . The result for

hexyl methacrylate was slightly lower than indicated by the previous experiments of Dainton (6).

No literature values are available for hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, ethyl acrylate or butyl acrylate.

Interpretation of the Results

As seen earlier, addition of a free radical to a vinyl monomer may occur in one of two ways;

$$R + H_2C = CXY \longrightarrow R\text{-}CH_2\text{-}CXY\text{-}$$

$$R + XYC = CH_2 \longrightarrow R\text{-}CXY\text{-}CH_2\text{-}$$

The former process leads to a head-to-tail (HT) polymer, the latter to a head-to-head, tail-to-tail (HHTT) polymer. The relative rate of the two processes depends on the energies of the corresponding complexes, and the following two factors are of primary importance:

1) In the radical $R\text{-}CH_2\text{-}CXY$ the substituents X and Y provide the possibility of resonance structures in which the unpaired electron resides on the radical, and this has the effect of stabilizing the radical. This resonance stabilization will also enter to some extent into the activated complex. No such resonance stabilization is possible in the case of the radical $R\text{-}CXY\text{-}CH_2\text{-}$ or its corresponding activated complex. This factor therefore favors the formation of HT polymers, and structural studies (64,65) in fact indicate that these are the most common.

2) Steric effects, on the other hand, tend to favor the HHTT arrangement, as is shown schematically in Figure 5. There is more steric interference in the case of an HT polymer than in a HHTT polymer, and this is also true in the case of the activated complexes. A polymer radical in which the odd electron is on the $-CH_2-$ group (I and II in Figure 5) will therefore prefer to add on to the $-CH_2$ end (I) rather than the -CXY end (II). Similarly a polymer radical with the end electron on the -CXY group will prefer to add on to the CXY end of the monomer (IV) rather than to the CH_2 end (III). As a result, the HHTT polymers tend to be prefered if there is much steric hindrance. In agreement with this Marvel and Cowan (66) have shown that the monomers

$$CH_2=\overset{Cl}{\overset{|}{C}}COOCH_3 \qquad \text{and} \qquad CH_2=\overset{Br}{\overset{|}{C}}COOCH_3$$

where considerable steric effects are expected, lead predominantly to the HHTT arrangement.

These considerations lead to an interpretation of the apparently paradoxical results that in both acrylate and methacrylate series the change from methyl to ethyl to n-butyl esters leads to a steady increase in the heat of polymerization. It must be supposed that the increased steric hindrance leads to an increase in the proportion of HHTT polymer, so that in the products there is actually less steric hindrance with the more bulky substituents than with the smaller ones.

INITIAL STATE

ACTIVATED STATE

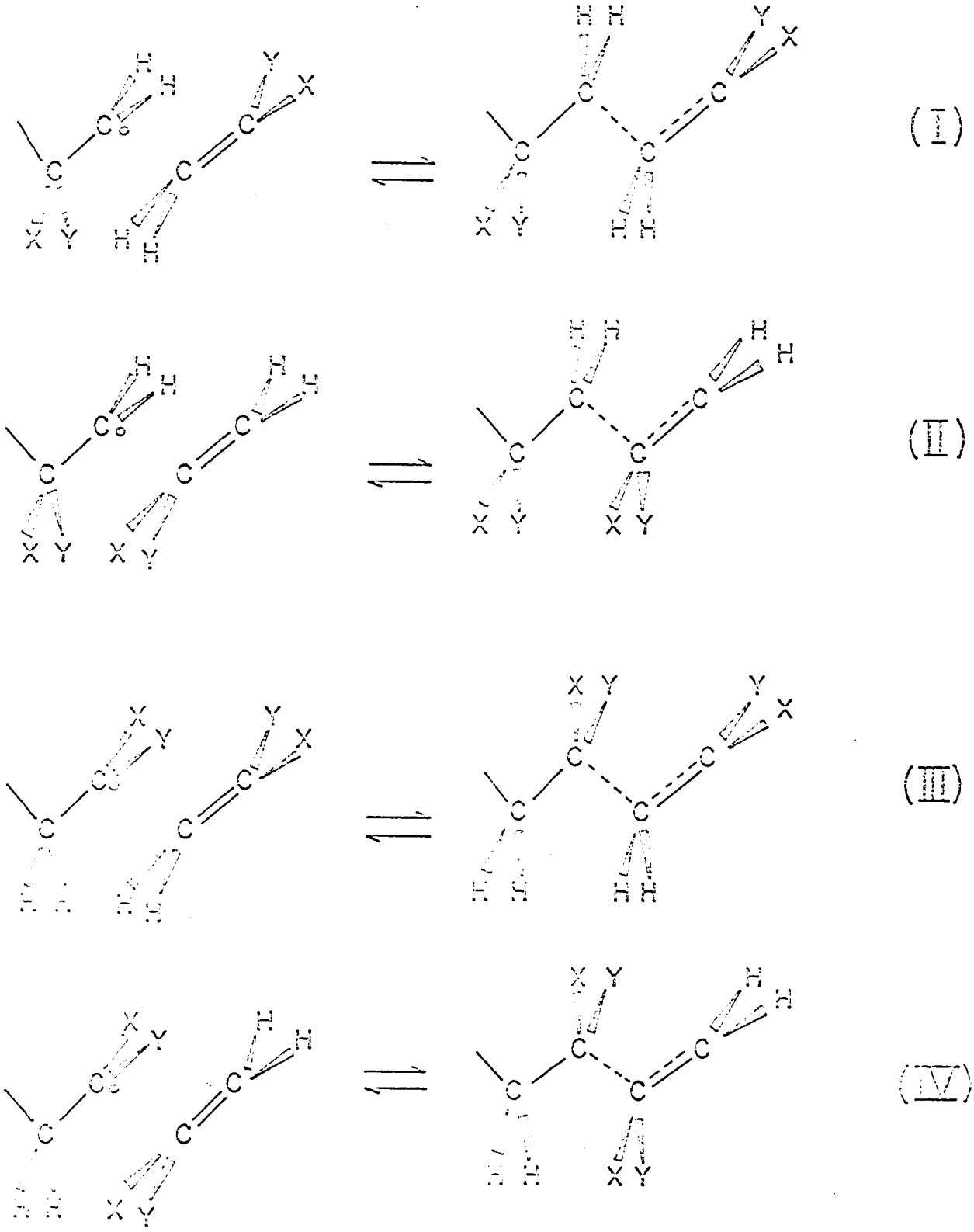


Figure 5 Initial and activated states in polymerisation

Hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate both exhibit lower heats of polymerization than do the monomers having no hydroxyl groups. The difference seems too large to explain on the basis of changes in the bond strengths, or by steric hindrance, brought about by the hydroxyl groups. The most likely explanation appears to be that in solution the hydroxyl group in the monomer is solvated, but that in the polymer chain the hydroxyl groups are only partially solvated. The heats of solvation of alcohols are in the range of 2.5 to 4 kcal per mole (67), so that the effects observed could be explained if only part of the solvation shell is removed on polymerization.

PART II

KINETICS OF POLYMERIZATION

INTRODUCTION

Kinetics of Emulsion Polymerization

McBain (26) and Harkins (27,28) studied strong soap solutions by means of X-ray diffraction, obtaining good diffraction patterns which tended to show that lamellar micelles are present in strong soap solutions. These micelles consist of a pile of three or more double layers of oriented soap molecules; each double layer is held together by the relatively weak attractive forces between the methyl groups of the soap, and are separated by layers of liquid water approximately 20 A.U. thick.

If a hydrocarbon is added to this system, it penetrates the micelle and splits the double layer of soap. Consequently the micelles consist of soap separated by water and oil. McBain coined the term 'solubilized' to describe the state of the oil within the micelle. This incorporation of the oil has the effect of increasing the distance between adjacent soap layers and this was reflected in a shift of the x-ray diffraction lines. If the monomer is not completely

solubilized some of it remains as suspended droplets in the aqueous phase.

The characteristics of emulsion polymerization led Harkins (29) to propose two principal loci of polymerization. One locus operative initially, when the monomer is present in the solubilized condition and in the form of droplets; and the other locus later on, when the character of the emulsion has been materially altered. The monomer droplets are orders of magnitude greater in mean radius than the micelles; but the latter present an immensely larger interfacial area; almost all of the radicals generated in the aqueous phase are therefore captured by the micelles. Polymerization is initiated in the micelles by the capture of the radical, and monomer is supplied to the growing radicals from the droplets in the surrounding solution. The original micelles containing monomer, through initiation of polymerization, become polymer particles, and these polymer particles rapidly grow larger than the original micelle due to the entrance of monomer from the droplets. Soon all the soap is absorbed on these polymer particles, the micelles disappear (2 - 3 % conversion), and from this point on the locus of polymerization is the polymer particles.

Smith and Ewart (30) provided a quantitative check on the mechanism of emulsion polymerization proposed by Harkins. Their argument is most easily developed by

considering the steady state portion of the polymerization process after the micelles have disappeared and the number of polymer particles has become constant. Under normal emulsion polymerization conditions the number of polymer particles amounts to 10^{13} - 10^{15} particles per cubic centimeter. We will take 10^{14} as an average value.

The rate of radical production depends on the temperature, amount and nature of the initiator employed, but 10^{13} radicals per cubic centimeter per second is a representative value. Therefore if all the initiator radicals enter polymer particles, a particle will aquire a radical once in about 10 seconds, on the average. Once in a particle, a radical proceeds to grow by adding monomer units at a rate equal to the rate constant for propagation process k_p, multiplied by the monomer concentration in the particles.

If a radical enters a particle that already contains a radical it will at once combine with it, and from this it follows that at any time one half of the polymer particles will contain one radical and the other half no radicals. If N is the total number of polymer particles the rate of polymerization is therefore given by

$$R_p = k_p [M] \frac{N}{2}$$

This expression has been confirmed for styrene systems by Smith (68, 69) and also by Morton (70, 71, 72), employing

"seeded" systems in which fresh initiator and styrene is added to a performed latex, containing no free soap, and in which the particle concentration is known by electron microscopic measurements or other means.

It is evident from the above expression that if $\frac{d[M]}{dt}$ N and $[M]$ are known k_p can be calculated. With styrene the result is in reasonable agreement with the measurements in homogeneous systems (68,69,70,71,72) and provides additional confirmation of the scheme.

The number of particles, N, in the rate expression, is shown by the Smith-Ewart theory to be proportional to the concentration of the emulsifier to the 0.6 power and the concentration of the initiator to the 0.4 power.

$$N \propto C_E^{0.6} \; C_I^{0.4}$$

A more recent theory of emulsion polymerization has been put forth by Medvedev (73). His assumption is that the initial formation of the polymer raises the viscosity of the interior of the monomer-polymer particles preventing radical penetration and therefore most polymerization takes place on the surface of the particles. He also assumes that the water-soluble initiator radical reacts with an emulsifier molecule in the water phase. This activated emulsifier molecule then enters the absorbed layer on the surface of the particle initiating a chain reaction. From these assumptions he finds

that the number of particles is proportional to the concentration of the emulsifier and of the initiator both to the 0.5 power. That is

$$N \propto C_E^{0.5} \; C_I^{0.5}$$

Recent investigations of the effect of emulsifier and initiator on the rates of polymerization (74) indicates this latter expression may indeed apply. This investigation (74) also shows that the water solubility of the monomer is relatively unimportant in determining the rate dependence and the particle number dependence; methyl methacrylate, butyl methacrylate and other monomers have the same dependence of rate and particle number on emulsifier, initiator and monomer concentrations over the range of variables investigated.

In the present studies the monomer concentration was approximately 0.2M and it is assummed that at this low concentration of monomer and a one percent emulsion, all the monomer is solubilized.

This is equivalent to saying that the monomer concentration in the particle is proportional to the overall monomer concentration. In comparing the rate constants for propagation of different monomers one must assume that N is the same in all cases. Recent work (74) has indicated that several monomers have the same dependence of the particle

number on emulsifier, initiator and monomer. Since all experiments were under identical conditions, the assumption of a constant N does not appear dangerous, especially since the nature of the monomers is not altered greatly from one monomer to another.

Thermal Method for Determining Rate Constants

The thermal method of following the kinetics of a reaction by the temperature change is particularly important where the reactions are too fast to use the usual chemical methods. As early as 1923 a thermal method of determining rate constants was suggested by Hartridge and Roughton (75) for a flow system. For reactions in non-flowing systems, Bell and Clunie (76) have given a theoretical treatment of first-order and second-order reactions and have verified their treatment experimentally. Their treatment requires that the heat of reaction and the cooling constant of the reaction cell be known. Their method also involves a knowledge of T_o, the temperature (or E.M.F. of the calorimeter) that would result if the reaction took place under adiabatic conditions; this is not conveniently obtained from the calorimeter data available. Other investigators have also focused attention on the relationship of temperature to time (77,78,79).

A method due to Baumgartner and Duhaut (80) is ideally suited to the problem and the experimental information

available. It allows deduction of the first-order rate constant from readily available experimental data. It has been used by Lovering and Laidler (81) in the determination of alcohol-isocyanate rate constants.

Lueck, Beste and Hall (82) have described a method of determining reaction kinetics in solution similar to that of Baumgartner. Their apparatus consisted of a constant temperature bath in which are immersed two identical glass reaction vessels. Each glass reaction cell is equipped with an efficient stirrer and a thermister. Each cell contains the same amount of reagent solution. One cell serves as the reaction cell and the other as a reference calorimeter cell. The thermisters are connected through an amplifier and a bridge to a recording potentiometer, which provides a measure of the temperature difference between the two calorimeter cells as the reaction proceeds. When the reagent is injected into the reaction cell, a plot of temperature difference against time resembles curve A of Figure 6. The initial sharp rise in temperature at time zero when the reagent is injected is caused by: a) the difference in temperature of the added reagent from the cell contents, and b) the heat of mixing of the reagent with the solvent. The reaction begins and heat is generated causing a further rise in temperature. However, heat is also being lost from the reaction cell to the bath. After a maximum temperature is reached, a gradual decline of ΔT_t, the temperature difference

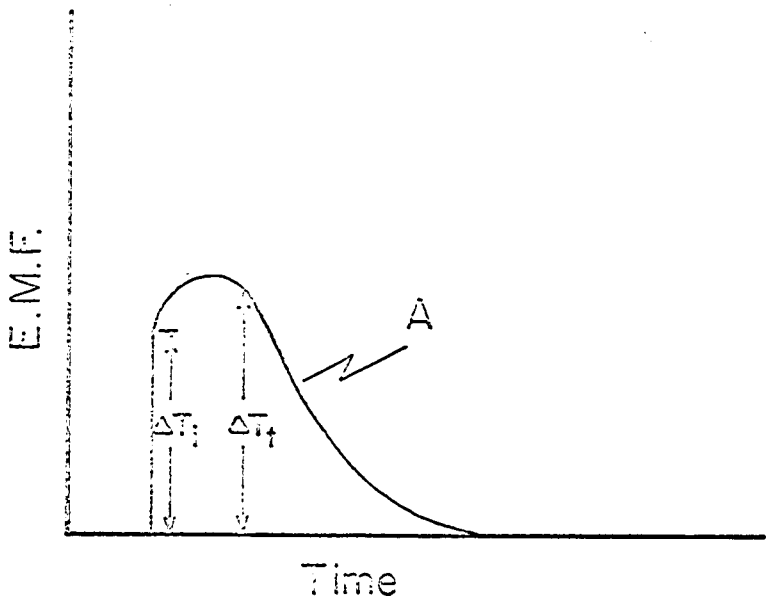


Fig. 1 Potentiometric tracing for a first order reaction

between reaction and reference cells at any time t, to zero occurs. They give the following derivation for the calculation of a first-order rate constant. Curve A will depend on k_1, the rate constant of the chemical reaction, and on the rate of cooling. The rate constant can be extricated from the curve A in the following manner. At any time t, the following heat balance equation holds

$$C_p \Delta T_t = Q_m + Q_r - Q_d \qquad (k)$$

where

C_p is the heat capacity of the reaction cell and contents in calories per temperature unit. It is assumed constant during the run.

ΔT_t is the temperature difference between the reaction and reference cells in appropriate units of time.

Q_m is that heat in calories which would be just sufficient to cause the rapid temperature rise, ΔT_i, which is observed when the given quantity of reagent at any temperature is mixed with the solution in given amount and concentration.

ΔT_i is the value of ΔT_t reached almost instantly after the injection of the reagent.

Q_r is the heat in calories evolved by the reaction of the given amount of reagent by time t.

Q_d is the heat in calories which has been dissipated from the reaction cell into the bath by time t.

Heat is now being lost to the bath throughout the run, and if Newtonian behavior is followed the heat lost can be expressed as

$$-\frac{1}{C_p}\frac{dQ_d}{dt} = K\Delta T_t = -\frac{d\Delta T_t}{dt} \qquad (l)$$

where K, in reciprocal minutes is a constant characteristic of the particular cell, stirrer and cell contents. That Newtonian behavior is indeed followed was demonstrated by plotting the logarithm of ΔT_t against t, as expressed in the following equation

$$\Delta T_t = \Delta T_i \, e^{Kt} \qquad (m)$$

Where K can be evaluated from the slope.

Integration of equation (l) gives

$$-\int_o^\tau dQ_d = -Q_d = KC_p \int_o^\tau \Delta T_t \, dt \qquad (n)$$

The term Q_m can be evaluated from the value of ΔT_i (see Figure 6).

$$Q_m = C_p \Delta T_i \qquad (o)$$

Substituting terms in equation k from their equivalents in equations (n) and (o) yields

$$Q_r = C_p \Delta T_t - C_p \Delta T_i + KC_p \int_o^\tau \Delta T_t \, dt \qquad (p)$$

Q_r is proportional to the concentration of product $[P]_t$ formed at time t.

$$\frac{Q_r}{Q_{r(\infty)}} = \frac{[P]_t}{[M]_o} \qquad (q)$$

in which $Q_{r(\infty)}$ is the total heat in calories formed by the complete reaction of the added reagent under the specific conditions and $[M]_o$ is the initial concentration of reagent.

By eliminating Q_r between equations (p) and (q).

$$[P]_t \quad \frac{C_p [M]_o}{Q_{r(\infty)}} \; X\left\{ \Delta T_t - \Delta T_i + K\int_o^{\infty} \Delta T_t \, dt \right\} \qquad (r)$$

Here the bracketed term involving experimentally accessible quantities is directly proportional to the product concentration. The values of ΔT_t and ΔT_i are read directly from the potentiometer tracing at various times and just after injection.

To calculate the fraction reacted, f, at any time we let $t = \infty$ in equation (r) and we obtain (s).

$$[P]_{\infty} = \frac{C_p [M]_o}{Q_{r(\infty)}} \left\{ 0 - \Delta T_i + K\int_o^{\infty} \Delta T_t \, dt \right\} \qquad (s)$$

Dividing (r) by (s) and letting $f = [P]_t / [P]_{\infty}$ we obtain (t)

$$f = \frac{\Delta T_t / K + \Delta T_i / K + \int_o^{\tau} \Delta T_t \, dt}{-\Delta T_i / K + \int_o^{\infty} \Delta T_t \, dt} = \qquad (t)$$

In our case $\Delta T_i = 0$, since the reactants were at thermal equilibrium and any heat of mixing on adding the initiator cancels because of the differential nature of the calorimeter. Therefore (t) has the form

$$f = \frac{\Delta T_t / K + \int_o^{\tau} \Delta T_t \, dt}{\int_o^{\infty} \Delta T_t \, dt}$$

The numerator is the sum of the heat evolved in attaining temperature t (area A Figure 7a), and the unevolved heat for the cooling from temperature t to the initial temperature (area B Figure 7c). The denominator is the total heat evolved.

The usual form of the first-order expression is

$$\ln \frac{a}{c} = kt$$

where

a = initial concentration

c = concentration at time t

k = rate constant

t = time

but $c = a - a_p f$

where a_p is the amount polymerized when the reaction has essentially stopped. Therefore from

$$\ln \frac{a}{a - a_p f} = kt \qquad (u)$$

a plot of $\ln \frac{a}{a-a_p f}$ versus t gives a line of slope k, a and a_p are determined analytically and f is calculated from the above expression from the data available on the recorder charts. The rate expression for emulsion polymerization has been shown to be

$$-\frac{d[M]}{dt} = k_p [M] \frac{N}{2} \qquad (x)$$

Since in our experiments the majority of polymerizations were carried out with a constant concentration of initiator and emulsifier, N would be approximately constant in all cases, and since N is very large the above expression (x) corresponds to pseudo-first-order kinetics.

We can, by the previously described thermal methods determine rate constants for the polymerizations.

These rate constants are proportional to k_p, the rate constant for propagation.

The method of Lueck et al has been used to determine the rate constants, for the polymerization reactions studied, from the calorimetric charts. These charts record the E.M.F. due to the heat produced by a reaction or by electrical heating as a function of time, and also the integral of the E.M.F. versus time curve as a function of time. Schematic curves of this type appear in Figure 7: curve 7a shows the variation of the E.M.F. with time due to a chemical reaction, and 7b is the integral of the curve 7a, also as a function of time; curve 7c shows the E.M.F. variation with time due to electrical heating, and 7d is the integral of this curve.

The procedure of extracting the rate constants from these charts is as follows. If the chemical reaction could be stopped at any time t, the reaction cell would cool off exactly in the manner it cools off after the current is turned off in an electrical calibration. The area under this curve is proportional to the amount of material reacted from time t = o to t = t.

Imaginary curves of this type can be obtained from the E.M.F. versus time plots for the chemical reaction, and for an electrical heating. The shaded area A in Figure 7a is a measure of the heat evolved from time t = o to t = t.

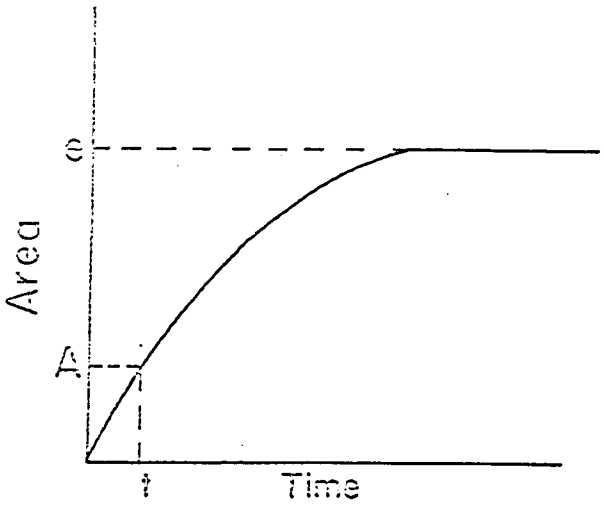


Figure 7b Integrator chart for a chemical reaction

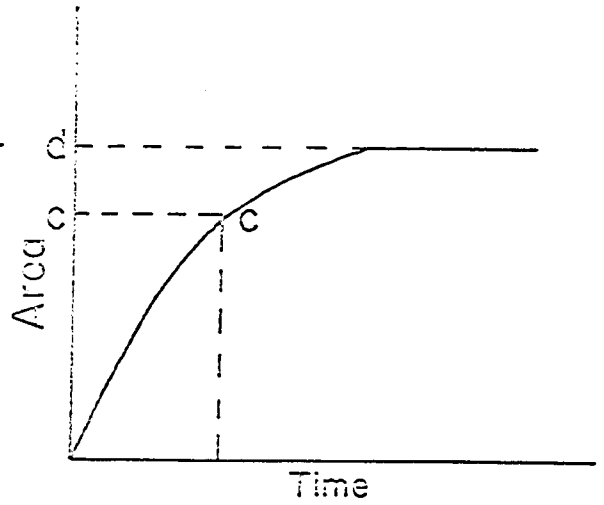


Figure 7d Integrator chart for an electrical heating

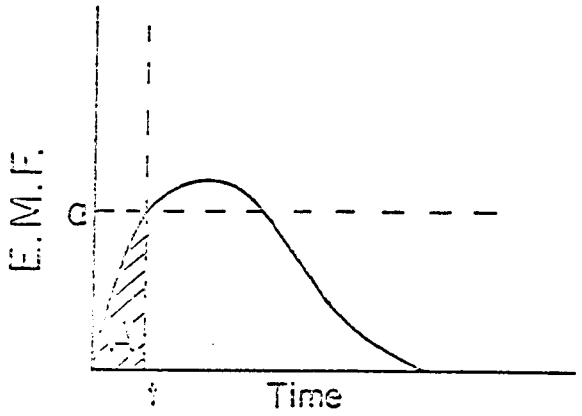


Figure 7a Amplifier chart for a chemical reaction

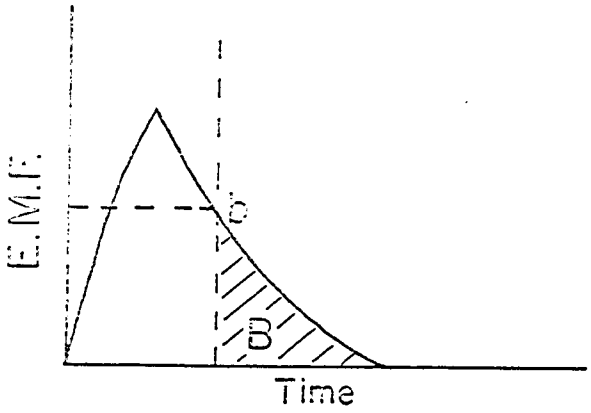


Figure 7c Amplifier chart for an electrical heating

Stopping the reaction at t, would mean the reaction cell would cool down according to its characteristics, as measured by a simple cooling curve, such as is obtained when an electrical heating is discontinued. Hence, the area of a simple cooling curve between E.M.F. = a and E.M.F. = o is a measure of the unevolved heat in the reaction cell when the reaction is stopped at time t. This is shown as the shaded area B in Figure 7c. The sum of area A in Figure 7a and area B in Figure 7c gives the total heat of reaction up to time t. This is a direct measure of the amount of reactant which has reacted at time t. The ratio of the heat evolved up to time t to the total heat evolved is a measure of the fraction reacted, f, up to time t. From this value of f and the analytical results of initial monomer and final monomer in the solution, we can calculate the rate constant from equation (u).

EXPERIMENTAL

Calculation of the Rate Constants from Calorimetric Data

The rate constants were obtained from the calorimetric charts in the following manner. The charts from a chemical reaction and the electrical calibration were arranged on a drawing board in the order shown in Figure 7. A series of times were selected at fixed intervals covering the initial part of the reaction, up to 50% completion.

The magnitude of the area A is obtained by reading the area directly from the curve of area versus time (see Figure 7b). Area B is obtained by constructing a line from a to b and then from b to c as shown in Figure 7. The magnitude of area B is obtained by subtracting area C (Figure 7d) from the total area d, of the electrical heating curve. The fraction, f, polymerized is then determined from the ratio of the sum of area A and area B to the total area e, (Figure 7b) due to the chemical reaction. The left hand side of equation (u) was then plotted against the appropriate time, for a number of different times, the rate constant is then given by the slope of this curve (see Figure 8).

EXPERIMENTAL RESULTS

The values of the rate constants obtained by the above method are given in Table XV. The average values with the standard deviation, for the constants are summarized in Table XVI.

The slope of the line in Figure 8 is $\frac{k_p N}{4.606}$ Since N is assumed constant in the case of different monomers, comparison of the slopes of the lines for different monomers is proportional to a comparison of the k_p's.

Fig. 4 Determination of the rate constant for experiment number one on methyl methacrylate

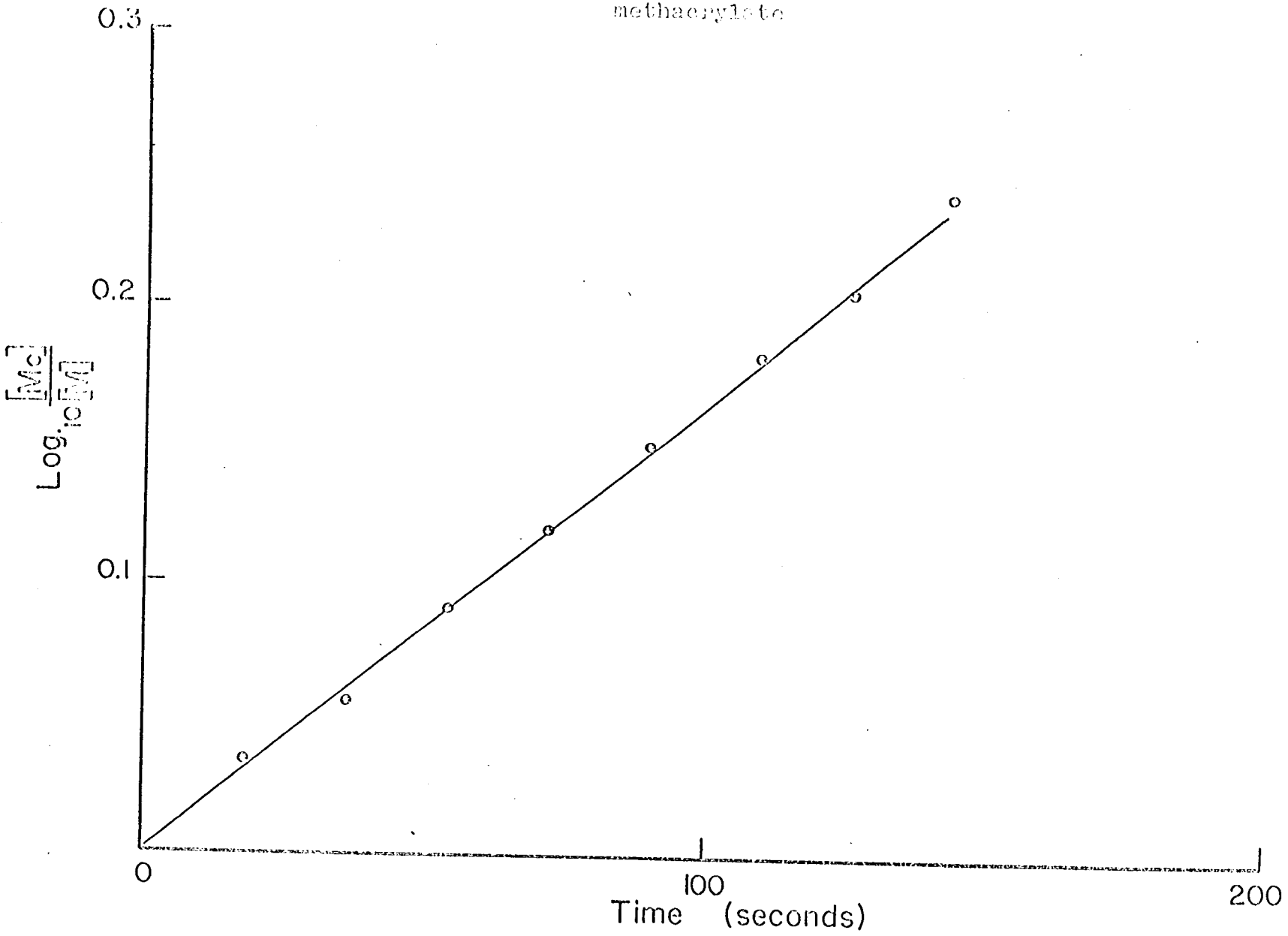


TABLE XV

Rate Constants from Thermal Data

Methacrylic acid		Methyl methacrylate		Ethyl methacrylate		Butyl methacrylate	
Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$
1	2.11	1	1.66	1	2.49	1	2.68
2	1.80	2	1.70	2	2.49	2	2.52
3	2.11	3	1.68	3	2.82	3	2.70
4	2.36	4	1.72	4	2.78	4	2.44
5	2.36	5	1.68	5	2.90	5	2.32
6	2.14	7	1.72	6	3.40	6	2.40
		8	1.68	7	3.04	7	2.44
		12	1.70	8	3.01	8	2.78
		13	1.67	9	3.60	9	2.78
		14	1.52			10	3.00
		15	1.60			11	2.90
						12	3.02

TABLE XV

Rate Constants from Thermal Data

Hexyl methacrylate		Acrylic acid		Methyl acrylate		Ethyl acrylate	
Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$
1	1.22	1	4.04	1	9.00	1	11.60
2	1.12	2	3.72	2	8.10	2	10.60
3	1.30	3	4.96	3	9.80	3	13.60
4	1.60	4	4.40	4	8.95	4	13.80
5	1.50	5	4.30	5	8.30	5	13.60
		6	3.70				

TABLE XV CONTINUED

Rate Constants from Thermal Data

Butyl acrylate		Hydroxyethyl methacrylate		2-Hydroxypropyl methacrylate	
Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$	Experiment number	$k_p \times 10^3$ sec.$^{-1}$
1	9.00	1	1.50	1	1.76
2	9.70	2	1.30	2	1.76
3	10.00	3	1.36	3	1.28
4	9.75	4	1.02	4	1.60
5	9.68	5	1.04	5	2.24
				6	1.60
				7	1.60

TABLE XVI

Summary of Rate Constants from Calorimetric Data T 25°C.

Monomer	Rate Constant x 10^3 $sec.^{-\frac{1}{2}}$
Methacrylic acid	2.15 ± 0.19
Methyl methacrylate	1.83 ± 0.14
Ethyl methacrylate	2.84 ± 0.28
Butyl methacrylate	2.66 ± 0.23
Hexyl methacrylate	1.35 ± 0.18
Acrylic acid	4.19 ± 0.43
Methyl acrylate	8.83 ± 0.60
Ethyl acrylate	12.64 ± 0.41
Butyl acrylate	9.62 ± 0.10
Hydroxyethyl methacrylate	1.24 ± 0.19
2-Hydroxypropyl methacrylate	1.97 ± 0.39

DISCUSSION

Comparison with Previous Results.

The rate constants available for the propagation step of polymerization from the literature are derived from bulk polymerization studies, and are not directly comparable to the present studies. However they do exhibit a maximum in the propagation rate constant between methyl and butyl methacrylate. The available data include 310 at 24°c for methyl methacrylate (83), 467 at 30°c for n-propyl methacrylate (84) and 362 at 30°c for n-butyl methacrylate (85) all in units of liters $mole^{-1}$ sec^{-1}.

For the acrylates, only values of 720 liters $mole^{-1}$ sec^{-1} at 30°Cfor methyl acrylate (86) and 13 liters $mole^{-1}$ sec^{-1} at 25°Cfor butyl acrylate (87) have been reported. These are also rate constants for the propagation step in bulk polymerizations. In our studies the rate constant for propagation is lower for methyl than for butyl acrylate. This is in contrast to the values mentioned above. However, it should be pointed out that in bulk polymerization of methyl acrylate the high value for the propagation rate constant may be due to auto-acceleration(88).

In order to compare our first order rate constant to a second order rate constant of simillar units to the values mentioned above we must assume [N] is of the order

of 10^{15}-10^{-16} molecules per cc. This is in the proper range for $[N]$ found by other investigations (68,69,70,71,72,74).

Interpretation of the Results

From Table XVI it can be observed that propagation rate constants of the acrylate esters are consistently higher than those of the corresponding methacrylate esters. There is considerably less steric hindrance to polymerization in the case of the acrylates (mono-substituted ethylenes) than in the methacrylates (di-substituted ethylenes). This has been shown in Part I, where the heats of polymerization of the acrylates are considerably higher than those of the methacrylates. Since there is less steric hindrance in the polymers of the acrylates than that in the methacrylates, one would indeed expect their rates of propagation to be higher than those of the methacrylates.

In the acrylate series, the rate propagation constants increase from acrylic acid to methyl acrylate through ethyl acrylate, but then decrease to butyl acrylate, similar behavior is also exhibited by the methacrylates. The rate constants for methacrylic acid and methyl methacrylate seem to show a deviation from this, but the values for the rate constants are within experimental error of one another. The decrease in rate of polymerization from ethyl to butyl to hexyl methacrylate is similar to the observed decrease in rates observed on going from ethyl to butyl acrylate.

The rates of polymerization show an increase in the rate of propagation on proceeding from methyl to ethyl esters of the monomers. The electron donating power of the ethyl group is greater than that of the methyl group; this seems to be responsible for the increase in k_p. Increased steric hindrance on proceeding from methyl to the ethyl ester must be less important than the electron donating power.

The k_p's for the butyl esters are lower than those of the ethyl esters. The effect of the electron-donating power on the double bond would be similar with both ethyl and butyl since the electrons must be shifted along a considerably longer chain in the butyl ester; steric effects now become the determining factor on the k_p's, and the k_p's decrease.

This is carried through to the hexyl esters where the electron donating power is approximately the same as with the ethyl and butyl esters, but where the increased steric hindrance causes the k_p's to decrease with increasing length of the alkyl ester chain. This tendency is exhibited in both the acrylate and methacrylate monomers.

Hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate both exhibit low rates of polymerization. This is further confirmation of the explanation, given in Part I, for the low heats of polymerization of these two monomers. If, on polymerization these monomers must lose part of the

solvation shell about the hydroxyl group, this would be a slow step in their polymerization and would be reflected in low rate constants.

PART III

HEATS OF VAPORIZATION

INTRODUCTION

A phase change such as the vaporization of a liquid is invariably associated with a change in heat content. Such a heat change is referred to as the "latent heat" of vaporization. This latent heat of vaporization represents the difference in heat contents of one gram or one mole of the two phases under consideration at the temperature and pressure at which the vaporization takes place.

A considerable amount of experimental work has been done on heats of combustion of compounds in the liquid and solid states, but relatively little work has been done on heats of vaporization. Such heats are required for the conversion of heats for the liquid state into heats relating to the gaseous state.

As a rule heat of vaporization data must be obtained indirectly from vapor pressure measurements by application of the Clausius-Clapeyron equation or application of simple empirical rules. Numerous empirical rules have been developed for approximating heat of vaporization data (89), but few are reliable.

Several types of calorimeters have been described (90), for the measurement of heats of vaporization. The calorimeters used are often similar to those used for determining heat capacities, the important modification being a method of measuring the amount of material vaporized. Most calorimeters operate at a temperature other than 25°C., and therefore the heats of vaporization obtained must be recalculated to 25°C. to be of the most use. Unfortunately these temperature corrections, when applied to heats of vaporization, reduce the accuracy of the calorimetric measurements.

It was decided to adapt the Calvet microcalorimeter for the direct measurement of heats of vaporization at 25°C. It was considered of particular interest to attempt to interpret the heats of vaporization in terms of additivity schemes, such as the one previously developed by Laidler (91).

EXPERIMENTAL

Materials

The alcohols used were Fisher certified reagents. They were dried by refluxing over freshly ignited calcium oxide for 4 hours, followed by fractionation through a 40-cm column packed with short lengths of 4-mm glass tubing. Only the middle fractions were retained.

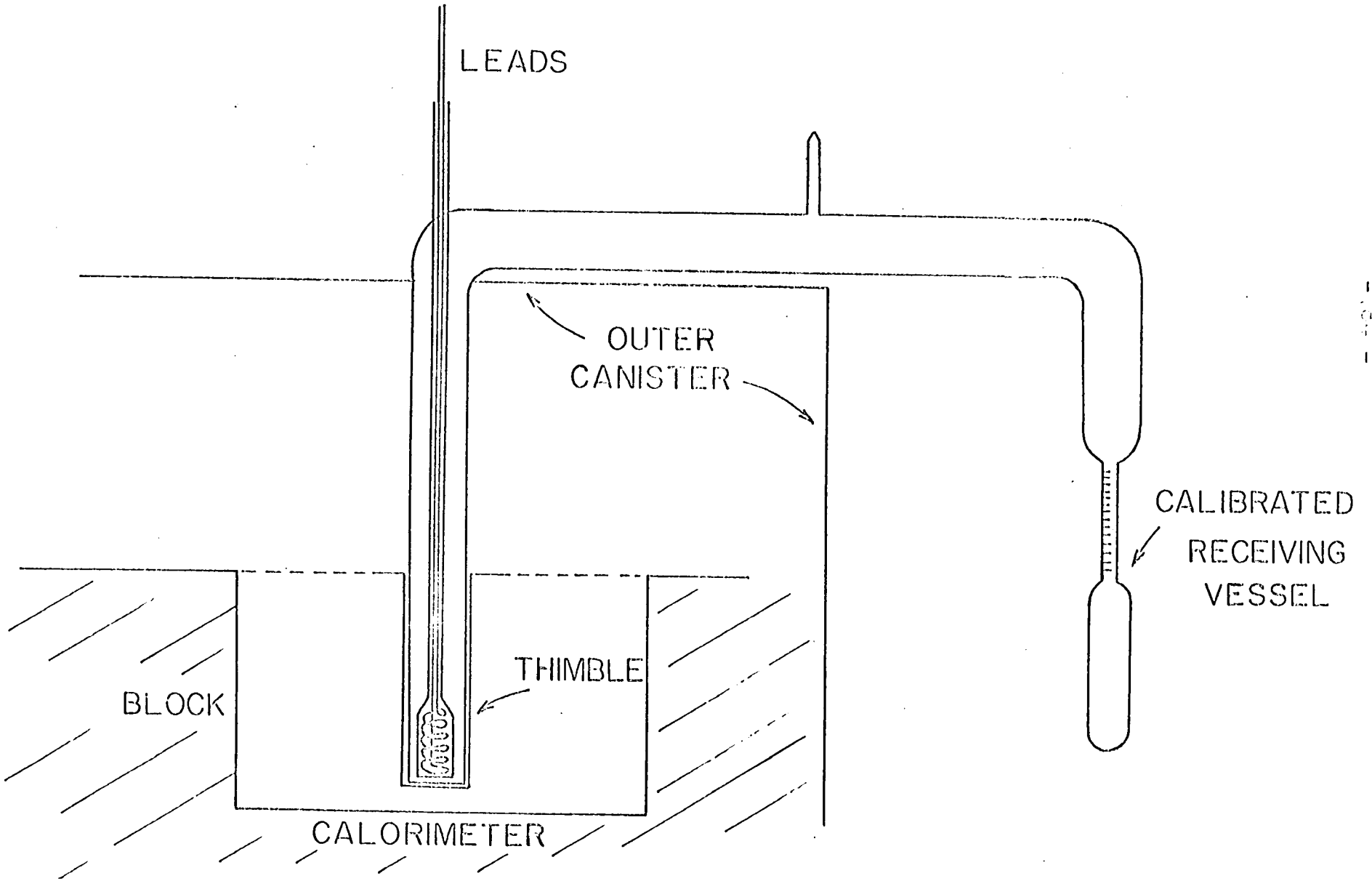
Calorimeter

The heats of vaporization were measured at 25°C using a differential microcalorimeter of the Calvet type as described in Part I. The apparatus for carrying out the vaporization, shown in Figure 1, consists of a U-tube which contains the purified alcohol. This tube, after being loaded with the appropriate amount of alcohol, was sealed directly to a vacuum line. It was then subjected to freeze drying to remove air that had become dissolved during loading. The U-tube was then evacuated to a pressure of approximately 0.5 mm, with the alcohol frozen in liquid air. The U-tube was then sealed off from the vacuum line by collapsing the walls of the tube.

The receiver consisted of a calibrated glass bulb of approximately 5-ml capacity connected to the U-tube by means of a calibrated capillary tube. The U-tube was placed in the calorimeter, and when it and the calorimeter had attained thermal equilibrium the distillation was started by raising a Dewar vessel of coolant on the receiving end of the U-tube. This was done by means of a raising and lowering device controlled from the exterior of the calorimeter cabin. The coolant consisted of liquid air, dry ice-acetone, or iced water, according to circumstances.

The heat required to cause vaporization was compensated for by the application of [illegible] to introduce [illegible] in the calorimeter [illegible]

Figure 9 Schematic diagram of the apparatus used in the measurement of heats of vaporization



timing device was used to record the duration of the passage of the current; the current was passed for 100 to 200 minutes, depending on the vapor pressure and the coolant. It was possible, by means of the elevating device, to control the rate of evaporation so that it would closely match the rate of heat delivered by the coil; in this way the amount of heat measured in the calorimeter was kept to a minimum, and the accuracy of the measurements was thereby greatly increased. The rates of evaporation ranged from about 2×10^{-4} mole/min to 5×10^{-4} mole/min.

When sufficient alcohol had been vaporized, so that the surface of the liquid was in the calibrated capillary tube, the coolant was lowered sufficiently to stop vaporization but only to such an extent that the alcohol in the receiver did not distill back into the U-tube. The heater was then turned off and the calorimeter allowed to come back to thermal equilibrium. During this period part of the alcohol in the calorimeter was vaporized, with the result that the conditions in the U-tube were the same as the initial conditions. The coolant was then lowered and the alcohol in the receiver allowed to return to 25°C; this was done in the thermostatted cabin, the temperature of which was controlled to 0.1°C. The volume was then recorded, and from a knowledge of its density it was then possible to calculate the weight of alcohol distilled.

The conditions were always adjusted so that there was a positive amount of heat evolved, indicated by a positive area

on the record. This area was reproduced by passing an electric current through the resistance in the cell for a known period of time. This excess heat was usually less than 1% of the total heat absorbed in the vaporization process.

Experiments with the U-tube empty and evacuated showed that there was negligible conduction of heat along the U-tube when the coolant was placed around the receiver. Experiments in which the amount of alcohol in the U-tube was varied showed no effect on the calculated heat of vaporization, indicating that there was negligible heat loss from the tube. Experiments in which the rate of vaporization was varied, using a different coolant and varying the potential across the resistance, gave results in good agreement with one another. This indicates negligible entrainment of liquid during the vaporization.

RESULTS

The results for each experiment are presented in Table XVII, and the results are summarized in Table XVIII. An estimate of the overall accuracy of the heat determinations may be arrived at as follows. The error in the measurement of time can be ignored as being much smaller (1 in 10,000) than the other errors. An average current was 0.0750 amp, and the uncertainty in this is 0.0001 amp. The total resistance was 73.675 ohms, and the uncertainty in this is about 0.010 ohms.

TABLE XVII

Heats of Vaporization of Aliphatic Alcohols at 25°C.

Experiment number	Moles vaporized	Heat required for vaporization Calories	Heat of vaporization Calories per mole
	CH_3OH Density 0.7866 gm. per ml. 25°C (100)		
1	0.1344	1208.7	8,990
2	0.1287	1160.8	9,020
3	0.1284	1157.8	9,020
	Mean 9,010 ± 13		
	C_2H_5OH Density 0.7851 gm. per ml. 25°C (100)		
1	0.0902	911.1	10,100
2	0.0908	914.5	10,070
3	0.0894	903.2	10.100
	Mean 10,090 ± 13		
	$n\text{-}C_3H_7OH$ Density 0.8001 gm. per ml. 25° (100)		
1	0.0730	812.4	11,130
2	0.0704	785.3	11,150
3	0.0703	781.7	11,120
	Mean 11,130 ± 10		

TABLE XVII CONTINUED

$(CH_3)_2CHOH$ Density 0.7810 gm. per ml. 25°C (100)

1	0.0700	735.1	10,500
2	0.0675	710.8	10,530
3	0.0683	719.2	10,530

Mean 10,520 ± 13

$CH_3(CH_2)_3OH$ Density 0.8059 gm. per ml. 25°C (100)

1	0.0581	707.7	12,180
2	0.0575	701.4	12,200
3	0.0575	701.2	12,190

Mean 12,190 ± 13

$(CH_3)_2CHCH_2OH$ Density 0.7979 gm. per ml. 25°C (100)

1	0.0558	664.3	11,910
2	0.0601	714.9	11,900
3	0.0589	700.8	11,900
4	0.0568	677.0	11,920

Mean 11,910 ± 9

TABLE XVII CONTINUED

$CH_3CH_2(CH_3)CHOH$ Density 0.8025 gm. per ml. 25°C (100)

1	0.0605	700.1	11,570
2	0.0575	664.8	11,560
3	0.0593	689.6	11,630
4	0.0581	673.6	11,590

Mean 11,590 ± 27

$(CH_3)_3COH$ Density 0.7810 gm. per ml. 25°C (100)

1	0.0565	606.2	10,730
2	0.0566	604.1	10,670
3	0.0560	599.8	10,710
4	0.0570	612.8	10,750

Mean 10,720 ± 30

$(CH_3)_2CH(CH_2)_2OH$ Density 0.8054 gm. per ml. 25°C (100)

1	0.0479	622.0	12,990
2	0.0475	616.1	12,970

Mean 12,980 ± 10

TABLE XVII CONTINUED

$CH_3CH_2(CH_3)CHCH_2OH$ Density 0.8110 gm. per ml. 25°C (100)

1	0.0494	639.2	12,940
2	0.0495	638.7	12,900

Mean 12,920 ± 20

$CH_3(CH_2)_2(CH_3)CHOH$ Density 0.8052 gm. per ml. 25°C (100)

1	0.0521	659.7	12,660
2	0.0488	618.8	12,680

Mean 12,670±10

$(CH_3CH_2)_2CHOH$ Density 0.8150 gm. per ml. 25°C (100)

1	0.0489	619.2	12,660
2	0.0499	630.7	12,640
3	0.0487	616.1	12,650

Mean 12,650 ± 8

TABLE XVII CONTINUED

$(CH_3)_2CH(CH_3)CHOH$ Density 0.8150 gm. per ml. 25°C (100)

1	0.0542	668.8	12,340
2	0.0610	752.1	12,330
3	0.0523	647.0	12,370

Mean 12,350 ± 17

$CH_3CH_2(CH_3)_2COH$ Density 0.8069 gm.per ml. 25°C (100)

1	0.0501	589.0	11,760
2	0.0494	579.8	11,740
3	0.0497	584.1	11,750

Mean 11,750 ± 8

TABLE XVIII

Summary of Experimental Heats of Vaporization and the Calculated Heats of Vaporization by the Additivity Scheme

Compound	Bonds	Heats of Vaporization Kilocalories per mole Calculated	Experimental
CH_3OH	$3P+A^1$	9.01	9.01±.13
CH_3CH_2OH	$3P+2S+A^1$	10.07	10.09±.13
$CH_3CH_2CH_2OH$	$3P+4S+A^1$	11.13	11.13±.10
$(CH_3)_2CHOH$	$6P+T+A^2$	10.53	10.52±.13
$CH_3(CH_2)_3OH$	$3P+6S+A^1$	12.19	12.19±.13
$(CH_3)_2CHCH_2OH$	$6P+2S+T+A^1$	11.89	11.91±.09
$CH_3CH_2(CH_3)CHOH$	$6P+2S+T+A^2$	11.59	11.59±.27
$(CH_3)_3COH$	$9P+A^3$	10.71	10.72±.30
$(CH_3)_2CH(CH_2)_2OH$	$6P+4S+T+A^1$	12.95	12.98±.10
$CH_3CH_2(CH_3)CHCH_2OH$	$6P+4S+T+A^1$	12.95	12.92±.20
$CH_3(CH_2)_2(CH_3)CHOH$	$6P+4S+T+A^2$	12.65	12.67±.10
$(CH_3CH_2)_2CHOH$	$6P+4S+T+A^2$	12.65	12.65±.08
$(CH_3)_2CH(CH_3)CHOH$	$9P+2T+A^2$	12.35	12.35±.17
$CH_3CH_2(CH_3)_2COH$	$9P+2S+A^3$	11.76	11.75±.08

These figures lead to an uncertainty of 2.9 cal in the electrical heat, or of 0.3%. The volume vaporized was approximately 5 ml, and the uncertainty 0.01 ml or 0.2%. The heat of vaporization per mole is the ratio of a measured heat to the volume, and this leads to an overall uncertainty of 0.5%.

The calculated heats of vaporization were obtained by the use of an additivity scheme of the same kind as previously given (91) for heats of formation. The contributions for the various bonds, obtained on the IBM 650 computer by the method of least squares, are as follows:

P	(primary C H bond)	606 cal/mole
S	(secondary C H bond)	530 cal/mole
T	(tertiary C H bond)	0 cal/mole
A^1	(C O H, in which C is primary)	7196 cal/mole
A^2	(C O H, in which C is secondary)	6894 cal/mole
A^3	(C.O H, in which C is tertiary)	5250 cal/mole

There is no contribution for a C-C bond.

DISCUSSION

The standard deviations of the experimental heats of vaporization are in all cases less than 0.3%, and in most cases are 0.1 to 0.2%. The technique employed therefore seems to provide a very reliable method of measuring the heats of vaporization.

The values obtained for methanol, ethanol, and n-propanol may be compared with the values given by Green (92) which are 9,070 ± 10, 10,180 ± 20, and 11,360 ± 10 cal/mole respectively. For higher members of this straight-chain series of aliphatic alcohols Green suggests the same increment per CH_2 unit for the heat of vaporization as is found per CH_2 unit in the straight-chain aliphatic hydrocarbon series. This value is 1200 ± 50 cal/mole per CH_2 unit; our value for the CH_2 unit increment is 1060 cal/mole.

Parks and Barton (93) obtained values for the heats of vaporization of i-propyl alcohol and t-butyl alcohol at 25°C from vapor pressure measurements; application of the Clausius-Clapeyron equation gives the values 10,600 ± 150 and 10,900 ± 200 cal/mole respectively, in good agreement with our experimental values.

Two methods most frequently employed in the calculation of the heat of vaporization at one temperature from the heat of vaporization at another temperature are due to Su (94) and Watson (95). These two methods have been applied to the data of Mathews (96), Ingle and Cody (97), Williamson and Harrison (98), and Weltner and Pitzer (99); the critical constants from the "International Critical Tables" (100) were used. The resulting values for the heats of vaporization at 25°C are shown in Tables XIX and XX.

TABLE XIX

Calculated Heats of Vaporization at 25°C (Cal. per mole)

Data of:	Mathews		Cody	
Method of:	Su	Watson	Su	Watson
CH_3OH	9,070	9,100	9,310	9,350
C_2H_5OH	10,240	10,310	10,510	10,590
$n\text{-}C_3H_7OH$	-	-	11,220	11,330
$i\text{-}C_3H_7OH$	10,700	10,770	10,490	10,550
$n\text{-}C_4H_9OH$	12,130	12,340	11,970	12,180
$i\text{-}C_4H_9OH$	11,780	12,020	-	-
$s\text{-}C_4H_9OH$	11,290	11,490	-	-

TABLE XX

Calculated Heats of Vaporization at 25°C (Calories per mole)

Temperature of measurement	Calculated values at 25°C Su	Watson
Data of Weltner and Pitzer (99) for methanol		
40	8,970	9,010
55	8,980	9,090
65	9,080	9,130
Data of Williamson and Harrison (98) for n-propanol		
60	11,310	11,420
73	11,310	11,390
81	11,300	11,420
Data of Williamson and Harrison (98) for i-propanol		
51	10,800	10,810
70	10,790	10,840
80	10,690	10,380

Pitzer and Williamson have determined the heats of vaporization of certain aliphatic alcohols at several temperatures. Results of the application of the method of Su and Watson to their data are given in Table XX.

For the lower-boiling aliphatic alcohols both temperature-dependent relationships predict heats of vaporization which are too high. The data of Pitzer lead to a value in better agreement with our value when the temperature of the measurement is closer to 25°C, that is, when the amount of correction is small. This is not the case with the data of Williamson and Harrison, where the predicted heat of vaporization is too high for both n-propyl and i-propyl alcohol, and the predicted value at 25°C is independent of the temperature of the measurement. For the higher-boiling alcohols both approximation methods give values that are too low. Adjustment of the exponent in Watson's equation allows one to fit different members of the series, but one cannot predict the heats of vaporization of a number of aliphatic alcohols using a constant exponent.

The agreement between our observed and calculated heats is very satisfactory, and is usually well within the standard deviation. This can be taken as confirming the accuracy of the measurements, and shows that the additivity scheme is as good as can be developed on the basis of the present experimental results.

Strictly speaking, an additivity scheme in terms of atoms or groups, rather than of bonds, would be preferable in the case of heats of vaporization. Simple atom schemes can, however, be shown to be equivalent to bond schemes. The use of the present bond scheme has the practical advantage that it is equivalent to the scheme used for heats of formation (91), so that gases and liquids can be treated in a uniform manner.

PART IV

ADDITIVITY

INTRODUCTION

The properties of chemical substances are conveniently classified as:

1) Colligative

2) Additive

3) Constitutive

The colligative properties, such as osmotic pressure and freezing point depression, are those that depend only on the number of molecules and not at all on their nature. The additive properties are those that depend only on the atoms or chemical bonds present in the molecule; strictly speaking, the only additive property is the molecular weight. Constitutive properties are those that depend not only on the number of atoms but on the way they are arranged in the molecule.

There are many properties, such as heat of formation and molar refraction, that show a certain degree of additivity but which also show constitutive effects. To a first approximation one can predict these properties on the basis of a pure additivity scheme, but if more accurate

predictions are required, account must be taken of the constitutive effects. It has become the practice to refer to these properties as additive even though they are not strictly so.

Experimental determination of all the physio-chemical properties of isomers of alkanes of practical interest would be a huge task, demanding a large expenditure in capital and time. Naturally, therefore, a great interest is taken in the development of theoretical, semi-empirical or even purely empirical methods of calculating the physico-chemical properties of alkanes and especially of the higher alkanes.

Rossini and his co-workers (101, 102) developed linear relationships between the heat of combustion of the n-alkanes and the number of carbon atoms. The linear variations were made a little more accurate (103) by the introduction of a small quadratic term.

Ewell (104) proposed that the heats of combustion of alkanes of branched structure are subject to an empirical law, based on the fact that each simple branching of the chain (producing a tertiary atom) changes its heat of combustion, as compared to the normal structure, by 1.8 kilo calories/mole. A complex branching (producing a quaternary C atom) changed the heat of combustion by 4.7 kilo calories/mole compared to a chain of the normal

structure. These changes were supposedly independent of the number or the relative position of the branches. This empirical rule met with limited success. Ewell also put forth an approximate empirical rule concerning the variation of the entropy of the alkane with the number of simple and complex branchings.

Other investigators studied other properties of the alkanes with respect to their structures and gave a series of empirical equations (105,106,107,108,109) for calculation of these properties.

Bernstein (110) set up a scheme for calculation of the energy of formation of the hydrocarbons and obtained interesting results, but the scheme is extremely unwieldly.

Tatevskii (111) proposed a scheme similar to that of Bernstein but which was more conveniently employed.

Laidler (91) proposed a scheme in which a fewer number of terms were used to express the structure of the molecule, and the calculated values compared reasonably well with experimental quantities.

A fuller survey of the fundamental methods of calculation of physico-chemical properties is given by Tatevskii (111). A comparison and an analysis of the discrepancies between the different methods is given along with an analysis of the theoretical questions concerned.

THE EMPIRICAL SCHEME

The scheme proposed here is closely related to that of Tatevskii, Bendarskii and Yarovoi (112). We define three types of carbon-hydrogen bonds P, S, and T, according to the number of other carbon atoms to which the carbon atom of the bond is attached.

For the saturated hydrocarbons we define six types of carbon-carbon (C-C) bonds, depending on the number of carbons attached to the two carbons involved in any such C-C bond. Table XXI gives a pictorial description of the bonds. In any type of compound the same terminology is used for C-H bonds, but new definitions are included for other functional groups.

The properties treated, all related to 25°C, include: molar volume, molar refraction, entropy of formation and heat of atomization. The hydrocarbon families to which the treatment has been applied include: saturated hydrocarbons, olefines, dienes and cyclic hydrocarbons.

Molar sound velocity and diamagnetic susceptibility are two other properties treated for the following families of compounds: saturated hydrocarbons, olefins, aromatics, aldehydes, ketones, alcohols, esters, and chloro derivatives. Alkynes have also been treated for molar sound velocity, but olefins and aldehydes have not been treated for this property because of the lack of experimental data.

TABLE XXI

Pictorial Description of the Bonds Involved in the Additivity Scheme

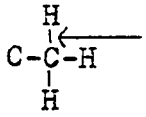
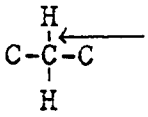
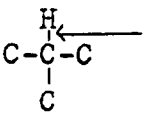
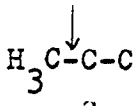
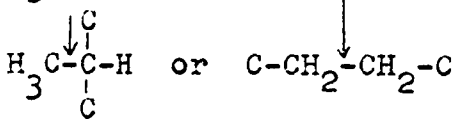
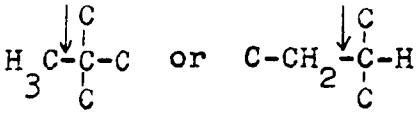
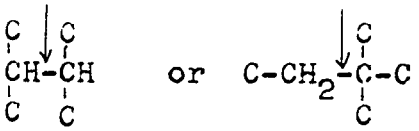
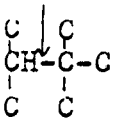
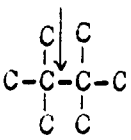
Bond	Symbol
Saturated Hydrocarbons	
C-H Bonds	
	P
	S
	T
C-C Bonds	
	C^1
	C^2
	C^3
	C^4
	C^5
	C^6

TABLE XXI CONTINUED

Olefines

C-C Bonds

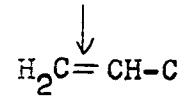
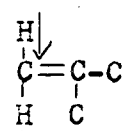
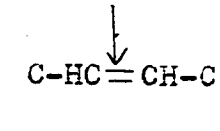
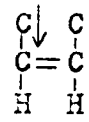
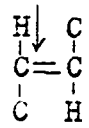
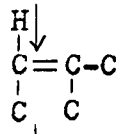
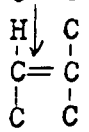
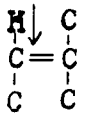
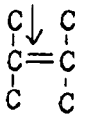
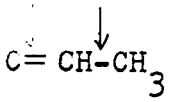
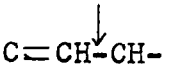
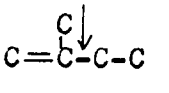
			C_2^1
	or		C_2^{2a}
	cis		C_2^{2b}
	trans		C_2^{2c}
			C_2^{3a}
	cis		C_2^{3b}
	trans		C_2^{3c}
			C_2^4
			$^2C_1^0$
			$^2C_1^1$
			$^2C_1^2$

TABLE XXI CONTINUED

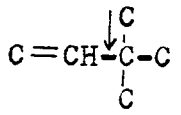
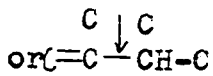
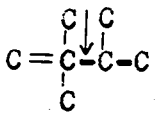
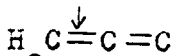
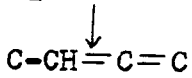
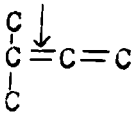
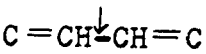
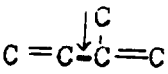
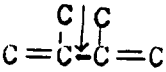
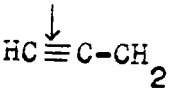
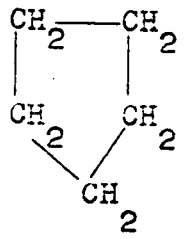
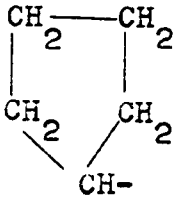
	or 	$_{2}C^{3}_{1}$
		$_{2}C^{4}_{1}$
Dienes		
		$_{2}C^{0}_{2}$
		$_{2}C^{1}_{2}$
		$_{2}C^{2}_{2}$
		$_{22}C^{0}_{1}$
		$_{22}C^{1}_{1}$
		$_{22}C^{2}_{1}$
Alkynes		
		C_{3}
		$_{3}C^{1}_{1}$

TABLE XXI CONTINUED

Cyclic Hydrocarbons



$^{0}_{0}5$



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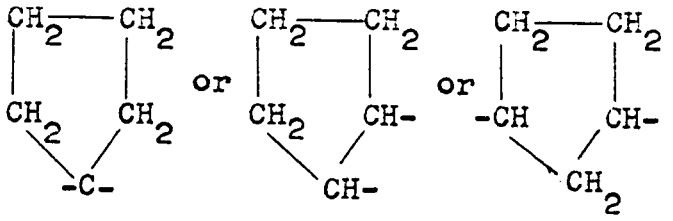
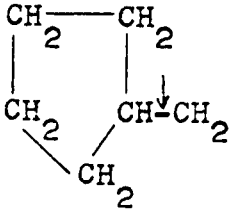
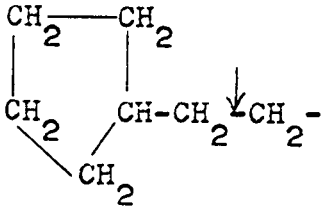


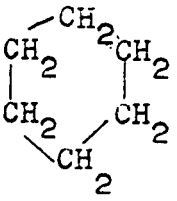
$^{2}_{0}5$



$^{1}_{c}5$

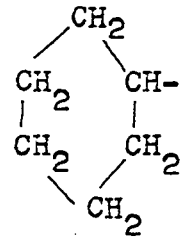


$^{2}_{c}5$

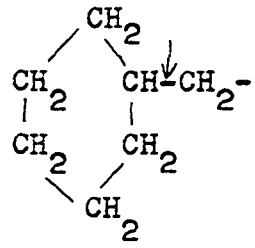


$^{0}_{0}6$

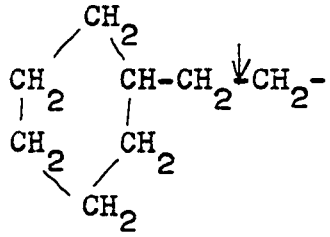
TABLE XXI CONTINUED



1_o6

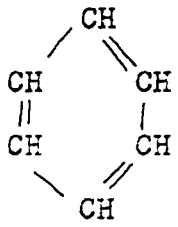


1_c6

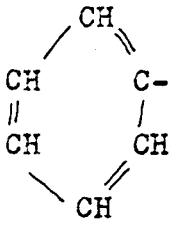


2_c6

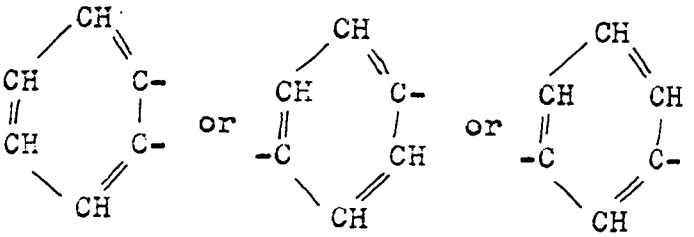
Aromatics



φ

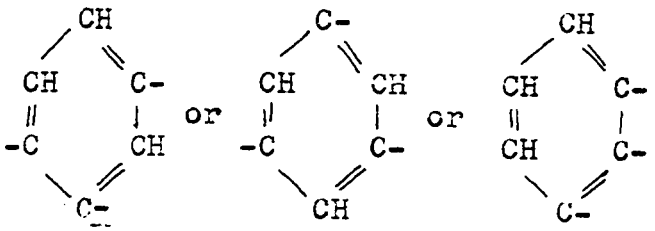


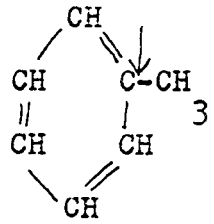
φ'

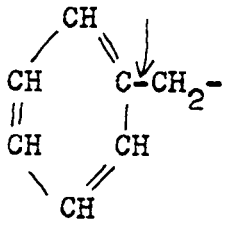


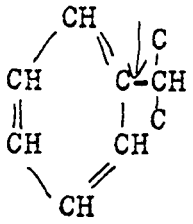
φ^2

TABLE XXI CONTINUED

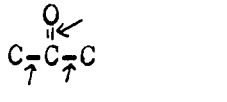
 φ^3

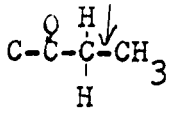
 $\varphi_{C_1^0}$

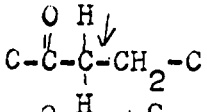
 $\varphi_{C_1^1}$

 $\varphi_{C_1^2}$

Ketones

 K

 $K_{C_1^0}$

 $K_{C_1^1}$

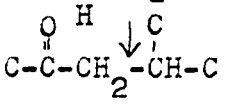
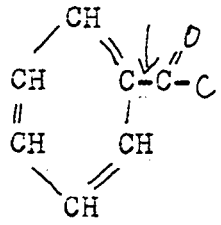
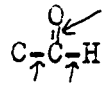
 $K_{C_1^2}$

TABLE XXI CONTINUED

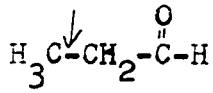


φC_1^K

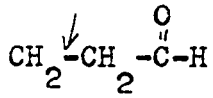
Aldehydes



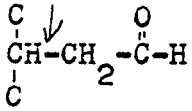
A1



C_1^{OA1}

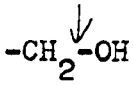


C_1^{1A1}

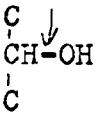


C_1^{2A1}

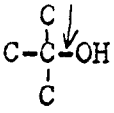
Alcohols



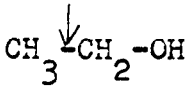
A^1



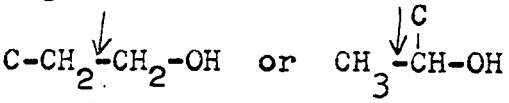
A^2



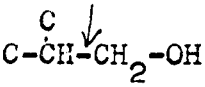
A^3



$A C_1^0$

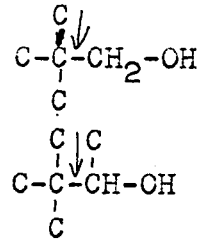


$A C_1^1$



$A C_1^2$

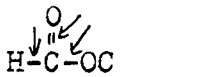
TABLE XXI CONTINUED



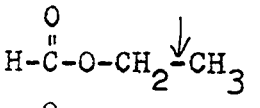
$A_{C_1^3}$

$A_{C_1^4}$

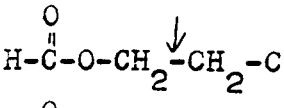
Formates



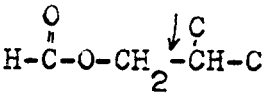
F



$F_{C_1^0}$

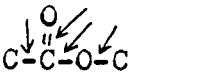


$F_{C_1^1}$

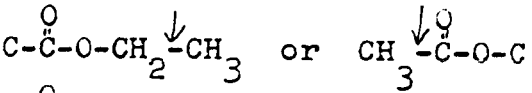


$F_{C_1^2}$

Esters



E



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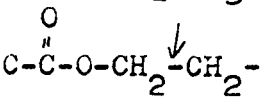
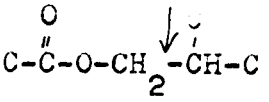
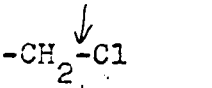


$E_{C_1^1}$

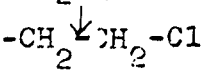


$E_{C_1^2}$

Chloro Derivatives

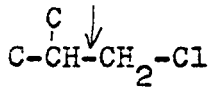


Cl

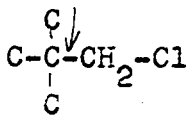


C_1^{Cl}

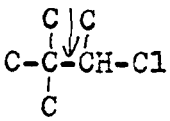
TABLE XXI CONTINUED



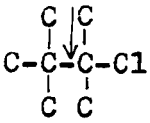
C_1^{2Cl}



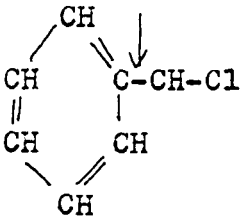
C_1^{3Cl}



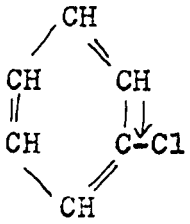
C_1^{4Cl}



C_1^{5Cl}



$\phi_{C_1}^{Cl}$



ϕ_{Cl}

PHYSICO CHEMICAL PROPERTIES TREATED

Molar Volumes

According to Glasstone (113a), Kopp (1855) was the first to discover that the molar volume was an additive property. The molar volume is equal to the product of the molecular weights M, and the specific volume v; the latter is equal to the reciprocal of the density d, and so it follows that:

$$\text{Molar volume} = Mv = \frac{M}{d}$$

If the molar volumes of isomeric compounds of similar constitution or compared at their respective boiling points the values are found to be almost identical. Also in a homolgous series of organic compounds, a constant difference of about 22.2 cc (113a) is found in the molar volume at the boiling points for each additional CH_2 group.

Molar Refraction:

The property of molar refraction is characteristic of both gaseous and liquid states, but it is usually measured on the liquid. When light passes from one medium to another, it almost invariably suffers refraction.

Theoretical work of Lorentz (113b) indicated that the molar refraction of a compound could be expressed as

$$M.R. = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$$

where M is the molecular weight, d is the density, n is the

refractive index and (M.R.) is the molar refraction. The presence of the factor $\frac{M}{d}$ shows that the molar refraction is a type of molar volume. Molar refraction exhibits additive and constitutive properties.

Entropy of Formation

Entropy of formation has been fitted by a number of empirical schemes (114,115) with varying degrees of success.

it is important to realize that both elements and compounds have entropies which are greater than zero at 298°K, and that the absolute entropy of a compound is not its entropy of formation from its elements. The entropy of formation of a compound is calculated by

$$\Delta S_f^\circ = S^\circ(\text{compound}) - S^\circ(\text{elements})$$

where the quantities on the right hand side of the equation are absolute entropies.

Heats of Combustion, Formation and Atomization

The heat of atomization, Q_a, used here can be defined as the energy required to dissociate one mole of a compound in the gaseous state at 25°C into its constituent atoms in their ground state at 25°C. Thermochemical data is generally given in terms of heats of formation, Q_f, which are the heats liberated when one mole of the substance is

produced from the elements in their standard states of gaseous hydrogen, oxygen and nitrogen, and carbon in the form of graphite. The data available at 25°C are considerably more abundant than any other temperature. Values at 25°C, therefore, are selected for the determination of the parameters for the additivity scheme. The calculation of heats of atomization from heats of formation, requires a knowledge of the heats of atomization of the relevant elements in standard states.

Considerable controversy has been associated with the heats of atomization of carbon. Cottrell (116) in a review of the subject, supports the value of 170 kcal./mole; the JANAF tables (117) gives a value of 170.89 kcal./mole, which has been used here.

Spectroscopic studies have established unequivocally the value for the heat of atomization of hydrogen.

The heats of atomization of hydrogen and carbon at 25°C. are as follows:

$$C \text{ (graphite)} = C\ (g, {}^3p) - 170.89 \text{ kcal.}$$

$$\tfrac{1}{2}H_2(g) = H(g) - 52.10 \text{ kcal.}$$

It is common practice in thermochemistry to associate a negative sign with exothermic processes. Here the usual procedure is reversed to avoid dealing with negative numbers; heats of combustion in this part are given with positive signs.

From the heat of atomization data given above, it is obvious that the heat of atomization, Q_a, is related to the heat of formation, Q_f, by the following equation:

$$Q_a = Q_f + 170.89\ n_C + 52.10\ n_H \qquad (1)$$

Here n_C and n_H are the numbers of atoms of carbon and hydrogen respectively. If the products of combustion of compounds of carbon and hydrogen are carbon dioxide and water, then the heat of formation is related to the heat of combustion, Q_c, by the following equation:

$$Q_f = Q_c + 94.05\ n_C + 34.16\ n_H \qquad (2)$$

This relationship is based upon the heat of formation values for carbon dioxide and liquid water of 94.05 and 68.32 $kcal.mole^{-1}$ respectively (118).

Substitution of equation (2) into equation (1) gives the following relationship between the heat of combustion and the heat of atomization at 25°C.:

$$Q_a = -Q_c + 264.94\ n_C + 86.26 n_H \qquad (3)$$

In view of the relationship between heats of combustion, formation and atomization it is necessary to devise a scheme for only one of the quantities. Here the quantity chosen is the heat of atomization.

Diamagnetic Susceptibility

Diamagnetic susceptibility arises from the fact that an electron in an orbital produces a magnetic field; the application of an external magnetic field gives rise to a magnetic field which opposes the external field. The orbital

field is equivalent to that produced by an electron moving in a circular orbit. The gram atomic susceptibility can be shown to be:

$$\chi_A = \frac{Ne^2}{6mc^2} \sum_i \overline{r_i^2} = -(2.832 \times 10^{10}) \sum_i \overline{r_i^2}$$

where $\overline{r_i^2}$ is the mean square radius of the orbit of the i-th electron. Since radii are of the order of 10^{-8} cm., χ_A values are of the order of 10^{-6} cc. These values show that roughly speaking susceptibilities of atoms and ions fall in line with the radii.

On the basis of this type of explanation a certain amount of additivity in molecular susceptibilities is to be expected. This matter was originally treated by Pascal, empirical additive constants are usually known as the "Pascal constants". He showed that diamagnetic susceptibilities may be expressed as:

$$\chi_o = \sum_i n_i \chi_i + \sum_j \lambda_j$$

where n_1 is the number of atoms of the i-th kind, x_1 is the additive contribution for an atom of the i-th kind and is a correction factor for certain special structures such as double bonds, aromatic rings etc.

Molar Sound Velocity

A considerable number of measurements of ultrasonic sound velocity have been made in recent years, and attempts have been made to interpret the results in the light of

molecular structure. An important advance was made by Rao (119) who recognized the significance of the property $(\frac{M}{\rho})V^{1/3}$ where V is the ultrasonic velocity, M the molecular weight and ρ the density. He showed that this quantity, which is conveniently referred to as the molar sound velocity, can be expressed additively in terms of contributions for the atoms and types of bonds. Lagerman (120) proposed an alternative additivity scheme in terms of individual bond contributions. Another bond additivity scheme was proposed by Weissler (121). Various similar relationships have been suggested, such as that of Lagermann and Dunbar (122), who showed that molar sound velocity is a linear function of the parachor and the molar refraction, both of the latter properties being expressible in terms of atom and bond additivity schemes.

CALCULATIONS

Table XXII gives the contribution of each bond to the value of the properties discussed above. The contributions where determined by a least squares procedure on an I.B.M. 1620 Computer.

Table XXII gives the contribution of each defined bond to the value of the property of the molecule. Multiplication of each bond involved in a structure by its multiplicity and summation of these values, yields the predicted value of the property for the molecule.

Table XXIII gives a number of compounds a code number. Tables XXIV and XXV give the experimental and calculated values of the different properties, along with arithmetic difference between the experimental and calculated values. Table XX gives a comparison of experimental and calculated values for molar volume and molar refraction, while Table XXI gives a comparison of experimental and calculated values for entropies and heats of atomization.

Tables XXVI to XXXIX give a comparison of calculated and experimental data for a number of different families of compounds for the properties of diamagnetic susceptibility and molar sound velocity.

The source of experimental data for the properties of molar volume, molar refraction, entropy and heat of atomization was from a tabulation of Rossini et al (123)

The source of experimental data for molar sound velocity and diamagnetic susceptibility is indicated by a superscript after the value of the property quoted in the tables.

TABLE XXII

Bond Contributions to the Properties

Symbol	Property Contribution at 25°C			
	Molecular Volume ml/mole	Molecular Refraction ml/mole	Entropy cal/deg mole	Heat of Atomization kcal/mole
P	15.111	1.8529	12.871	98.013
S	15.971	1.9277	15.363	96.848
T	15.505	1.8697	18.301	95.196
C^1	-18.577	0.5946	-21.369	86.252
C^2	-16.184	0.7630	-21.469	86.388
C^3	-15.059	0.8437	-19.918	85.895
C^4	-16.537	0.7951	-19.062	84.693
C^5	-18.804	0.7123	-13.942	82.319
C^6	-22.768	0.4664	- 9.403	77.602
C_2^1	14.965	3.7478	-61.660	77.117
C_2^{2a}	21.428	3.5712	-111.442	2.148
C_2^{2b}	27.230	4.2721	-117.866	3.428
C_2^{2c}	27.927	4.3921	-119.116	4.428
C_2^{3a}	35.224	4.2502	-167.210	-72.209
C_2^{3b}	34.427	4.1329	-169.633	-72.469
C_2^{3c}	34.197	4.1230	-168.824	-72.469
C_2^4	40.714	4.0000	-220.000	-150.000
$^2C_1^0$	-28.176	0.5457	40.444	159.996
$^2C_1^1$	-25.534	0.8439	38.055	160.156

TABLE XXII CONTINUED

Symbol	Property Contributions at 25°C			
	Molecular Volume ml/mole	Molecular Refraction ml/mole	Entropy cal/deg mole	Heat of Atomization kcal/mole
$^{2}C_{1}^{2}$	-23.356	0.9894	38.089	159.926
$^{2}C_{1}^{3}$	-22.643	1.0115	39.528	159.115
$^{2}C_{1}^{4}$	-23.830	0.9409	-	156.676
$^{2}C_{2}^{0}$	2.240	3.850	1.855	119.000
$^{2}C_{2}^{1}$	17.539	4.530	-58.558	95.463
$^{2}C_{2}^{2}$	26.749	4.290	-109.517	19.184
$^{22}C_{1}^{0}$	-37.127	2.266	92.239	238.08
$^{22}C_{1}^{1}$	-35.442	2.312	92.121	237.11
$^{22}C_{1}^{2}$	-32.592	2.090	-	-
$^{0}C^{5}$	15.923	0.052	23.715	-6.51
$^{1}O^{5}$	19.370	0.258	27.134	-5.31
$^{2}O^{5}$	24.235	0.448	-	-
$^{1}C^{5}$	-17.370	0.633	-23.096	86.767
$^{2}C^{5}$	-15.464	0.786	-21.417	86.323
$^{0}O^{6}$	+14.192	0.907	15.738	-0.57
$^{1}O^{6}$	18.820	0.312	18.697	1.15
$^{1}C^{6}$	-18.257	0.574	-22.897	85.94
$^{2}C^{6}$	-15.425	0.789	-21.466	86.33

TABLE XXII CONTINUED

Symbol	Property Contributions at 25°C	
	Magnetic Susceptibility c.g.s. units x 10^6	Molar Sound Velocity $\frac{c.c.}{mole}\left(\frac{m.}{sec}\right)^{1/3}$
P	4.224	111.558
S	4.174	114.637
T	4.691	106.346
C^o	1.956	
C^1	2.991	-53.061
C^2	3.097	-42.335
C^3	3.188	-42.142
C^4	3.431	-49.874
C^5	4.587	-68.247
C_2^0	-4.696	-
C_2^1	4.000	-
C_2^2	4.604	-
C_2^3	5.648	-
C_2^4	1.700	-
$^2C_1^o$	1.789	-
$^2C_1^1$	2.128	-
$^2C_1^2$	1.766	-
$^2C_2^0$	5.331	-
$^2C_2^1$	5.398	-
C_3	-	236.88
$^3C_1^1$	-	-22.04

TABLE XXII CONTINUED

Symbol	Property Contributions at 25°C	
	Magnetic Susceptibility c.g.s. units x 10^6	Molar Sound Velocity $\frac{c.c.}{mole}(\frac{m}{sec})^{1/3}$
φ	26.704	339.2
φ^1	27.000	373.5
φ^2	28.116	400.8
φ^3	-	410.1
φ_1^0	2.433	-70.8
φ_1^1	3.227	-67.9
φ_1^2	3.101	-86.3
K	8.616	108.9
$K_{C_1}^0$	3.299	-44.7
$K_{C_1}^1$	3.722	-27.2
$K_{C_1}^2$	3.724	-56.9
$\varphi_{C_1}^K$	-	-4.2
A1	10.778	-
C_1^{OA1}	2.522	-
C_1^{1A1}	2.782	-
C_1^{2A1}	3.610	-
A^1	8.94	85.82
A^2	8.35	60.65
A^3	-	23.07
$A_{C_1}^0$	3.61	-26.88

TABLE XXII CONTINUED

Symbol	Property Contributions at 25°C	
	Magnetic Susceptibility c.g.s. units x 10^6	Molar Sound Velocity $\frac{c.c.}{mole}(\frac{m}{sec})^{1/3}$
$A_{C_1^1}$	3.78	-15.38
$A_{C_1^2}$	4.21	-14.17
$A_{C_1^3}$	4.10	-12.56
$A_{C_1^4}$	-	-17.11
F	18.23	-
$F_{C_1^0}$	3.24	-
$F_{C_1^1}$	3.83	-
$F_{C_1^2}$	4.01	-
E	16.91	169.6
$E_{C_1^0}$	3.41	-35.5
$E_{C_1^1}$	3.85	-24.4
$E_{C_1^2}$	4.40	-17.9
C1	21.293	174.8
C_1^{C1}	2.003	-5.4
C_1^{2C1}	2.508	42.9
C_1^{3C1}	3.218	-
C_1^{4C1}	-	197.2
C_1^{5C1}	-	278.7
$\phi_{C_1^{C1}}$	1.800	-
ϕ_{C1}	-	210.6

TABLE XXIII

Code Numbers and Bond Contributions Assigned to Molecules

Code Number	Molecule	Bond Symbols
1	n- propane	$6P+2S+2C^1$
2	n- butane	$6P+4S+2C^1+C^2$
3	n- pentane	$6P+6S+2C^1+2C^2$
4	n- hexane	$6P+8S+2C^1+3C^2$
5	n- heptane	$6P+10S+2C^1+4C^2$
6	n- octane	$6P+12S+2C^1+5C^2$
7	n- nonane	$6P+14S+2C^1+6C^2$
8	n- decane	$6P+16S+2C^1+7C^2$
9	n- undecane	$6P+18S+2C^1+8C^2$
10	n- dodecane	$6P+20S+2C^1+9C^2$
11	n- tridecane	$6P+22S+2C^1+10C^2$
12	2-methylpropane	$9P+T+3C^2$
13	2-methylbutane	$9P+2S+T+C^1+2C^2+C^3$
14	2,2-dimethyl-propane	$12P+4C^3$
15	2-methylpentane	$9P+4S+T+C^1+3C^2+C^3$
16	3-methylpentane	$9P+4S+T+2C^1+C^2+2C^3$
17	2,2-dimethyl-butane	$12P+2S+C^1+3C^3+C^4$
18	2,3-dimethyl-butane	$12P+2T+4C^2+C^4$
19	2-methylhexane	$9P+6S+T+C^1+4C^2+C^3$

TABLE XX111 CONTINUED

Code Number	Molecule	Bond Symbols
20	3-methylhexane	$9P+6S+T+2C^1+2C^2+2C^3$
21	3-ethylpentane	$9P+6S+T+3C^1+3C3$
22	2,2-dimethyl-pentane	$12P+4S+C^1+C^2+3C^3+C^4$
23	2,3-dimethyl-pentane	$12P+2S+2T+C^1+3C^2+C^3+C^4$
24	2,4-dimethyl-pentane	$12P+2S+2T+4C^2+2C^3$
25	3,3-dimethyl-pentane	$12P+4S+2C^1+2C^3+2C^4$
26	2,2,3-trimethyl-butane	$15P+T+2C2+3C^3+C^5$
27	2-methylheptane	$9P+8S+T+C^1+5C^2+C^3$
28	3-methylheptane	$9P+8S+T+2C^1+3C^2+2C^3$
29	4-methylheptane	$9P+8S+T+2C^1+3C^2+2C^3$
30	3-ethylhexane	$9P+8S+T+3C^1+C^2+3C^3$
31	2,2-dimethyl-hexane	$12P+6S+C^1+2C^2+3C^3+C^4$
32	2,3-dimethyl-hexane	$12P+4S+2T+C^1+4C^2+C^3+C^4$
33	2,4-dimethyl-hexane	$12P+4S+2T+C^1+3C^2+3C^3$
34	2,5-dimethyl-hexane	$12P+4S+2T+5C^2+2C^3$
35	3,3-dimethyl-hexane	$12P+6S+2C^1+C^2+2C^3+2C^4$
36	3,4-dimethyl-hexane	$12P+4S+2T+2C^1+2C^2+2C^3+C^4$

TABLE XX111 CONTINUED

Code Number	Molecule	Bond Symbols
37	2-methyl-3-ethyl-pentane	$12P+4S+2T+2C^1+2C^2+2C^3+C^4$
38	3-methyl-3-ethyl-pentane	$12P+6S+3C^1+C^3+3C^4$
39	2,2,3-trimethyl-pentane	$15P+2S+T+C^1+C^2+4C^3+C^5$
40	2,2,4-trimethyl-pentane	$15P+2S+T+2C^2+4C^3+C^4$
41	2,3,3-trimethyl-pentane	$15P+2S+T+C^1+2C^2+2C^3+C^4+C^5$
42	2,3,4-trimethyl-pentane	$15P+3T+5C^2+2C^4$
43	2-methyloctane	$9P+10S+T+C^1+6C^2+C^3$
44	3-methyloctane	$9P+10S+T+C^1+4C^2+2C^3$
45	4-methyloctane	$9P+10S+T+2C^1+4C^2+2C^3$
46	3-ethylheptane	$9P+10S+T+3C^1+2C^2+3C^3$
47	4-ethylheptane	$9P+10S+T+3C^1+2C^2+3C^3$
48	2,2-dimethyl-heptane	$12P+8S+C^1+3C^2+3C^3+C^4$
49	2,3-dimethyl-heptane	$12P+6S+2T+C^1+5C^2+C^3+C^4$
50	2,4-dimethyl-heptane	$12P+6S+2T+C^1+4C^2+3C^3$
51	2,5-dimethyl-heptane	$12P+6S+2T+C^1+4C^2+3C^3$
52	2,6-dimethyl-heptane	$12P+6S+2T+6C^2+2C^3$

TABLE XX111 CONTINUED

Code Number	Molecule	Bond Symbols
53	3,3-dimethyl-heptane	$12P+8S+2C^1+2C^2+2C^3+2C^4$
54	3,4-dimethyl-heptane	$12P+6S+2T+2C^1+3C^2+2C^3+C^4$
55	3,5-dimethyl-heptane	$12P+6S+2T+2C^1+2C^2+4C^3$
56	4,4-dimethyl-heptane	$12P+8S+2C^1\ 2C^2+2C^3+2C^4$
57	2-methyl-3-ethyl-hexane	$12P+6S+2T+2C^1+3C^2+2C^3+C^4$
58	2-methyl-4-ethyl-hexane	$12P+6S+2T+2C^1+2C^2+4C^3$
59	3-methyl-3-ethyl-hexane	$12P+8S+3C^1+C^2+C^3+3C^4$
60	3-methyl-4ethyl-hexane	$12P+6S+2T+3C^1+C^2+3C^3+C^4$
61	2,2,3-trimethyl-hexane	$15P+4S+T+C^1+2C^2+4C^3+C^5$
62	2,2,4-trimethyl-hexane	$15P+4S+T+C^1+C^2+5C^3+C^4$
63	2,2,5-trimethyl-hexane	$15P+4S+T+3C^2+4C^3+C^4$
64	2,3,3-trimethyl-hexane	$15P+4S+T+C^1+3C^2+2C^3+C^4+C^5$
65	2,3,4-trimethyl-hexane	$15P+2S+3T+C^1+4C^2+C^3+2C^4$
66	2,3,5-trimethyl-hexane	$15P+2S+3T+5C^2+2C^3+C^4$
67	2,4,4-trimethyl-hexane	$15P+4S+T+C^1+2C^2+3C^3+2C^4$

TABLE XX111 CONTINUED

Code Number	Molecule	Bond Symbols
68	3,3,4-trimethyl-hexane	$15P+4S+T+2C^1+C^2+3C^3+C^4+C^5$
69	3,3-diethylpentane	$12P+5S+4C^1+4C^4$
70	2,2-dimethyl-3-ethylpentane	$15P+4S+T+2C^1+5C^3+C^5$
71	2,3-dimethyl-3-ethylpentane	$15P+4S+T+2C^1+2C^2+C^3+2C^4+C^5$
72	2,4-dimethyl-3-ethylpentane	$15P+2S+3T+C^1+4C^2+C^3+2C^4$
73	2,2,3,3-tetra-methylpentane	$18P+2S+C^1+5C^3+C^4+C^6$
74	2,2,3,4-tetra-methylpentane	$18P+2T+3C^2+3C^3+C^4+C^5$
75	2,2,4,4-tetra-methylpentane	$18P+2S+6C^3+2C^4$
76	2,3,3,4-tetra-methylpentane	$18P+2T+4C^2+2C^3+2C^5$
77	1-propene	$3P+2S+T+{}^2C_1^0+C_2^1$
78	1-butene	$3P+4S+T+C^1+{}^2C_1^1+C^1$
79	1-pentene	$3P+6S+T+C^1+C^2+{}^2C_1^1+C_2^1$
80	1-hexene	$3P+8S+T+C^1+2C^2+{}^2C_1^1+C_2^1$
81	1-heptene	$3P+10S+T+C^1+3C^2+{}^2C_1^1+C_2^1$
82	1-octene	$3P+12S+T+C^1+4C^2+{}^2C_1^1+C_2^1$
83	1-nonene	$3P+14S+T+C^1+5C^2+{}^2C_1^1+C_2^1$
84	1-decene	$3P+16S+T+C^1+6C^2+{}^2C_1^1+C_2^1$
85	cis-2-butene	$6P+2T+{}^2C_1^0+C_2^{2b}$

TABLE XX111 CONTINUED

Code Number	Molecule	Bond Symbols
86	trans-2-butene	$6P+2T+2^2C_1^0+C_2^{2c}$
87	2-methyl-1-propene	$6P+2S+2^2C_1^1+C_2^{2a}$
88	cis-2-pentene	$6P+2S+2T+C^1+^2C_1^0+^2C_1^1+C_2^{2b}$
89	trans-2-pentene	$6P+2S+2T+C^1+^2C_1^0+^2C_1^1+C_2^{2c}$
90	2-methyl-1-butene	$6P+4S+C^1+C^2+^2C_1^1+^2C_1^2+C_2^{2a}$
91	2-methyl-2-butene	$9P+T+^2C_1^0+2^2C_1^1+C_2^{3a}$
92	cis-2-hexene	$6P+4S+2T+C^1+C^2+^2C_1^0+^2C_1^1+C_2^{2b}$
93	trans-2-hexene	$6P+4S+2T+C^1+C^2+^2C_1^0+^2C_1^1+C_2^{2c}$
94	cis-3-hexene	$6P+4S+2T+2C^1+2^2C_1^1+C_2^{2b}$
95	trans-3-hexene	$6P+4S+2T+2C^1+2^2C_1^1+C_2^{2c}$
96	2-methyl-1-pentene	$6P+6S+C^1+C^2+^2C_1^1+^2C_1^2+C_2^{2a}$
97	3-methyl-1-pentene	$6P+4S+2T+C^1+C^2+C^3+^2C_1^2+C_2^1$
98	4-methyl-1-pentene	$6P+4S+2T+2C^2+C^3+^2C_1^1+C_2^1$
99	2-methyl-2-pentene	$9P+2S+T+C^1+3^2C_1^1+C_2^{3a}$
100	3-methyl-cis-2-pentene	$9P+2S+T+C^1+^2C_1^0+^2C_1^1+^2C_1^2+C_2^{3b}$
101	3-methyl-trans-2-pentene	$9P+2S+T+C^1+^2C_1^0+^2C_1^1+^2C_1^2+C_2^{3c}$
102	4-methyl-cis-2-pentene	$9P+3T+2C^2+^2C_1^0+^2C_1^2+C_2^{2b}$
103	4-methyl-trans-2-pentene	$9P+3T+2C^2+^2C_1^0+^2C_1^2+C_2^{2c}$
104	2-ethyl-1-butene	$6P+6S+2C^1+2^2C_1^2+C_2^{2a}$

TABLE XX111 CONTINUED

Code Number	Molecule	Bond Symbols
105	2,3-dimethyl-1-butene	$9P+2S+T+2C^{2}+{}^{2}C_{1}^{1}+{}^{2}C_{1}^{3}+C_{2}^{2a}$
106	3,3-dimethyl-1-butene	$9P+2S+T+3C^{3}+{}^{2}C_{1}^{3}+C_{2}^{1}$
107	2,3-dimethyl-2-butene	$12P+4{}^{2}C_{1}^{1}+C_{2}^{4}$
108	cis-2-heptene	$6P+6S+2T+C^{1}+2C^{2}+{}^{2}C_{1}^{0}+{}^{2}C_{1}^{1}+C_{2}^{2b}$
109	trans-2-heptene	$6P+6S+2T+C^{1}+2C^{2}+{}^{2}C_{1}^{0}+{}^{2}C_{1}^{1}+C_{2}^{2c}$
110	cis-3-heptene	$6P+6S+2T+2C^{1}+C^{2}+2{}^{2}C_{1}^{1}+C_{2}^{2b}$
111	trans-3-heptene	$6P+6S+2T+2C^{1}+C^{2}+2{}^{2}C_{1}^{1}+C_{2}^{2c}$
112	2-methyl-1-hexene	$6P+8S+C^{1}+2C^{2}+{}^{2}C_{1}^{1}+{}^{2}C_{1}^{2}+C_{2}^{2a}$
113	3-methyl-1-hexene	$6P+6S+2T+C^{1}+2C^{2}+C^{3}+{}^{2}C_{1}^{2}+C_{2}^{1}$
114	4-methyl-1-hexene	$6P+6S+2T+C^{1}+C^{2}+2C^{3}+{}^{2}C_{1}^{1}+C_{2}^{1}$
115	5-methyl-1-hexene	$6P+6S+2T+3C^{2}+C^{3}+{}^{2}C_{1}^{1}+C_{2}^{1}$
116	2-methyl-2-hexene	$9P+4S+T+C^{1}+C^{2}+3{}^{2}C_{1}^{1}+C_{2}^{3a}$
117	2-ethyl-1-pentene	$6P+8S\ 2C^{1}+C^{2}+2{}^{2}C_{1}^{2}+C_{2}^{2a}$
118	3-ethyl-1-pentene	$6P+6S+2T+2C^{1}+2C^{3}+{}^{2}C_{1}^{2}+C_{2}^{1}$
119	2,3-dimethyl-1-pentene	$9P+4S+T+C^{1}+C^{2}+C^{3}+{}^{2}C_{1}^{0}+{}^{2}C_{1}^{3}+C_{2}^{2a}$
120	3-ethyl-2-pentene	$9P+4S+T+2C^{1}\ {}^{2}C_{1}^{0}+2{}^{2}C_{1}^{2}+C_{2}^{3a}$
121	2,3-dimethyl-2-pentene	$12P+2S+C^{1}+3{}^{2}C_{1}^{1}+{}^{2}C_{1}^{2}+C_{2}^{4}$
122	2,4-dimethyl-2-pentene	$12P+2T+2C^{2}+2{}^{2}C_{1}^{1}+{}^{2}C_{1}^{2}+C_{2}^{3a}$

TABLE XX111 CONTINUED

Code Number	Molecule	Bond Symbols
123	4,4-dimethyl-cis-2-pentene	$12P+2T+3C^3+2C_1^0+2C_1^3+C_2^{2b}$
124	4,4-dimethyl-trans-2-pentene	$12P+2T+3C^3+2C_1^0+2C_1^3+C_2^{2c}$
125	3-methyl-2-ethyl-1-butene	$9P+4S+T+C^1+2C^2+2C_1^2+2C_1^3+C_2^{2a}$
126	2,3,3-trimethyl-1-butene	$12P+2S+3C^3+2C_1^0+2C_1^4+C_2^{2a}$
127	1,2-butadiene	$3P+2S+T+2C_1^0+2C_2^0+2C_2^1$
128	1,3-butadiene	$4S+2T+2C_2^1+22C_1^0$
129	1,2-pentadiene	$3P+4S+T+C^1+2C_1^1+2C_2^0+2C_2^1$
130	1,cis-3-pentadiene	$3P+2S+3T+2C_1^0+C_2^1+C_2^{2b}+22C_1^0$
131	1,trans-3-pentadiene	$3P+2S+3T+2C_1^0+C_2^1+C_2^{2c}+22C_1^0$
132	1,4-pentadiene	$6S+2T+2^2C_1^1+2C_2^1$
133	2,3-pentadiene	$6P+2T+2^2C_1^0+2^2C_2^1$
134	3-methyl-1,2-butadiene	$6P+2S+2^2C_1^1+2C_2^0+C_2^2$
135	2-methyl-1,3-butadiene	$3P+4S+T+2C_1^1+C_2^1+C_2^{2a}+22C_1^1$
136	1,2-hexadiene	$3P+6S+T+C^1+C^2+2C_1^1+2C_2^0+2C_2^1$
137	1,cis-3-hexadiene	$3P+4S+3T+C^1+2C_1^1+22C_1^0+C_2^1+C_2^{2b}$
138	1,trans-3-hexadiene	$3P+4S+3T+C^1+2C_1^1+22C_1^0+C_2^1+C_2^{2c}$
139	1,cis-4-hexadiene	$3P+4S+3T+2C_1^0+2^2C_1^1+C_2^1+C_2^{2b}$

TABLE XXIII CONTINUED

Code Number	Molecule	Bond Symbols
140	1,trans-4-hexadiene	$3P+4S+3T+{}^2C_1^0+2{}^2C_1^1+C_2^1+C_2^{2c}$
141	1,5-hexadiene	$8S+2T+2C_2^1+2{}^2C_1^1+C^2$
142	2,3-hexadiene	$6P+2S+2T+C^1+{}^2C_1^0+{}^2C_1^1+2{}^2C_2^1$
143	cis-2-cis-4-hexadiene	$6P+4T+2{}^2C_1^0+{}^{22}C_1^0+2C_2^{2b}$
144	cis-2-trans-4-hexadiene	$6P+4T+2{}^2C_1^0+{}^{22}C_1^0+C_2^{2b}+C_2^{2c}$
145	trans-2-trans-4-hexadiene	$6P+4T+2{}^2C_1^0+{}^{22}C_1^0+2C_2^{2c}$
146	3-methyl-1,2-pentadiene	$6P+4S+C^1+{}^2C_1^1+{}^2C_1^2+{}^2C_2^0+{}^2C_2^2$
147	4-methyl-1,2-pentadiene	$6P+2S+2T+2C^2+{}^2C_1^2+{}^2C_2^0+{}^2C_2^1$
148	2-methyl-1,cis-3-pentadiene	$6P+2S+2T+{}^2C_1^0+{}^2C_1^1+{}^{22}C_1^1+C_2^{2a}+C_2^{2b}$
149	3-methyl-1,cis-3-pentadiene	$6P+2S+2T+{}^2C_1^0+{}^2C_1^1+{}^{22}C_1^1+C_2^1+C_2^{3b}$
150	3-methyl-1,trans-3-pentadiene	$6P+2S+2T+{}^2C_1^0+{}^2C_1^1+{}^{22}C_1^1+C_2^1+C_2^{3c}$
151	4-methyl-1,3-pentadiene	$6P+2S+2T+2{}^2C_1^1+{}^{22}C_1^0+C_2^1+C_2^{3a}$
152	2-methyl-1,4-pentadiene	$3P+6S+T+2{}^2C_1^1+{}^2C_1^2+C_2^1+C_2^{2a}$
153	3-methyl-1,4-pentadiene	$3P+4S+3T+C^2+2{}^2C_2^2+2C_2^1$
154	2-methyl-1,3-butadiene	$9P+T+{}^2C_1^0+{}^2C_2^1+{}^2C_2^2+2{}^2C_1^1$

TABLE XXIII CONTINUED

Code Number	Molecule	Bond Symbols
155	2-ethyl-1,3-butadiene	$3P+6S+T+C^{1}+{}^{2}C_{1}^{2}+C_{2}^{1}+C_{2}^{2a}+{}^{22}C_{1}^{1}$
156	2,3-dimethyl-1,3-butadiene	$6P+4S+2^{2}C_{1}^{1}+{}^{22}C_{1}^{2}+2C_{2}^{2a}$
157	cyclopentane	$10S+5C^{2}+O^{5}$
158	methylcyclopentane	$3P+8S+T+4C^{2}+2C^{3}+1O^{5}$
159	ethylcyclopentane	$3P+10S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+1O^{5}$
160	n-propylcyclopentane	$3P+12S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+{}^{2}C^{5}+1O^{5}$
161	n-butylcyclopentane	$3P+14S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+2^{2}C^{5}+1O^{5}$
162	n-pentylcyclopentane	$3P+16S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+3^{2}C^{5}+1O^{5}$
163	n-hexylcyclopentane	$3P+18S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+4^{2}C^{5}+1O^{5}$
164	n-heptylcyclopentane	$3P+20S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+5^{2}C^{5}+1O^{5}$
165	n-octylcyclopentane	$3P+22S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+6^{2}C^{5}+1O^{5}$
166	n-nonylcyclopentane	$3P+24S+T+3C^{2}+3C^{3}+{}^{1}C^{5}+7^{2}C^{5}+1O^{5}$
167	1,1-dimethylcyclopentane	$6P+8S+3C^{2}+2C^{3}+2C^{4}+{}^{2}O^{5}$
168	cis-1,2-dimethylcyclopentane	$6P+6S+2T+4C^{2}+2C^{3}+C^{4}+{}^{2}O^{5}$
169	trans-1,2-dimethylcyclopentane	$6P+6S+2T+4C^{2}+2C^{3}+C^{4}+{}^{2}O^{5}$

TABLE XXIII CONTINUED

Code Number	Molecule	Bond Symbols
170	isopropylcyclo-pentane	$6P+8S+2T+3C^2+2C^3+C^4+2^2C^5+1_05$
171	1-methyl-1-ethyl-cyclopentane	$6P+10S+3C^2+4C^3+1C^5+1_05$
172	cyclohexane	$12S+6C^2+0_06$
173	methylcyclohexane	$3P+10S+T+5C^2+2C^3+1_06$
174	ethylcyclohexane	$3P+12S+T+4C^2+3C^3+1C^6+1_06$
175	n-propylcyclo-hexane	$3P+14S+T+4C^2+3C^3+1C^6+2C^6+1_06$
176	n-butylcyclo-hexane	$3P+16S+T+4C^2+3C^3+1C^6+2^2C^6+1_06$
177	n-pentylcyclo-hexane	$3P+18S+T+4C^2+3C^3+1C^6+3^2C^6+1_06$
178	n-hexylcyclo-hexane	$3P+20S+T+4C^2+3C^3+1C^6+4^2C^6+1_06$
179	n-heptylcyclo-hexane	$3P+22S+T+4C^2+3C^3+1C^6+5^2C^6+1_06$
180	n-octylcyclo-hexane	$3P+24S+T+4C^2+3C^3+1C^6+6^2C^6+1_06$

TABLE XXIV

Comparison of Experimental and Calculated Values for Molar Volume and Molar Refraction at 25°C

Code Number	Molar Volume ml/mole Experimental	Molar Volume ml/mole Calculated	Molar Volume ml/mole Difference	Molar Refraction ml/mole Experimental	Molar Refraction ml/mole Calculated	Molar Refraction ml/mole Difference
1	89.48	85.45	4.03	-	-	-
2	101.43	101.21	0.22	20.64	20.78	-0.14
3	116.104	116.970	-0.87	25.286	25.399	-0.113
4	131.598	132.728	-1.13	29.928	30.017	-0.089
5	147.46	148.49	-1.03	34.565	34.636	-0.071
6	163.53	164.24	-.71	39.209	39.254	-0.045
7	179.67	180.00	-0.33	43.855	43.872	-0.017
8	195.91	195.76	0.15	48.503	48.491	0.012
9	212.21	211.52	0.69	53.140	53.109	0.031
10	228.58	227.28	1.30	57.783	57.729	0.054
11	244.89	243.03	1.86	62.41	62.346	0.064
12	105.48	102.95	2.53	-	-	-
13	117.38	117.44	-0.06	25.315	25.366	-0.051
14	123.31	121.10	2.21	25.780	25.610	0.170
15	132.88	133.20	-0.32	29.962	29.984	-0.022
16	130.61	131.93	-1.32	29.818	29.896	-0.078
17	133.71	132.98	0.73	29.947	30.011	-0.064
18	131.16	131.07	0.09	29.831	29.821	0.010
19	148.58	148.96	-0.38	34.599	34.602	-0.003

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Molar Volume ml/mole Calculated	Molar Volume ml/mole Difference	Molar Refraction ml/mole Experimental	Molar Refraction ml/mole Calculated	Molar Refraction ml/mole Difference
20	146.71	147.69	-0.98	34.469	34.515	-0.046
21	144.39	146.42	-2.03	34.292	34.427	-0.135
22	149.65	148.74	0.91	34.629	34.629	-
23	145.03	145.56	-0.53	34.335	34.352	-0.017
24	149.93	149.43	0.50	34.632	34.569	0.063
25	145.41	144.87	0.54	34.345	34.412	-0.067
26	146.09	145.82	0.27	34.387	34.433	-0.046
27	164.61	164.72	-0.11	39.248	39.221	0.027
28	162.77	163.45	-0.68	39.119	39.133	0.014
29	163.05	163.45	-0.40	39.136	39.133	0.003
30	161.00	162.18	1.18	38.960	39.045	-0.085
31	165.27	164.50	0.77	39.271	39.248	0.023
32	161.31	161.32	-0.01	39.002	38.970	0.030
33	164.07	163.92	0.15	39.149	39.100	0.049
34	165.70	165.19	0.51	39.283	39.187	0.096
35	161.80	160.63	1.17	39.035	39.031	0.004
36	159.72	160.05	0.33	38.873	38.883	-0.010
37	159.70	160.05	-0.34	38.859	38.883	-0.024
38	157.87	156.76	1.11	38.734	38.814	-0.080
39	160.41	160.31	0.10	38.944	38.963	-0.019

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Molar Volume ml/mole Calculated	Molar Volume ml/mole Difference	Molar Refraction ml/mole Experimental	Molar Refraction ml/mole Calculated	Molar Refraction ml/mole Difference
40	166.08	164.97	1.11	39.280	39.215	0.065
41	158.14	157.71	0.43	38.777	38.834	-0.057
42	159.75	159.19	0.56	38.896	38.808	0.088
43	180.76	180.47	0.29	43.90	43.84	0.06
44	178.92	179.21	-0.29	43.75	43.75	-
45	179.12	179.21	-0.09	43.79	43.751	0.039
46	177.4	177.90	-0.50	43.7	43.66	0.04
47	146.7	177.94	-1.24	43.5	43.66	-0.16
48	181.50	180.26	1.24	43.93	43.87	0.06
49	177.61	177.08	0.53	43.65	43.59	0.06
50	180.1	179.68	0.42	43.7	43.72	-0.02
51	180.4	179.68	0.72	43.9	43.72	0.18
52	181.94	180.95	0.99	43.94	43,806	0.134
53	177.90	176.39	1.51	43.7	43.65	0.05
54	176.29	175.81	0.48	43.57	43.501	0.069
55	178.40	178.41	-0.01	43.70	43.63	0.07
56	177.9	176.39	1.51	43.6	43.65	-0.05
57	176.4	175.81	0.59	43.7	43.50	0.20
58	178.4	178.41	-0.01	43.7	43.63	0.07
59	174.0	172.52	1.48	43.3	43.43	-0.13
60	173.8	174.54	0.74	43.4	43.41	-0.01
61	176.8	176.07	0.73	43.63	43.58	0.05

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Calculated	Difference	Molar Refraction ml/mole Experimental	Calculated	Difference
62	180.18	179.46	0.72	43.78	43.75	0.03
63	182.38	180.73	1.65	43.95	43.83	0.12
64	174.7	173.47	1.23	43.5	43.45	0.05
65	174.39	173.68	0.71	43.39	43.34	0.05
66	178.65	177.55	1.10	43.65	43.56	0.09
67	178.108	176.858	1.250	43.665	43.62	0.048
68	172.98	172.20	0.78	43.35	43.36	-0.01
69	171.00	168.64	2.36	43.13	43.22	-0.09
70	175.44	174.80	0.64	43.49	43.49	-
71	171.00	169.60	1.40	43.0	43.24	-0.24
72	174.70	173.68	1.02	43.42	43.34	0.08
73	170.321	170.763	-0.442	43.228	43.28	-0.052
74	174.433	173.938	-0.495	43.446	43.42	0.026
75	179.213	180.512	-1.299	43.886	43.86	0.026
76	170.743	170.546	0.197	43.211	43.256	-0.044
77	83.273	79.569	3.704	-	-	-
78	95.285	95.476	-0.291	-	-	-
79	110.384	111.334	-0.950	24.868	24.944	-0.076
80	125.892	127.092	-1.200	29.504	29.562	-0.058
81	141.744	142.850	-1.106	34.144	34.181	-0.037
82	157.850	158.608	-0.758	38.790	38.789	-0.009
83	174.041	174.399	-0.325	43.429	43.418	0.011
84	190.330	190.124	0.206	48.078	48.036	0.042

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Molar Volume ml/mole Calculated	Molar Volume ml/mole Difference	Molar Refraction ml/mole Experimental	Molar Refraction ml/mole Calculated	Molar Refraction ml/mole Difference
85	91.17	92.55	-1.38	-	-	-
86	93.76	93.25	-0.51	-	-	-
87	95.43	92.97	2.46	-	-	-
88	107.78	108.56	-0.78	24.95	24.969	-0.019
89	109.05	109.25	-0.20	25.03	25.089	-0.059
90	108.71	108.51	0.20	24.86	24.827	0.033
91	106.74	107.48	-0.74	24.97	25.030	-0.060
92	123.34	124.32	-0.98	29.56	29.587	-0.027
93	124.90	125.02	-0.12	29.65	29.708	-0.058
94	124.69	124.57	0.12	29.69	29.717	-0.027
95	125.14	125.27	-0.13	29.77	29.837	-0.067
96	124.33	124.27	0.06	29.26	29.446	-0.086
97	126.97	127.35	-0.38	29.51	29.506	0.004
98	127.63	127.56	0.07	29.56	29.529	0.031
99	123.49	123.49	-	29.78	29.778	0.002
100	121.23	121.23	-	29.51	29.508	0.002
101	122.00	122.00	-	29.50	29.498	-0.002
102	126.70	125.84	0.86	29.68	29.618	0.062
103	126.78	126.54	0.24	29.77	29.738	0.032
104	122.91	124.05	-1.14	29.41	29.423	-0.013
105	125.03	124.33	0.70	29.46	29.354	0.106
106	129.89	130.59	-0.70	29.59	29.692	-0.102
107	119.64	119.91	-0.27	29.60	29.610	-0.010

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Calculated	Difference	Molar Refraction ml/mole Experimental	Calculated	Difference
108	139.50	140.08	-0.58	34.0	34.205	-0.205
109	140.88	140.08	0.80	34.30	34.325	-0.025
110	140.52	140.32	0.20	34.31	34.335	-0.025
111	141.51	141.02	0.49	34.43	34.455	-0.025
112	140.54	140.03	0.51	34.12	34.064	0.056
113	142.1	143.11	1.01	34.0	34.125	-0.125
114	141.43	142.05	-0.62	34.08	34.06	0.020
115	142.79	143.32	-0.53	34.16	34.147	0.013
116	139.50	139.25	0.25	34.41	34.396	0.014
117	139.50	139.81	-0.31	34.00	34.041	-0.041
118	141.94	141.84	0.10	34.06	34.037	0.023
119	140.10	136.18	3.92	34.02	33.586	0.434
120	137.15	138.57	-1.42	34.14	34.221	-0.081
121	135.72	135.45	0.27	34.22	34.206	-0.014
122	142.05	140.77	1.28	34.54	34.428	0.112
123	141.23	143.58	-2.35	34.22	34.335	-0.115
124	143.44	144.27	-0.83	34.41	34.455	-0.045
125	138.1	139.87	-1.77	34.0	33.949	0.051
126	140.16	137.51	2.65	33.98	33.679	0.301
127	83.7	84.38	-0.68	-	-	-
128	87.96	87.70	0.26	-	-	-
129	99.06	100.39	-1.33	24.950	24.958	-0.008
130	99.30	100.69	-1.39	25.804	25.855	-0.051

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Molar Volume ml/mole Calculated	Molar Volume ml/mole Difference	Molar Refraction ml/mole Experimental	Molar Refraction ml/mole Calculated	Molar Refraction ml/mole Difference
131	101.51	101.38	0.13	26.046	26.855	-0.809
132	103.88	105.70	-1.82	24.367	24.489	-0.182
133	98.72	100.40	-1.68	25.246	25.008	0.238
134	100.9	100.53	0.37	24.8	24.801	-0.001
135	100.78	100.14	0.64	25.425	25.614	-0.189
136	115.66	116.15	0.49	29.59	29.576	0.014
137	117.3	116.69	0.61	30.60	30.603	-0.003
138	117.3	117.39	-0.09	30.6	30.723	-0.123
139	118.2	118.68	-0.48	29.4	29.132	0.268
140	118.2	119.38	-1.18	29.4	29.252	0.148
141	119.42	121.46	-2.04	29.01	29.107	-0.097
142	121.7	116.41	5.29	29.0	29.756	-0.756
143	114.9	113.67	1.23	30.7	30.498	0.202
144	114.9	114.36	0.54	30.7	30.618	0.082
145	114.9	115.06	-0.16	30.7	30.738	-0.038
146	115.7	116.07	-0.37	29.4	29.396	-0.004
147	116.8	117.67	-0.87	29.6	29.608	-0.008
148	115.0	113.13	1.87	30.5	30.257	0.243
149	112.5	112.86	-0.36	30.2	30.296	-0.095
150	112.5	113.63	-1.13	30.2	30.285	-0.085
151	115.0	115.61	-0.61	30.8	30.664	0.136
152	119.2	118.63	0.57	29.0	28.991	0.009

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Molar Volume ml/mole Calculated	Molar Volume ml/mole Difference	Molar Refraction ml/mole Experimental	Molar Refraction ml/mole Calculated	Molar Refraction ml/mole Difference
153	119.0	122.78	-3.78	29.0	28.13	0.87
154	116.3	116.55	-0.25	29.6	29.599	0.001
155	115.4	115.68	-0.28	30.50	30.210	0.291
156	113.74	113.75	-0.01	29.75	29.748	0.002
157	94.713	94.713	-	23.144	23.144	-
158	113.122	113.122	-	27.847	27.847	-
159	128.819	128.819	-	32.416	32.416	-
160	145.292	145.312	-0.02	37.067	37.057	0.01
161	161.67	161.75	-0.08	41.70	41.70	-
162	178.15	178.26	-0.11	46.35	46.34	0.01
163	194.62	194.73	-0.11	50.99	50.98	0.01
164	211.11	211.21	-0.10	55.64	55.62	0.02
165	227.60	227.68	-0.08	60.28	60.26	0.02
166	244.09	244.17	-0.08	64.92	64.90	0.02
167	130.925	130.925	-	32.49	32.55	-0.06
168	127.829	130.346	-2.517	32.30	32.41	-0.11
169	131.46	130.346	1.114	32.51	32.41	0.01
170	145.236	142.679	2.557	37.02	36.88	0.14
171	144.468	143.588	0.880	36.92	37.19	-0.27
172	108.74	108.74	-	27.72	27.72	-
173	128.33	128.33	-	32.52	32.52	-
174	143.14	143.14	-	37.03	37.03	-
175	159.84	159.66	0.18	41.69	41.67	0.02

TABLE XXIV CONTINUED

Code Number	Molar Volume ml/mole Experimental	Molar Volume ml/mole Calculated	Molar Volume ml/mole Difference	Molar Refraction ml/mole Experimental	Molar Refraction ml/mole Calculated	Molar Refraction ml/mole Difference
176	176.31	176.17	0.14	46.33	46.32	0.01
177	192.82	192.69	0.13	50.98	50.96	0.02
178	209.32	209.20	0.12	55.62	55.61	0.01
179	225.82	225.72	0.01	60.26	60.25	0.01
180	242.32	242.24	0.08	64.90	64.89	0.01

TABLE XXV

Comparison of Experimental and Calculated Values for Entropy and Heat of Atomization, Q_a, at 25°C

Code Number	Entropy cal/deg mole Experimental	Entropy cal/deg mole Calculated	Entropy cal/deg mole Difference	Q_a kcal/mole Experimental	Q_a kcal/mole Calculated	Q_a kcal/mole Difference
1	64.51	65.21	-0.70	954.30	954.28	0.02
2	74.12	74.47	-0.35	1234.71	1234.36	0.35
3	83.40	83.72	-0.32	1514.66	1514.45	0.21
4	92.83	92.99	-0.16	1794.71	1794.53	0.18
5	102.24	102.24	-	2074.73	2074.61	0.12
6	111.55	111.50	0.05	2354.75	2354.70	0.05
7	120.86	120.76	0.10	2634.76	2634.78	-0.02
8	130.17	130.06	0.11	2914.78	2914.87	-0.09
9	139.48	139.27	0.21	-	-	-
10	148.79	148.53	0.26	-	-	-
11	158.09	157.78	0.31	-	-	-
12	70.42	69.73	0.69	1236.71	1236.48	0.23
13	82.12	80.64	1.48	1516.58	1515.93	0.65
14	73.23	74.78	-1.55	1519.33	1519.74	-0.41
15	90.95	89.90	1.05	1796.41	1796.02	0.39
16	90.77	91.55	-0.78	1795.77	1795.39	0.38
17	85.62	84.99	0.63	1799.11	1798.48	0.63
18	87.42	86.12	1.30	1797.24	1796.79	0.45
19	100.35	99.6	0.75	2076.44	2076.10	0.34

TABLE XXV CONTINUED

Code Number	Entropy cal/deg mole Experimental	Calculated	Difference	Q_p kcal/mole Experimental	Calculated	Difference
20	101.37	100.81	0.56	2075.80	2075.47	0.33
21	98.30	102.46	-4.16	2075.18	2074.84	0.34
22	93.85	94.25	-0.40	2079.13	2078.57	0.56
23	98.96	97.02	1.94	2077.46	2076.25	1.21
24	94.80	96.08	-1.28	2078.14	2077.59	0.55
25	95.53	95.21	0.32	2078.01	2077.23	0.78
26	91.60	94.73	-3.13	2078,80	2078.17	0.63
27	108.81	108.41	0.40	2356.44	2356.18	0.26
28	110.32	110.06	0.26	2355.76	2355.56	0.20
29	108.35	110.06	-1.71	2355.63	2355.56	0.07
30	109.51	111.71	-2.20	2355.33	2354.93	0.40
31	103.06	103.51	-0145	2358.64	2358.65	-0.01
32	106.11	106.28	-0.17	2356.07	2356.33	-0.26
33	106.51	106.98	-0.47	2357.37	2357.04	0.33
34	104.93	105.33	-0.40	2358.15	2357.67	0.48
35	104.70	104.46	0.24	2357.55	2357.31	0.24
36	107.15	107.93	-0.78	2355.84	2355.70	0.14
37	105.43	107.93	-2.50	2355.41	2355.70	-0.29
38	103.48	105.42	-1.94	2356.32	2357.94	0.35
39	110.62	105.64	4.98	2357.54	2357.63	-0.09
40	101.15	100.52	0.63	2358.51	2360.14	-1.63

TABLE XXV CONTINUED

Code Number	Entropy cal/deg mole Experimental	Entropy cal/deg mole Calculated	Entropy cal/deg mole Difference	Q kcal/mole Experimental	Q kcal/mole Calculated	Q kcal/mole Difference
41	103.14	104.95	-.81	2356.66	2356.92	-0.26
42	102.31	102.50	-0.19	2356.91	2356.91	-0.20
77	63.80	66.42	-2.62	820.37	820.04	0.35
78	73.04	73.39	-0.35	1100.39	1100.15	0.24
79	82.65	82.65		1380.45	1380.24	0.21
80	91.93	91.91	0.02	1660.50	1660.32	0.18
81	101.24	101.16	0.08	1940.53	1940.43	0.13
82	110.55	110.42	0.13	2220.55	2220.49	0.06
83	119.86	119.68	0.18	2500.56	2500.57	-0.01
84	129.17	128.94	0.23	2780.58	2780.66	-0.08
85	71.90	76.85	-4.95	1102.03	1101.89	0.14
86	70.86	75.60	-4.74	1103.03	1102.89	0.14
87	70.17	72.62	-2.45	1104.41	1104.23	0.18
88	82.76	83.82	-1.06	1381.96	1382.00	-0.04
89	81.36	82.57	-1.21	1383.04	1383.00	0.04
90	81.73	82.01	-0.28	1384.13	1383.95	0.18
91	80.92	83.48	-2.56	1385.62	1385.41	0.21
92	92.37	93.08	-0.71	1662.10	1662.08	0.02
93	90.97	91.83	0.86	1663.10	1663.08	0.02
94	90.73	90.79	-0.06	1662.10	1662.11	-0.01

TABLE XXV CONTINUED

Code Number	Entropy cal/deg mole Experimental	Entropy cal/deg mole Calculated	Entropy cal/deg mole Difference	Heat kcal/mole Experimental	Heat kcal/mole Calculated	Heat kcal/mole Difference
95	89.59	89.54	-0.05	1663.10	1663.11	-0.01
96	91.34	91.27	0.07	1664.10	1664.04	0.06
97	90.06	88.95	1.11	1661.56	1661.44	0.12
98	87.89	88.82	-0.93	1662.20	1661.81	0.39
99	90.45	90.45	-	1665.50	1665.52	-0.02
100	90.45	90.45	-	1664.86	1664.87	-0.01
101	91.26	91.26	-	1664.86	1664.87	-0.01
102	89.23	88.47	0.76	1663.80	1663.83	-0.03
103	88.02	87.22	0.80	1664.80	1664.83	-0.03
104	90.01	91.40	-1.39	1663.46	1663.67	-0.21
105	87.39	88.07	-0.68	1665.32	1665.20	0.12
106	82.16	82.98	-0.82	1664.79	1664.93	-0.14
107	86.67	86.67	-	1664.45	1666.78	-0.33
108	-	-	-	1942.13	1942.17	-0.04
109	-	-	-	1943.13	1943.17	-0.04
110	-	-	-	1942.13	1942.19	-0.06
111	-	-	-	1943.13	1943.19	-0.06
112	-	-	-	1944.14	1944.12	0.02
113	-	-	-	1941.60	1941.52	0.08
114	-	-	-	1941.60	1941.26	[illegible]
115	-	-	-	1942.24	1941.89	-0.65
116	-	-	-	1945.54	1945.60	-0.06

TABLE XXV CONTINUED

Code Number	Entropy cal/deg mole Experimental	Entropy cal/deg mole Calculated	Entropy cal/deg mole Difference	kcal/mole Differ- mental	kcal/mole Calculated	kcal/mole Difference
117	-	-	-	1943.50	1943.75	-0.25
118	-	-	-	1940.98	1940.90	0.08
119	-	-	-	1945.16	1944.50	0.66
120	-	-	-	1944.28	1944.85	-0.57
121	-	-	-	1946.76	1946.50	0.26
122	-	-	-	1947.24	1947.35	-0.11
123	-	-	-	1946.53	1946.77	-0.24
124	-	-	-	1947.53	1947.77	-0.24
125	-	-	-	1945.16	1944.92	0.24
126	-	-	-	1946.50	1946.36	0.14
127	70.03	71.38	-1.35	957.39	957.39	-
128	66.62	66.97	-0.35	969.83	970.10	-0.27
129	79.7	78.35	1.35	1236.47	1237.50	-1.03
130	77.5	77.40	-0.10	1252.57	1251.94	0.63
131	76.4	76.15	0.25	1252.67	1252.94	-0.27
132	79.7	81.57	-1.87	1246.07	1246.03	0.04
133	77.6	77.60	-	1238.17	1238.18	-0.01
134	76.4	76.40	-	1240.27	1240.27	-
135	75.44	75.44	-	1253.17	1253.16	[illegible]
157	70.00	70.00	-	1393.91	1393.91	-
158	81.24	81.24	-	1676.04	1676.04	-

TABLE XXV CONTINUED

Code Number	Entropy cal/deg mole Experimental	Entropy cal/deg mole Calculated	Entropy cal/deg mole Difference	Δ kcal/mole Experimental	Δ kcal/mole Calculated	Δ kcal/mole Difference
159	90.42	90.42	-	1956.01	1956.01	-
160	99.73	99.73	-	2236.12	2236.03	0.09
161	109.04	109.04	-	2516.04	2516.05	-0.01
162	118.35	118.35	-	2796.06	2796.07	-0.01
163	127.66	127.66	-	3076.07	3076.09	-0.02
164	136.96	136.97	-0.01	3356.09	3356.11	-0.02
165	146.27	146.28	-0.01	3636.11	3636.13	-0.02
166	155.58	155.59	-0.01	3916.12	3916.15	-0.03
172	71.28	71.28	-	1679.97	1679.97	-
173	82.06	82.06	-	1962.63	1962.63	-
174	91.44	91.44	-	2241.78	2241.78	-
175	100.27	100.70	-0.43	2522.02	2521.81	0.21
176	109.59	109.96	-0.38	2801.81	2801.84	-0.03
177	118.89	119.22	-0.33	3081.88	3081.87	0.01
178	128.20	128.48	-0.28	3361.89	3361.90	-0.01
179	137.51	137.74	-0.23	3641.91	3641.93	-0.02
180	146.82	147.00	-0.18	3921.93	3921.96	-0.03

TABLE XXVI

Molar Magnetic Susceptibilities of Paraffins

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
1	Ethane	$6P+C^0$	27.3^{124}	27.3	-
2	n-Propane	$6P+2S+2C^1$	39.6^{125}	39.67	-0.07
3	n-Butane	$6P+4S+2C^1+C^2$	57.4^{124}	51.12	6.28
4	1-Butane	$9P+T+3C^2$	51.7^{125}	52.00	-0.30
5	n-Pentane	$6P+6S+2C^1+3C^2$	63.05^{126}	62.56	0.49
6	2-Methylbutane	$9P+2S+T+C^1+2C^2+C^3$	64.40*	63.43	0.97
7	2,2-Dimethyl-propane	$12P+4C^3$	63.10^{125}	63.44	-0.34
8	n-Hexane	$6P+8S+2C^1+3C^2$	73.84*	74.01	-0.17
9	2-Methylpentane	$9P+4S+T+C^1+3C^2+C^3$	75.26^{126}	74.87	0.39
10	3-Methylpentane	$9P+4S+T+2C^1+C^2+2C^3$	75.52^{126}	74.86	0.66
11	2,2-Dimethyl-butane	$12P+2S+C^1+3C^3+C^4$	76.24^{126}	75.02	1.22
12	2,3-Dimethyl-butane	$12P+2T+4C^2+C^4$	76.22^{126}	75,89	0.33
13	n-Heptane	$6P+10S+2C^1+4C^2$	85.31*	85.45	-0.14

TABLE XXVI CONTINUED

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
14	2-Methylhexane	$9P+6S+T+C^1+4C^2+C^3$	86.24[126]	86.32	-0.08
15	3-Ethylpentane	$9P+6S+T+3C^1+3C^3$	86.21[126]	86.29	-0.08
16	2,2-Dimethylpentane	$12P+4S+C^1+C^2+3C^3+C^4$	86.97[126]	86.47	0.50
17	2,3-Dimethylpentane	$12P+2S+2T+C^1+3C^2+C^3+C^4$	87.51[126]	87.32	0.19
18	2,4-Dimethylpentane	$12P+2S+2T+4C^2+2C^3$	87.48[126]	87.32	0.30
19	2,2,3-Trimethylbutane	$15P+T+2C^2+3C^3+C^5$	88.36[126]	88.40	-0.04
20	n-Octane	$6P+12S+2C^1+5C^2$	96.86*	96.90	-0.22
21	3-Methylheptane	$9P+8S+T+2C^1+3C^2+2C^3$	97.99[126]	97.75	0.24
22	4-Methylheptane	$9P+8S+T+2C^1+3C^2+2C^3$	97.30[127]	97.75	-0.45
23	3-Ethylhexane	$9P+8S+T+3C^1+C^2+3C^3$	97.76[127]	97.73	0.03
24	2,3-Dimethylhexane	$12P+4S+2T+C^1+4C^2+C^3+C^4$	98.56*	98.76	-0.20
25	3,4-Dimethylhexane	$12P+4S+2T+2C^1+2C^2+2C^3+C^4$	99.06[126]	98.75	0.31
26	2,5-Dimethylhexane	$12P+4S+2T+5C^2+2C^3$	98.15[126]	98.63	-0.48

TABLE XXVI CONTINUED

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
27	2,2,3-Trimethylpentane	$15P+2S+T+c^1+c^2+4c^3+c^5$	99.86^{126}	99.83	0.03
28	2,2,4-Trimethylpentane	$15P+2S+T+2c^2+4c^3+c^4$	98.34^{126}	98.78	-0.44
29	2,3,4-Trimethylpentane	$15P+3T+5c^2+2c^4$	99.75^{127}	99.78	-0.03
30	n-Nonane	$6P+14S+2c^1+6c^2$	108.07*	108.35	-0.28
31	4-Methyloctane	$9P+10S+T+2c^1+4c^2+2c^3$	109.63^{128}	109.19	0.44
32	n-Decane	$6P+16S+2c^1+7c^2$	119.62*	119.80	-0.18
33	4-Methylnonane	$9P+12S+T+2c^1+5c^2+2c^3$	121.39^{128}	120.64	-0.75
34	2,6-Dimethyloctane	$12P+8S+2T+c^1+5c^2+3c^3$	122.54^{128}	121.50	1.04
35	n-Undecane	$6P+18S+2c^1+8c^2$	131.84^{128}	131.23	0.61
36	3,4-Dimethylnonane	$12P+10S+2T+2c^1+5c^2+2c^3+c^4$	134.70^{128}	133.08	1.62
37	2,4-Dimethylnonane	$12P+10S+2T+c^1+6c^2+3c^3$	134.68^{128}	132.95	1.73
38	n-Hexadecane	$6P+28S+2c^1+13c^2$	187.63	188.46	-0.83

Mean Deviation 0.63

* Average Value

TABLE XXVII

Molar Magnetic Susceptibilities of Unsaturated Compounds

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
1	$CH_2=CH_2$	$4S+C_2^0$	12.0[124]	12.0	-
2	$CH_3-CH=CH_2$	$3P+2S+T+C_2^1+{}^2C_1^0$	31.5[125]	31.5	-
3	trans-$CH_3-CH=CH-CH_3$	$6P+2T+C_2^2+2{}^2C_1^0$	43.3[125]	42.9	0.4
4	cis - $CH_3CH=CH-CH_3$	$6P+2T+C_2^2+2{}^2C_1^0$	42.6[126]	42.9	-0.3
5	$(CH_3)_2C=CH_2$	$6P+2S+2{}^2C_1^1+C_2^2$	44.4[125]	42.9	1.5
6	$CH_3-CH=C(CH_3)2$	$9P+T+{}^2C_1^0+2{}^2C_1^1+C_2^3$	54.4[125]	54.4	-
7	$CH_3CH=C=CHCH_3$	$6P+2T+2{}^2C_1^0+{}^2C_2^1$	49.1[129]	49.1	-
8	$(CH_3)_2C=C(CH_3)_2$	$12P+4{}^2C_1^1+C_2^4$	65.9[125]	65.9	-
9	$CH_3CH=C=CHCH_2CH_3$	$6P+2S+2T+C^1+{}^2C_1^1+{}^2C_1^0+2{}^2C_2^1$	60.9[129]	60.9	-
10	$CH_3(CH_2)_3CH=C=CH_2$	$3P+8S+T+C^1+2C^2+{}^2C_1^1+{}^2C_2^1+{}^2C_2^0$	73.5[129]	72.8	0.7
11	$(CH_3)_2CHCH_2CH=C=CH_2$	$6P+4S+2T+2C_1^2+C_1^3+{}^2C_1^1+{}^2C_2^1+{}^2C_2^0$	73.6[129]	73.7	-0.1

TABLE XXVII CONTINUED

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
12	$CH_3CH=C=CH(CH_2)_2CH_3$	$6P+4S+2T+{}^2C_1^0+2{}^2C_2^1+{}^2C_1^1+C^2+C^1$	72.1[129]	72.2	-0.1
13	$(CH_3)_2CHCH_2CH=CHCH_2CH_3$	$9P+4S+3T+2C_1^2+C_1^3+2{}^2C_1^1+C_2^2+C^1$	88.0[130]	90.0	-2.0
14	$CH_3(CH_2)_4CH=C=CH_2$	$3P+10S+T+C^1+3C^2+{}^2C_2^1+{}^2C_2^0$	83.6[129]	84.2	-0.6
15	$(CH_3)_2CHCH_2CH=C(CH_3)CH_2CH_3$	$12P+4S+2T+2C_1^2+C^1+C^3+2{}^2C_1^1+C_2^3+{}^2C_1^2$	100.6[130]	100.8	-0.2
16	$CH_3(CH_2)_3C(CH_3)=CH(CH_2)_2CH_3$	$9P+10S+T+2C^1+3C^2+{}^2C_1^2+2{}^2C_1^1+C_2^3$	111.6	111.4	0.2

Mean Deviation 0.4

TABLE XXVIII

Molar Magnetic Susceptibilities of Aromatic Compounds

	Compound	Contributions	Molar Susceptibility x10^6 Experimental	Calculated	Difference
1	Benzene	$\phi + 6T$	54.85^{128}	54.85	-
2	Toluene	$\phi' + 5T + 3P + {}^{\phi}C_1^0$	65.56*	65.56	-
3	Ethylbenzene	$\phi' + 5T + 3P + 2S + C^1 + {}^{\phi}C_1^1$	77.29*	77.69	-0.40
4	o-Xylene	$\phi^2 + 6P + 4T + 2\,{}^{\phi}C_1^0$	77.81^{132}	77.09	0.72
5	m-Xylene	$\phi^2 + 6P + 4T + 2\,{}^{\phi}C_1^0$	76.50^{131}	77.09	-0.59
6	p-Xylene	$\phi^2 + 6P + 4T + 2\,{}^{\phi}C_1^0$	76.97^{128}	77.09	-0.12
7	n-Propylbenzene	$\phi' + 5T + 3P + 4S + C^1 + C^2 + {}^{\phi}C_1^1$	89.09*	89.15	-0.05
8	i-Propylbenzene	$\phi' + 6P + 6T + 2C^2 + {}^{\phi}C_1^2$	89.69*	89.79	-0.1-
9	n-Butylbenzene	$\phi' + 3P + 6S + 5T + C^1 + 2C^2 + {}^{\phi}C_1^1$	100.74*	100.59	0.16
10	i-Butylbenzene	$\phi' + 6P + 2S + 6T + 2C^2 + C^3 + {}^{\phi}C_1^1$	101.74*	101.45	0.29
11	sec-Butylbenzene	$\phi' + 6P + 2S + 6T + C^1 + C^2 + C^3 + {}^{\phi}C_1^2$	101.31^{131}	101.22	0.09
12	t-Butylbenzene	$\phi' + 9P + 5T + 3C^3 + {}^{\phi}C_1^3$	102.50^{132}	102.50	-
13	n-Amylbenzene	$\phi' + 3P + 8S + 5T + C^1 + 3C^2 + {}^{\phi}C_1^1$	112.55^{128}	112.03	0.52

TABLE XXVIII CONTINUED

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
14	1-Phenyl-2-methylbutane	$\varphi' + 6P + 4S + 6T + C^1 + C^2 + 2C^3 + \varphi C_1^1$	113.53[128]	112.89	0.64
15	n-Hexylbenzene	$\varphi' + 3P + 10S + 5T + C^1 + 4C^2 + \varphi C_1^1$	124.23[128]	123.47	0.76
16	p-diisopropyl benzene	$\varphi^2 + 12P + 6T + 4C^2 + \varphi C_1^2$	124.77[131]	125.54	-0.77
17	n-Heptylbenzene	$\varphi' + 3P + 12S + 5T + C^1 + 5C^2 + \varphi C_1^1$	134.41[126]	134.92	-0.51
18	1-Phenyl-4,6,6-trimethylheptane	$\varphi' + 12P + 8S + 6T + 3C^2 + 5C^3 + C^4 + \varphi C_1^1$	173.90[128]	171.12	2.78
19	Dibenzyl	$2\varphi' + 4S + 10T + C^2 + 2\varphi C_1^1$	127.79[131]	127.16	0.63
20	1,6-Diphenylhexane	$2\varphi' + 12S + 10T + 5C^2 + 2\varphi C_1^1$	171.81[126]	172.93	-1.12
		Mean Deviation	0.53		

TABLE XXIX

Molar Magnetic Susceptibilities of Aldehydes and Ketones

	Compound	Contributions	Molar Susceptibility x 10^6 Experimental	Calculated	Difference
1	Acetone	$6P+K$	33.96*	33.96	-
2	Ethylmethylketone	$6P+2S+K+{}^{K}C_1^0$	45.60[138]	45.60	-
3	Methyl-n-propylketone	$6P+4S+C^1+K+{}^{K}C_1^1$	57.41[133]	57.37	0.04
4	Diethylketone	$6P+4S+K+2{}^{K}C_1^0$	57.32[133]	57.25	0.07
5	Ethyl-n-propylketone	$6P+6S+C^1+K+{}^{K}C_1^0+{}^{K}C_1^1$	69.03[133]	69.02	0.01
6	n-Amyl methyl ketone	$6P+8S+C^1+2C^2+K+{}^{K}C_1^1$	80.50[133]	80.26	0.24
7	n-Butyl ethyl ketone	$6P+8S+C^1+C^2+K+{}^{K}C_1^0\ {}^{K}C_1^1$	80.73[133]	80.46	0.27
8	Di-n-propylketone	$6P+8S+2C^1+K+2{}^{K}C_1^1$	80.45[133]	80.78	-0.33
9	n-Hexylmethyl ketone	$6P+10S+C^1+3C^2+K+{}^{K}C_1^1$	92.08[133]	91.70	0.38
10	Methylisopropyl ketone	$9P+T+K+2{}^{K}C_1^1$	58.45[133]	58.77	-0.32
11	Methylisobutyl ketone	$9P+2S+T+2C^2+K+{}^{K}C_1^2$	70.05[133]	69.59	0.46
12	Diisopropyl ketone	$12P+2T+K+4{}^{K}C_1^1$	81.14[133]	83.57	-2.43
13	t-Butylmethyl ketone	$12P+K+3{}^{K}C_1^2$	69.86[133]	70.48	-0.62

TABLE XXIX CONTINUED

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
14	Diisobutyl ketone	$12P+4S+2T+4C_1^2+K+2^KC_1^2$	104.30[133]	105.22	-0.92
15	Di-t-butyl ketone	$18P+K+6^KC_1^2$	104.06[133]	107.00	-2.94
16	Acetonyl acetone	$6P+4S+2K+^KC_1^1$	62.51[134]	62.99	-0.48
17	Acetophenone	$3P+5T+\varphi^1+K+^KC_1^\varphi$	72.65[134]	71.74	0.91
18	Propiophenone	$18P+2S+5T+\varphi^1+K+^KC_1^\varphi{}^KC_1^O$	83.73[134]	83.39	0.34
19	Benzyl methyl ketone	$3P+2S+5T+\varphi^1+K+^\varphi C_1^1$	83.44[134]	83.32	0.12
20	Dibenzyl ketone	$4S+10T+2\varphi^1+K+2^\varphi C_1^1$	131.70[134]	132.70	-1.00
21	Benzophenone	$10T+2\varphi^1+K+2^KC_1^\varphi$	109.60[134]	108.80	0.80
22	Acetaldehyde	$3P+A1$	22.70[133]	23.45	-0.75
23	Propionaldehyde	$3P+2S+A1+C_1^{OA1}$	34.32[133]	34.32	-
24	n-Butyraldehyde	$3P+4S+C^1+A1+C_1^{1A1}$	46.08[133]	45.92	0.16
25	i-Butyraldehyde	$6P+T+A1+2C_1^{1A1}$	46.38[133]	46.38	-
26	n-Hexaldehyde	$3P+8S+C^1+2C^2+A1+C_1^{1A1}$	69.40[133]	68.81	0.59
27	Diethylacetaldehyde	$6P+4S+T+2C^1+A1+2C_1^{2A1}$	70.71[133]	70.70	0.01

Mean Deviation 0.52

TABLE XXX

Molar Magnetic Susceptibilities of Alcohols

	Compound	Contributions	Molar Susceptibility x 10^6 Experimental	Calculated	Difference
1	CH_3OH	$3P+A^1$	21.60[135]	21.60	-
2	C_2H_5OH	$3P+2S+A+{}^{1A}C_1^0$	33.55[135]	33.55	-
3	$n\text{-}C_3H_7OH$	$3P+4S+C^1+{}^{A}C_1^1+A^1$	45.18[135]	45.05	0.13
4	$1\text{-}C_3H_7OH$	$6P+T+2{}^{A}C_1^1+A^2$	45.79[135]	45.40	0.37
5	$n\text{-}C_4H_9OH$	$3P+6S+C^1+C^2+{}^{2A}C_1^1+A^1$	56.54[135]	56.49	0.05
6	$1\text{-}C_4H_9OH$	$6P+2S+T+2C^2+{}^{A}C_1^2+A'$	57.70[136]	57.11	0.59
7	$C_2H_5CHOHCH_3$	$6P+2S+T+C^1+{}^{A}C_1^2+{}^{A}C_1^1\ A^2$	57.68[135]	57.68	-
8	$n\text{-}C_5H_{11}OH$	$3P+8S+C^1+2C^2+{}^{A}C_1^1+A^1$	66.8[136]	67.93	-1.13
9	$n\text{-}C_6H_{13}OH$	$3P+10S+C^1+3C^2+{}^{A}C_1^1+A^1$	79.2[126]	79.37	-0.17
10	$n\text{-}C_7H_{15}OH$	$3P+12S+C^1+4C^2+{}^{A}C_1^1+A^1$	89.0[136]	90.81	-1.81
11	$n\text{-}C_9H_{19}OH$	$3P+16S+C^1+6C^2+{}^{A}C_1^1+A^1$	101.6[136]	113.69	-12.09
12	$CH_2OH(CH_2)_4CH_2OH$	$12S+3C^2+2{}^{A}C_1^1+2A^1$	84.30[126]	84.78	-0.48
13	CH_2OHCH_2OH	$4S+2A^1+{}^{A}C_1^1$	38.80[126]	40.34	-1.54
14	$CH_2OHCHOHCH_2OH$	$4S+T+2A^1+A^2+2{}^{A}C_1^1$	57.06[126]	55.16	1.90

Mean Deviation (excluding number 11) 0.58

TABLE XXXI

Molar Magnetic Susceptibilities of Esters

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
1	Methyl formate	$3P+F$	30.89[137]	30.89	-
2	Ethyl formate	$3P+2S+{}^{F}C_1^0+F$	42.47[137]	42.47	-
3	n-Butyl formate	$3P+4S+C^1+C^2+{}^{F}C_1^1+F$	65.83[138]	65.83	-
4	i-Butyl formate	$6P+2S+T+2C^2+{}^{F}C_1^2+F$	66.79[138]	66.79	-
5	i-Amyl formate	$6P+4S+T+2C^2+C^3+{}^{F}C_1^1+F$	78.38[138]	78.16	0.22
6	Methyl acetate	$6P+E$	42.23[137]	42.23	-
7	Ethyl acetate	$6P+2S+{}^{E}C_1^0+E$	53.98[139]	53.98	-
8	n-Propyl acetate	$6P+4S+C^1+{}^{E}C_1^1+E$	65.75[139]	65.75	-
9	i-Propyl acetate	$9P+T+2{}^{E}C_1^1+E$	67.04[138]	67.28	-0.24
10	n-Butyl acetate	$6P+6S+C^1+C^2+{}^{E}C_1^1+E$	77.00[139]	77.19	-0.19
11	i-Butyl acetate	$9P+2S+T+2C^2+{}^{E}C_1^2+E$	78.52[138]	78.52	-
12	n-Amyl acetate	$6P+8S+C^1+2C^2+{}^{E}C_1^1+E$	89.06[139]	88.63	0.43
13	i-Amyl acetate	$9P+4S+T+2C^2+C^3+{}^{E}C_1^1+E$	89.40[126]	89.50	-0.10

TABLE XXXI CONTINUED

	Compounds	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
14	n-Hexyl acetate	$6P+10S+C^1+3C^2+{}^EC_1^1+E$	100.90[137]	100.07	0.83
15	Methyl propionate	$6P+2S+{}^EC_1^0+E$	54.06[138]	53.98	0.08
16	Ethyl propionate	$6P+4S+2{}^EC_1^0+E$	65.75[138]	65.73	0.02
17	i-Amyl propionate	$9P+6S+T+2C^2+C^3+{}^EC_1^0+{}^EC_1^1+E$	101.73[138]	101.25	0.48
18	Methyl-n-butyrate	$6P+4S+C^1+{}^EC_1^1+E$	65.83[138]	65.75	0.08
19	Ethyl-n-butyrate	$6P+6S+C^1+{}^EC_1^0+{}^EC_1^1+E$	77.43[138]	77.50	-0.07
20	Ethyl-i-butyrate	$9P+2S+T+{}^EC_1^0+2{}^EC_1^1+E$	78.32[138]	79.03	-0.71
21	i-Amyl-n-butyrate	$9P+8S+T+C^1+2C^2+C^3+2{}^EC_1^1+E$	113.52[138]	109.87	3.65
22	n-Amyl valerate	$6P+14S+2C^1+3C^2+2{}^EC_1^1+E$	124.55	123.59	0.96

Mean Deviation 0.37

TABLE XXXII

Molar Magnetic Susceptibilities of some Chloro Derivatives

	Compound	Contributions	Molar Susceptibility x 10^6 (c.g.s. units) Experimental	Calculated	Difference
1	$C_2H_5CH_2Cl$	$3P+4S+C_1^{1Cl}+Cl+C^1$	56.10^{126}	56.66	-0.56
2	$CH_3(CH_2)_3Cl$	$3P+6S+C_1^{1Cl}+Cl+C^1+C^2$	67.10^{126}	67.10	-
3	$CH_3CH_2CHClCH_3$	$6P+2S+T+C^1+C_1^{1Cl}+C_1^{2Cl}+Cl$	67.40^{126}	67.18	0.22
4	$(CH_3)_2CHCH_2Cl$	$6P+2S+T+2C^2+C_1^{2Cl}+Cl$	68.6*	68.38	0.22
5	$(CH_3)C(CH_2Cl)_2$	$6P+4S+2C^3+2C_1^{3Cl}+2Cl$	96.9^{140}	97.01	-0.11
6	$CH_3C(CH_2Cl)_3$	$3P+6S+C^3+3C_1^{3Cl}+3Cl$	114^{140}	114.41	-0.44
7	$(CH_2Cl)_4C$	$8S+4C_1^{3Cl}+4Cl$	129^{140}	131.80	-2.80

Mean Deviation 0.62

TABLE XXXIII

Molar Sound Velocities of Paraffins

	Compound	Contributions	Molar Sound Velocity (c.c./mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
1	n-pentane	$6P+6S+2C^1+2C^2$	1179[141]	1166	13
2	1-pentane	$9P+2S+T+C^1+2C^2+C^3$	1170[141]	1160	10
3	n-hexane	$6P+8S+2C^1+3C^2$	1357*	1353	4
4	n-heptane	$6P+10S+2C^1+4C^2$	1536[141]	1540	-4
5	2-methylhexane	$9P+6S+T+C^1+4C^2+C^3$	1533[142]	1534	-1
6	3-methylhexane	$9P+6S+T+2C^1+2C^2+2C^3$	1522[142]	1523	-1
7	3-ethylpentane	$9P+6S+T+3C^1+3C^3$	1512[142]	1513	-1
8	2,2-dimethylpentane	$12P+4S+C^1+C^2+3C^3+C^4$	1526[142]	1526	-
9	3,3-dimethylpentane	$12P+4S+2C^1+2C^2+2C^4$	1505[142]	1507	-2
10	2,3-dimethylpentane	$12P+2S+2T+C^1+3C^2+C^3+C^4$	1512[142]	1508	4
11	2,4-dimethylpentane	$12P+2S+2T+4C^2+2C^3$	1526[142]	1527	-1
12	2,2,3-trimethylbutane	$15P+T+2C^2+3C^3+C^5$	1499[142]	1500	-1
13	n-octane	$6P+12S+2C^1+5C^2$	1725[141]	1727	-2
14	2methylheptane	$9P+8S+T+C^1+5C^2+C^3$	1718[143]	1721	-3
15	3-methylheptane	$9P+8S+T+2C^1+3C^2+2C^3$	1712[143]	1710	2

TABLE XXXIII CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c./mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
16	3-ethylhexane	$9P+8S+T+3C^1+3C^3$	1698[143]	1700	-2
17	2,2-dimethylhexane	$12P+6S+C^1+2C^2+3C^3+C^4$	1714[143]	1712	2
18	3,3-dimethylhexane	$12P+6S+2C^1+C^2+2C^3+2C^4$	1693[143]	1694	-1
19	3-methyl-3-ethyl-pentane	$12P+6S+3C^1+C^3+3C^4$	1673[143]	1676	-3
20	2,3dimethylhexane	$12P+4S+T+C^1+4C^2+C^3+C^4$	1695[143]	1695	-
21	2,4-dimethylhexane	$12P+4S+2T+C^1+3C^2+3C^3$	1709[143]	1703	6
22	2,5-dimethylhexane	$12P+4S+2T+5C^2+2C^3$	1718[143]	1713	5
23	3,4-dimethylhexane	$12P+4S+2T+2C^1+2C^2+2C^3+C^4$	1688[143]	1685	3
24	2-methyl-3ethyl-pentane	$12P+4S+2T+2C^1+2C^2+2C^3+C^4$	1681[143]	1685	-4
25	2,2,3-trimethyl-pentane	$15P+2S+T+C^1+C^2+4C^3+C^5$	1679[143]	1677	2
26	2,2,4-trimethyl-pentane	$15P+2S+T+2C^2+4C^3+C^4$	1706[143]	1706	-
27	2,23-trimethyl-pentane	$15P+2S+T+C^1+2C^2+2C^3+C^4+C^5$	1668[143]	1669	-1

TABLE XXXIII CONTINUED

	Compound	Contributions	Experimental	Molar Sound Velocity (c.c./mole)(m/sec)$^{1/3}$ Calculated	Difference
28	2,3,4-trimethylpentane	$15P+3T+5C^2+2C^4$	1681[143]	1681	-
29	n-nonane	$6P+14S+2C^1+6C^2$	1923[141]	1914	9
30	n-decane	$6P+16S+2C^1+7C^2$	2097[144]	2101	-4
31	dodecane	$6P+20S+2C^1+9C^2$	2482[144]	2475	7
32	tetradecane	$6P+24S+2C^1+11C^2$	2856[144]	2849	7

Mean Deviation 3.3

TABLE XXXIV

Molar Sound Velocities of Alkynes

	Compound	Contributions	Molar Sound Velocity $(cc./mole)(m/sec)^{1/3}$ Experimental	Calculated	Difference
1	1-Pentyne	$3P+4S+T+C^1+C^2+C_3+3C_1^1$	1017^{145}	1019	-2
2	1-Hexyne	$3P+6S+T+C^1+2C^2+C_3+3C_1^1$	1203^{145}	1206	-3
3	1-Heptyne	$3P+8S+T+C^1+3C^2+C_3+3C_1^1$	1392^{145}	1393	-1
4	1-Octyne	$3P+10S+T+C^1+4C^2+C_3+3C_1^1$	1581^{145}	1580	1
5	4-Octyne	$6P+8S+2C^1+2C^2+2^3C_1^1+C_3$	1561^{145}	1588	-27
6	1-Decyne	$3P+14S+T+C^1+6C^2+3C_1^1+C_3$	1955^{145}	1954	1
7	5-Decyne	$6P+12S+2C^1+4C^2+2^3C_1^1+C_3$	1960^{145}	1962	-2
8	1-Dodecyne	$3P+18S+T+C^1+8C^2+3C_1^1+C_3$	2331^{145}	2328	3
9	1,8-Nonadicyne	$10S+2T+4C^2+2C_3+2^3C_1^1$	1635^{145}	1619	16
10	3-Butyn-1-ol	$4S+T+A^1+C_3+3C_1^1+{}^AC_1^1$	853^{145}	850	3

Mean Deviation 5.9

TABLE XXXV

Molar Sound Velocities of Aromatic Compounds

	Compound	Contributions	Molar Sound Velocity $(c.c./mole)(m/sec)^{1/3}$ Experimental	Calculated	Difference
1	Benzene	$6T + \varphi$	977[141]	977	-
2	Toluene	$3P+5T+\varphi^1+{}^{\varphi}C_1^0$	1169[141]	1165	4
3	Ethylbenzene	$3P+2S+5T+\varphi^1+{}^{\varphi}C_1^1\ C^1$	1348[141]	1348	-
4	1-Propylbenzene	$6P+6T+\varphi^1+{}^{\varphi}C_1^2+2C^2$	1510[141]	1510	-
5	O-Xylene	$6P+4T+\varphi^2+2{}^{\varphi}C_1^0$	1350[141]	1354	-4
6	p-Xylene	$6P+4T+\varphi^2+2{}^{\varphi}C_1^0$	1357[141]	1354	3
7	m-Xylene	$6P+4T+\varphi^2+2{}^{\varphi}C_1^0$	1356[141]	1354	2
8	1,3,5-Trimethylbenzene	$9P+3T+\varphi^3+3{}^{\varphi}C_1^0$	1544[141]	1521	23
9	1,2,4-Trimethylbenzene	$9P+3T+\varphi^3+3{}^{\varphi}C_1^0$	1523[141]	1521	2
10	1,2,3-Trimethylbenzene	$9P+3T+\varphi^3+3{}^{\varphi}C_1^0$	1506[141]	1521	-15

Mean Deviation 5.3

TABLE XXXVI

Molar Sound Velocities of Alcohols

	Compound	Contributions	Molar Sound Velocity (c.c./mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
1	Methyl alcohol	$3P + A^1$	420.5[141]	420.5	-
2	Ethyl alcohol	$3P + 2S + {}^{A}C_1^0 + A^1$	622.9[141]	622.9	-
3	n-Propyl alcohol	$3P + 4S + C^1 + {}^{A}C_1^0 + A^1$	799.3[141]	799.1	0.2
4	i-Propyl alcohol	$6P + T + 2{}^{A}C_1^1 + A^2$	805.6[141]	805.6	-
5	n-Butyl alcohol	$3P + 6S + C^1 + C^2 + {}^{A}C_1^0 + A^1$	990.4[141]	986.1	4.3
6	i-Butyl alcohol	$6P + 2S + T + 2C^2 + A^1 + {}^{A}C_1^2$	988.1[141]	992.0	-3.9
7	s-Butyl alcohol	$6P + 2S + T + C^1 + {}^{A}C_1^1 + {}^{A}C_1^2 + A^2$	985.8[141]	983.0	2.8
8	t-Butyl alcohol	$9P + 3{}^{A}C_1^2 + A^3$	985.6[141]	984.6	1.0
9	n-Amyl alcohol	$3P + 8S + C^1 + 2C^2 + {}^{A}C_1^0 + A^1$	1177[141]	1173	4
10	i-Amyl alcohol	$6P + 4S + T + 3C^2 + A^1 + {}^{A}C_1^2$	1173[146]	1179	-6
11	t-amyl alcohol	$9P + 2S + C^1 + {}^{A}C_1^3 + 2{}^{A}C_1^2 + A^3$	1160[146]	1162	-2
12	2-Methylbutyl alcohol	$6P + 4S + T + C^1 + C^2 + C^3 + {}^{A}C_1^2 + A^1$	1170[146]	1168	2.0
13	Pentanol-3	$6P + 4S + T + 2C^1 + 2{}^{A}C_1^2 + A^2$	1164[146]	1160	4

TABLE XXXVI CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c./mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
14	n-Hexyl alcohol	$3P+10S+C^1+3C^2+A^1+{}^{A}C_1^1$	1367^{141}	1371	-4.0
15	2-Ethylbutyl alcohol	$6P+6S+T+2C^1+2C^3+{}^{A}C_1^2+A^1$	1347^{146}	1345	2.0
16	4-Methylpentanol-2	$9P+2S+2T+2C^2+C^3+{}^{A}C_1^1+{}^{A}C_1^2+A^2$	1357^{146}	1350	7
17	n-Heptanol	$3P+12S+C^1+4C^2+{}^{A}C_1^1+A^1$	1556^{141}	1558	-2
18	Heptanol-2	$6P+8S+T+C^1+3C^2+{}^{A}C_1^2+{}^{A}C_1^1+A^2$	1552^{146}	1544	8
19	2,4-Dimethylpentanol-3	$12P+3T+4C^2+2{}^{A}C_1^3+A^2$	1521^{146}	1524	-
20	n-Octanol	$3P+14S+C^1+5C^2+{}^{A}C_1^1+A^1$	1751^{146}	1745	6
21	n-Nonanol	$3P+16S+C^1+6C^2+{}^{A}C_1^1+A^1$	1945^{141}	1932	13
22	n-Decylanol	$3P+18S+C^1+7C^2+{}^{A}C_1^1+A^1$	2137^{141}	2119	18
23	5-Ethylnonanol-2	$9P+12S+2T+2C^1+3C^2+{}^{A}C_1^1+{}^{A}C_1^2+A^2$	2290^{146}	2264	26
24	n-Dodecylanol	$3P+22S+C^1+9C^2+{}^{A}C_1^1+A^1$	2514^{146}	2493	21
25	n-Tetradecylanol	$3P+26S+C^1+11C^2+{}^{A}C_1^1+A^1$	2911^{147}	2867	34

TABLE XXXVI CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c/mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
26	n-$C_{18}H_{37}OH$	$3P+34S+C^1+15C^2+{}^AC_1^1+A^1$	3666^{147}	3615	51
27	$(CH_3)_2^1$-PrCOH	$12P+T+2C^2+2{}^AC_1^2+{}^AC_1^4+A^3$	1338^{148}	1338	-
28	$CH_3(C_2H_5)_2COH$	$9P+4S+2C^1+{}^AC_1^2+2{}^AC_1^3+A^3$	1342^{148}	1340	2
		Mean Deviation 8.0			

TABLE XXXVII

Molar Sound Velocities of Ketones

	Compound	Contributions	Molar Sound Velocity (c.c/mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
1	Acetone	$6P+K$	778.5^{*}	776.5	-
2	Methyl ethyl	$6P+2S+K+{}^{K}C_1^0$	956.3^{*}	963.0	6.7
3	Diethyl	$6P+4S+K+2{}^{K}C_1^0$	1161^{119}	1148	13
4	Methyl hexyl	$6P+10S+C^1+3C^2+K+{}^{K}C_1^1$	1720^{119}	1717	3
5	4-heptanone	$6P+8S+2C^1+K+2{}^{K}C_1^1$	1521^{141}	1534	-13
6	Methylnonyl	$6P+16S+C^1+6C^2+K+{}^{K}C_1^1$	2282^{141}	2278	4
7	Methyl phenyl	$\varphi^1+3P+5T+K$	1338^{140}	1349	-11
8	Ethyl phenyl	$\varphi^1+3P+2S+5T+K+{}^{K}C_1^0$	1519^{140}	1533	-14
9	Propyl phenyl	$\varphi^1+3P+4S+5T+C^1+{}^{K}C_1^1+K$	1709^{140}	1709	-
10	Butyl phenyl	$\varphi^1+3P+6S+5T+C^1+C^2+{}^{K}C_1^1+K$	1896^{140}	1896	-
11	Amyl phenyl	$\varphi^1+3P+8S+5T+C^1+2C^2+{}^{K}C_1^1+K$	2084^{140}	2083	1
12	Hexyl phenyl	$\varphi^1+3P+10S+5T+C^1+3C^2+{}^{K}C_1^1+K$	2275^{149}	2457	6
13	Heptyl phenyl	$\varphi^1+3P+12S+5T+C^1+4C^2+{}^{K}C_1^1+K$	2463^{149}	2457	10

TABLE XXXVII CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c./mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
14	Octyl phenyl	$\varphi^1 + 3P + 14S + 5T + C^1 + 5C^2 + {}^{K}C_1^1 + K$	2654^{149}	2644	10
15	2,5-Dimethylphenyl-methyl	$\varphi^3 + 9P + 3T + K + {}^{K}C_1^{\varphi} + 2\,{}^{\varphi}C_1^0$	1696^{149}	1697	-1
16	2,5-Dimethylphenyl-ethyl	$\varphi^3 + 9P + 2S + 3T + K + {}^{K}C_1^0 + {}^{K}C_1^{\varphi} + 2\,{}^{\varphi}C_1^0$	1880^{149}	1881	-1
17	2,5-Dimethylphenyl-propyl	$\varphi^3 + 9P + 4S + 3T + K + {}^{K}C_1^{\varphi} + {}^{K}C_1^1 + C^1 + 2\,{}^{\varphi}C_1^0$	2069^{149}	2075	-6
18	2,5-Dimethylphenyl-butyl	$\varphi^3 + 9P + 6S + 3T + K + {}^{K}C_1^{\varphi} + {}^{K}C_1^1 + C^1\,C^2\,2\,C_1^0$	2258^{149}	2262	-4
19	2,5-Dimethylphenyl-amyl	$\varphi^3 + 9P + 8S + 3T + K + {}^{K}C_1^{\varphi} + {}^{K}C_1^1 + C^1 + 2C^2 + 2\,{}^{\varphi}C_1^0$	2445^{149}	2448	-3
20	2,5-Dimethylphenyl	$\varphi^3 + 9P + 10S + 3T + K + {}^{K}C_1^{\varphi} + {}^{K}C_1^1 + C^1 + 3C^2 + 2\,{}^{\varphi}C_1^0$	2634^{149}	2635	-1

TABLE XXXVII CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c/mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
21	2,5-Dimethylphenylheptyl	$\varphi^3 + 9P + 12S + 3T + K + {}^{K}C_1^{\varphi} + {}^{K}C_1^1 + C^1 + 4C^2 + 2{}^{\varphi}C_1^0$	2826[149]	2822	4
22	2,5-Dimethylphenyloctyl	$\varphi^3 + 9P + 14S + 3T + K + {}^{K}C_1^{\varphi} + {}^{K}C_1^1 + C^1 + 5C^2 + 2{}^{\varphi}C_1^0$	3011[149]	3009	2
23	2,5-Dimethylphenylnonyl	$\varphi^3 + 9P + 16S + 3T + K + {}^{K}C_1^{\varphi} + {}^{K}C_1^1 + C^1 + 6C^2 + 2{}^{\varphi}C_1^0$	3206[149]	3196	10
24	Acetonyl acetone	$6P + 4S + 2K + {}^{K}C_1^1$	1320[141]	1319	1
25	4-Methyl acetophenone	$6P + \varphi^2 + {}^{\varphi}C_1^0 + {}^{\varphi}C_1^K + K + 4T$	1526[150]	1529	-3
26	4-Ethyl acetophenone	$6P + 2S + \varphi^2 + {}^{\varphi}C_1^1 + C^1 + {}^{\varphi}C_1^K + K + 4T$	1704[150]	1708	-4
27	4-Isopropyl acetophenone	$9P + \varphi^2 + 2C_1^2 + {}^{\varphi}C_1^2 + {}^{\varphi}C_1^K + K + 5T$	1883[150]	1916	-33
28	4-t-Butyl acetophenone	$12P + 4T + \varphi^2 + 3C^3 + {}^{\varphi}C_1^3 + {}^{\varphi}C_1^K + K$	2073[150]	2069	4
29	4-Methyl propiophenone	$6P + 2S + 4T + \varphi^2 + K + {}^{\varphi}C_1^0 + {}^{K}C_1^0 + {}^{K}C_1^{\varphi}$	1706[150]	1714	-8

TABLE XXXVII CONTINUED

	Compound	Contributions	Molar Sound Velocity $(c.c/mole)(m/sec)^{1/3}$ Experimental	Calculated	Difference
30	4-Ethyl propiophenone	$6P+4S+4T+\varphi^2+K+\varphi C_1^1+C^1+{}^KC_1^0+{}^KC_1^\varphi$	1889^{150}	1893	-4
31	4-Isopropyl propiophenone	$9P+2S+5T+\varphi^2+K+\varphi C_1^2+2C^2+{}^KC_1^0+{}^KC_1^\varphi$	2074^{150}	2055	19
32	4-t-Butyl propiophenone	$12P+2S+4T+\varphi^2+K+\varphi C_1^3+3C^3+{}^KC_1^0+{}^KC_1^\varphi$	2252^{150}	2254	-2
33	Isobutyrophenone	$6P+6T+\varphi^1+2{}^KC_1^1+{}^KC_1^\varphi+K$	1704^{150}	1709	-5
34	4-Methyl isobutyrophenoone	$9P+5T+\varphi^2+K+2{}^KC_1^1+{}^KC_1^\varphi+\varphi C_1^0$	1894^{150}	1916	-22
35	4-Ethyl isobutyrophenone	$9P+2S+5T+\varphi^2+K+2{}^KC_1^1+{}^KC_1^\varphi+\varphi C_1^1+C'$	2079^{150}	2095	-16
36	4-Isopropyl isobutryophenone	$12P+6T+\varphi^2+K+2{}^KC_1^1+{}^KC_1^\varphi+\varphi C_1^2+2C^2$	2268^{150}	2251	11
37	4-t-butyl isobutryophenone	$15P+5T+\varphi^2+K+2{}^KC_1^1+{}^KC_1^\varphi+\varphi C_1^3+3C^3$	2439^{150}	2456	-17

TABLE XXXVII CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c./mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
38	t-Butyl phenyl ketone	$9P+K+3{}^{K}C_1^2+{}^{K}C_1^{\varphi}+\varphi^1+5T$	1880^{150}	1880	-
39	4-Methyl Pivalophenone	$12P+K+3{}^{K}C_1^2+{}^{K}C_1^{\varphi}+\varphi^2+4T \quad C_1^0$	2072^{150}	2028	44
40	Benzyl acetone	$3P+4S+5T+K+\varphi^1+{}^{\varphi}C_1^1+{}^{K}C_1^1$	1721^{141}	1748	-27

Mean Deviation 8.5

TABLE XXXVIII

Molar Sound Velocities of Esters

	Compound	Contributions	Molar Sound Velocity (c.c/mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
1	Methyl acetate	$6P+E$	839.2*	839.2	-
2	Ethyl acetate	$6P+2S+E+{}^{E}C_1^0$	1037^{119}	1033	4
3	Propyl acetate	$6P+4S+E+{}^{E}C_1^0+C^1$	1214*	1220	-6
4	i-Propyl acetate	$9P+T+E+2{}^{E}C_1^1$	1224^{152}	1232	-8
5	Butyl acetate	$6P+6S+E+{}^{E}C_1^1+C^1+C^2$	1407*	1407	-
6	i-Butyl acetate	$9P+2S+T+E+{}^{E}C_1^2+2C^2$	1408*	1407	1
7	Amyl acetate	$6P+8S+E+{}^{E}C_1^1+C^1+2C^2$	1593*	1594	-1
8	i-Amyl acetate	$9P+4S+T+E+{}^{E}C_1^1+C^3+2C^2$	1591^{152}	1588	3
9	Hexyl acetate	$6P+10S+E+{}^{E}C_1^1+C^1+3C^2$	1783^{152}	1781	2
10	Heptyl acetate	$6P+12S+E+{}^{E}C_1^1+C^1+4C^2$	1973^{152}	1968	5
11	Methyl propionate	$6P+2S+{}^{E}C_1^0+E$	1031^{151}	1033	-2
12	Ethyl propionate	$6P+4S+2{}^{E}C_1^0+E$	1222^{151}	1227	-5
13	Ethyl butyrate	$6P+6S+C^1+{}^{E}C_1^1+E+{}^{E}C_1^0$	1395^{151}	1414	-19

TABLE XXXVIII CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c/mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
14	Ethyl Caprylate	$6P+14S+C^1+4C^2+E_{C_1^0}+E_{C_1^1}+E$	2135^{153}	2161	-26
15	Ethyl formate	$E^f+3P+2S+E_{C_1^0}$	884.7^{151}	857.3	27.4
16	i-Butyl formate	$E^f+6P+2S+T+2C^2_7+E_{C_1^2}$	1196^{151}	1231	-35
17	i-Amyl formate	$E^f+6P+4S+T+2C^2_7+C^3+E_{C_1^1}$	1420^{151}	1412	8

Mean Deviation 8.9

TABLE XXXIX

Molar Sound Velocities of some Chloro Derivatives

	Compound	Contributions	Molar Sound Velocity (c.c./m.l.)(m/sec)$^{1/3}$ Experimental	Calculations	Difference
1	$(CH_2Cl)_2$	$4S+2Cl+C_1^{2Cl}$	845.8[141]	850.9	-5.1
2	CH_3CHCl_2	$3P+T+C_1^{2Cl}+2Cl$	843.7[141]	833.6	10.3
3	$(CHCl_2)_2$	$2T+C_1^{4Cl}+4Cl$	1109[154]	1109	-
4	C_2HCl_5	$T+5Cl+C_1^{5Cl}$	1259[141]	1259	-
5	C_3H_7Cl	$3P+4S+C^1+C_1^{1Cl}+Cl$	909.4*	910.3	-0.9
6	$CH_3CHClCH_2Cl$	$3P+2S+T+C_1^{1Cl}+C_1^{2Cl}+2Cl$	1028[154]	1058	-30
7	C_4H_9Cl	$3P+6S+C^1+C^2+C_1^{1Cl}+Cl$	1093[141]	1097	-4
8	$C_5H_{11}Cl$	$3P+10S+C^1+3C^2+C_1^{1Cl}+Cl$	1478[141]	1471	7
9	$C_6H_{13}Cl$	$3P+14S+C^1+5C^2+C_1^{1Cl}+Cl$	1850[141]	1845	5
10	$C_{10}H_{21}Cl$	$3P+18S+C^1+7C^2+C_1^{1Cl}+Cl$	2257[141]	2219	38
11	C_6H_5Cl	$\varphi^1+{}_\varphi Cl+5T$	1109*	1116	-7
12	$o\text{-}C_6H_4Cl_2$	$\varphi^2+2\,{}_\varphi Cl+4T$	1227[154]	1247	-20
13	$m\text{-}C_6H_4Cl_2$	$\varphi^2+2\,{}_\varphi Cl+4T$	1244[141]	1247	-3
14	$1,2,4\text{-}C_6H_3Cl_3$	$\varphi^3+3\,{}_\varphi Cl+3T$	1361[151]	1361	-

TABLE XXXIX CONTINUED

	Compound	Contributions	Molar Sound Velocity (c.c/mole)(m/sec)$^{1/3}$ Experimental	Calculated	Difference
15	o-$C_6H_4CH_3Cl$	$\varphi^2+3P+5T+\varphi_{Cl}+\varphi_{C_1^0}$	1282[154]	1301	-19
16	m-$C_6H_4CH_3Cl$	$\varphi^2+3P+5T+\varphi_{Cl}+\varphi_{C_1^0}$	1300[141]	1301	-1
17	p-$C_6H_4CH_3Cl$	$\varphi^2+3P+4T+\varphi_{Cl}+\varphi_{C_1^0}$	1294[154]	1301	-7
18	$C_6H_5CH_2Cl$	$\varphi^1+2P+5T+Cl$	1304[141]	1309	-5

Mean Deviation 9.0

DISCUSSION

The success of the additivity scheme lies in its ability to reproduce known physico-chemical properties, and to predict properties which have not been subjected to experiment. Comparison of the predicted properties and the experimental properties has been shown in the preceeding Tables XXIV to XXXIX. Agreement is favorable in most cases for all properties. Often the lower molecular weight members of a family exhibit large differences between calculated and experimental values indicating the unreliability of the additivity scheme for these compounds. The agreement improves as one proceeds to higher molecular weight members.

Differences between calculated and experimental values of molar volume are greater than one percent in only a few cases.

Calculated molar refraction values are generally closer than 1% to the experimental values; there are only three compounds in which the discrepancy is greater than 1%. Generally the deviation is only a few tenths of one percent.

Calculated and experimental values of entropy agree to approximately 1%. However some large discrepancies appear, casting doubt on the experimental data.

Heats of atomization are accurately predicted

by the additivity scheme. The calculated and experimental values differing by approximately one-tenth of a percent.

Molar sound velocity data available are adequately explained by the scheme employed here. Calculated values are generally within the experimental errors. In those cases where there are large deviations between the experimental and calculated values, it is likely that the experimental results are in error.

The additivity scheme employed here also adequately predicts the diamagnetic susceptibility within experimental error. Again large discrepancies in calculated and experimental data cast doubt on the experimental data available.

The additivity scheme proposed is a reliable method of predicting the properties of compounds not yet subjected to experiment. The scheme is generally applicable to other properties and to new series of compounds with the addition of suitable parameters.

CLAIMS TO ORIGINAL RESEARCH

1) A reaction cell assembly suitable for the determination of heats of polymerization has been constructed.

2) A satisfactory procedure for determining unsaturation quantitatively by bromination has been developed.

3) A number of heats of polymerization of acrylate and methacrylate monomers have been determined.

4) A study of the relative rates of propagation of polymerization has been carried out for some acrylate and methacrylate monomers.

5) A reaction cell assembly has been constructed for the measurement of heats of vaporization at 25°C.

6) The heats of vaporization of a series of aliphatic alcohols have been determined by means of the Calvet microcalorimeter.

7) A suitable additivity scheme for prediction of heat of vaporization of aliphatic alcohols at 25°C has been developed.

8) An additivity scheme has been developed and applied to molar volume, molar refraction, entropy of formation and heats of atomization at 25°C.

9) An additivity scheme has been applied to diamagnetic susceptibilities with satisfactory results.

10) An additivity scheme has been applied to molar sound velocity with satisfactory results.

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