ABSTRACTS OF DOCTORAL DISSERTATIONS
1956

DENSITY FLUCTUATIONS IN FLUIDIZED BEDS

Peter K. Baumgarten, Chemical Engineering

Gas-fluidized beds of small particles are subject to density fluctuations which reduce rates of heat transfer and chemical reaction by impairing gas-solid contact. The fluctuations can be characterized by assuming that gas bubbles free of solids rise through a dense phase of uniform density.

The problem was investigated by measuring continuously the fluctuating absorption of a horizontal beam of gamma radiation. The experiments were carried out with air-fluidized beds of spherical glass beads and cracking catalyst in a 3-in. × 6-in. × 6-ft. rectangular column. Equations developed from statistical considerations permitted calculation of the average bubble size from the variance of the density fluctuations and the time-average bed density.

Results indicated that gas bubbles developed spontaneously owing to an influx of gas from the dense phase. The bubbles grew until they either collided with the walls or burst through the surface of the bed. The volume of the gas rising in the form of bubbles amounted to as much as half of the total gas flow. Fluidization was most uniform with cracking catalyst, for which the density of the dense phase was appreciably less than the density of the fluidized bed at the minimum fluidizing velocity.

HEAT TRANSFER AND FLUID FRICTION DURING TURBULENT FLOW THROUGH A BAFFLED CYLINDRICAL SHELL AND TUBE HEAT EXCHANGER

George A. Brown, Chemical Engineering

The shell side heat transfer coefficient and pressure drop were determined for a cylindrical baffled heat exchanger designed to eliminate or minimize internal leakage. Results were determined

for nine combinations of three baffle cuts and four baffle spacings covering the range of industrial importance. Overall heat transfer coefficients were compared with results previously obtained in the research program on simple cross-flow exchangers. A correction factor based on cylindrical exchanger geometry was determined for predicting heat transfer coefficients from published cross-flow data.

The pressure drop was measured across single window and cross-flow sections. The total pressure drop across the exchanger was found to be closely approximated by a summation of the results for the single sections. An estimation of exchanger pressure drop based on use of the velocity head concept and published cross-flow data was found to represent the total measured pressure drop to within ten per cent.

GAS FILM MASS TRANSFER ON BUBBLE–CAP TRAYS

Norman N. Hochgraf, Chemical Engineering

Murphree vapor tray efficiencies were determined for the distillation of mixtures of acetone and benzene. For this binary pair the majority of the resistance to mass transfer is in the gas film. The experimental equipment consisted of a 2-foot diameter, 5 tray distillation column having 41 $1\frac{1}{2}$ inch diameter bubble-caps on each tray.

Measurements of tray efficiencies were made over a wide range of conditions: gas rates from 1.3 to 6.4 ft./sec., liquid rates from 18 to 64 gal./min., and pressures from 19 to 93 psia. In addition, data were taken on the visual froth heights, tray pressure drop, and liquid holdup on an operating tray.

The measured tray efficiencies, corrected so as to represent only gas film resistance, were used to test an assumed mechanism of vapor-liquid contact on distillation trays. The data appear to verify the hypothesis that the major operating variables (gas rate, liquid rate, and pressure) affect tray efficiency only insofar as they affect the nominal, or average, time of contact of the gas with the liquid. This conclusion holds only for situations where liquid mixing can be considered nearly complete. The nominal residence time ap-

proach was found to correlate satisfactorily the effects on efficiency of gas rate and liquid rate found in other studies. No bubble tray data other than those of this study are known which are suitable for checking the effect of pressure on tray efficiency.

I. OXIDATION OF SECONDARY ALCOHOLS
II. THE CINEOLES

Erik Kissa, Chemistry

The oxidation of secondary alcohols with peroxides and with triphenylmethyl carbonium ion was studied. t-Butyl hydroperoxide in t-butyl alcohol oxidized benzpinacolyl alcohol to β-benzopinacolone (88%) and methyl-t-amylcarbinol to methyl-t-amyl ketone (62%). The oxidation of benzpinacolyl alcohol with t-butyl hydroperoxide or with hydrogen peroxide in acid medium yielded tetraphenylethylene, β-benzopinacolone, benzophenone and a resin. It was shown that the possible initial cleavage products benzaldehyde and triphenylcarbinol would be oxidized further under the same conditions. Benzaldehyde and triphenylcarbinol were also oxidized in neutral medium: t-butyl hydroperoxide in t-butyl alcohol oxidized benzaldehyde to benzoic acid (87%) and triphenylcarbinol to benzophenone, triphenylmethyl peroxide and a resin. Benzpinacolyl alcohol was not oxidized by di-t-butyl peroxide or by triphenylmethyl peroxide.

The reaction between isopropyl alcohol and triphenylcarbinol in the presence of sulfuric acid yielded acetone (65%), triphenylmethane (93%) and benzophenone (1%). When pinacolyl alcohol was taken instead of isopropyl alcohol the yield of benzophenone was increased (8%). t-Butyl alcohol did not react with triphenylcarbinol.

The heats of reaction of the cineoles with phosphoric acid were compared and the heats of combustion of 1,4-cineole, 1,8-cineole, tetrahydrofurane, 1,4-epoxycyclohexane, tetrahydropyran and 1,4-cis-terpin were determined.

THE SORPTION OF BORON COMPOUNDS

Klaus Robert Lange, Chemistry

The sorption of diborane, deutero-diborane and trimethyl borane is described on palladium black and coconut charcoal. The sorption of diborane is given on silica-alumina and other sorbents, including sulfides and clays. Pressures range up to 70 cm.Hg.

Adsorption on palladium is physical. From the data the arrangement of the molecules of diborane on the surface is deduced. A flat configuration is impossible.

Adsorption on charcoal is physical. The heat of adsorption is in the range of the maximum theoretical heat of physical adsorption. A degree of activation is noted, indicating activated physical adsorption.

Silica-alumina, treated to produce surfaces of varying acidity, show the Lewis acid nature of diborane. Adsorption increases as acidity decreases.

The pyrolysis of diborane is shown to be enhanced by palladium black, coconut charcoal and 5% palladium on carbon. Charcoal gives the fastest decomposition. In no case could products be isolated; polymeric material seems to be formed on the surface.

1,4,4–TRIALKYLPYRROLIDINETRIONES

Richard E. Ludwig, Chemistry

The purpose of this study was to find a means of preparing 1,4,4-trialkylpyrrolidine-2,3,5-triones and to prove their structure. The isomeric 2-dialkylmethyleneoxazolidine-4,5-diones were prepared and their structure was investigated. The chemical properties of the pyrrolidinetriones and the oxazolidinediones were studied with emphasis on alcoholysis, hydrolysis, and ozonolysis.

Eight trialkylpyrrolidinetriones were prepared by rearrangement of the isomeric oxazolidinediones in ethanol and five new oxazolidinediones were prepared by the condensation of oxalyl chloride with a trialkylacetamide.

Although the direct synthesis of a trialkylpyrrolidinetrione was

unsuccessful, several methods of rearranging an oxazolidinedione to the isomeric pyrrolidinetrione were found.

A study of the products resulting from the ozonolysis of several oxazolidinediones substantiated the presence of a double bond in this structure. The pyrrolidinetriones were unaffected by ozone. The position of the double bond in 1,4-diphenyl-3-phenylimino-maleimide has also been established by ozonolysis.

In an effort to distinguish between the two isomeric structures, the effect of aniline, ethanolic potassium hydroxide, bromine in carbon tetrachloride, potassium permanganate in acetone, and several alcohols on oxazolidinediones and pyrrolidinetriones were studied. Differentiation is also possible through the use of the infrared spectra of these compounds.

FURTHER STUDIES IN ADDITIONS TO THE DOUBLE BOND OF BICYCLO [2.2.1] HEPTENE–2 AND ITS DERIVATIVES

Jerome S. Luloff, Chemistry

This dissertation deals mainly with two problems. The first objective is to determine the steric course of addition of hydrogen bromide to bicyclo [2.2.1] heptene-2, norbornylene. Deuterium bromide is employed as the reactant under both polar and non-polar conditions and the distribution of deuterium is determined. An apparatus for the determination of deuterium oxide in D_2O-H_2O mixtures is described.

The second objective is to determine the structure of the product of reaction of bromine and tricyclo [2.2.1.0^{2,6}] heptane, nortricyclene. Dipole moment determinations and chemical techniques are employed. The addition product of hydrogen bromide and *exo*-5-bromobicyclo [2.2.1] heptene-2, *exo*-dehydronorbornyl bromide, is also described.

A number of reaction mechanisms are suggested.

A KINETIC STUDY OF THE ALCOHOLYSIS OF DECABORANE

Thrygve R. Meeker, Chemistry

Specific bimolecular rate constants for the reaction of decaborane with various alcohols in several solvents have been determined and heats of activation and Arrhenius frequency factors obtained for some cases and relative rate constants for several other cases. The specific rate constants (10^{-7} liter mole^{-1} sec.$^{-1}$) and energies of activation (kcal./mole) for the reaction in benzene solution at 25.20° C. were: Alcohol (k – E_a); Methyl (7.27 – 3.16), Ethyl (5.20 – 25.7), n-Propyl (5.35 – 24.5), Isopropyl (2.01 – 15.9), n-Butyl (6.70 – 25.5), Isobutyl (4.79 – 20.7), and sec.-Butyl (3.80 – 16.3). All specific rate constants were $\pm$ 0.15 $\times$ 10^{-7} liter mole^{-1} sec.$^{-1}$ and the energies of activation $\pm$ 0.5 kcal./mole.

The change in the rate constant with the dielectric constant of the medium and with the molecular volume of the alcohol was found to be consistent with Kirkwood's equation:

$$\ln k' = \ln k'_0 - \left(\frac{N}{R\,T}\right)\left(\frac{D-1}{2D+1}\right)\left(\frac{u_A^2}{r_A^3} + \frac{u_B^2}{r_B^3} - \frac{u_M^{\ddagger 2}}{r_M^{\ddagger 3}}\right),$$

where u is the dipole moment, r is the molecular radius, and D is the dielectric constant of the medium. The adequacy of this equation was shown by the fact that the ln k'_0 was the same for the primary alcohols except for methanol and by its ability to represent the effect of changing the dielectric constant of the medium. Since this equation represents only external electrostatic effects, it was not surprising that the branched alcohols yielded a different value of ln k'_0.

A qualitative discussion of the results of this work with reference to the ionization energies and polarizabilities of the alcohols concerned, the effect of replacing hydrogen with deuterium in the decaborane and in the alcohol, and the success of the Hirschfelder calculation of the energy of activation lead to the conclusion that the initial step in the reaction process is the rupture of the boron-hydrogen bond of the decaborane but not that of the oxygen-hydrogen bond of the alcohol. The total reaction is represented as

$$B_{10}H_{14} + 30\ ROH \rightarrow 22\ H_2 + 10\ B(OR)_3$$
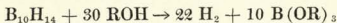
on the basis of the volume of gas produced and the yield of borate ester produced.

THE ADDITION OF SULFENYL HALIDES TO NORBORNENE AND RELATED TOPICS

Robert K. Miller, Chemistry

2,4-Dinitrobenzenesulfenyl chloride, 2,4-dinitrobenzenesulfenyl bromide, and *p*-toluenesulfenyl chloride have been added to norbornene and the structures of the products investigated. In all cases the predominant product was the *endo*-3-halo-*exo*-norbornylaryl sulfide which results from *trans*-2,3 addition of the sulfenyl halide to the double bond. Small amounts of nortricyclyl-2,4-dinitrophenyl sulfide result from the addition of the nitro sulfenyl halides, but the analogous compound does not occur during the addition of *p*-toluenesulfenyl chloride to norbornene.

The structures of the sulfenyl halide-norbornene reaction products have been determined by chlorinolysis in acetic acid-water. This reaction has been shown to be a good method of structural identification of cycloalkyl aryl sulfides. In the course of the structure determinations, some new dihalonorbornanes and halonorbornyl acetates have been identified and their properties reported.

An auxiliary method of structure determination used was the measurement of dipole moments. Structural complexities limit the usefulness of this method when norbornene-sulfenyl halide adducts are involved, but, as has been previously reported, the method is quite useful in the investigation of dihalonorbornane structures.

SOLVENT AND SUBSTITUTE EFFECTS IN ACID CATALYZED REACTIONS

Martin B. Price, Chemistry

A study has been made of the kinetics of several acid catalyzed reactions in aqueous solvents. The experimental work concerned the hydrolysis of methyl orthobenzoates and p-substituted methyl

orthobenzoates. The preparations of several of the p-substituted methyl orthobenzoates, as well as several imino ester hydrochlorides, (intermediates in the preparation of the orthoesters) are described. The catalysis has been determined to be of the general acid type. A Bronsted catalytic coefficient has been determined (alpha = 0.74). A Hammett $\sigma \rho$ relationship has been applied for the lyonium catalyzed reaction ($\rho = -2.02$), as well as the undissociated acid catalyzed reaction (non-linear). Criteria are discussed and experimental evidence included for the determination of involvement of solvent in the reaction transition state.

THE REACTION OF NITROGEN OXIDES WITH BENZALDEHYDE

Norman B. Ratiner, Chemistry

A reaction of benzaldehyde with nitric oxide has been discovered.

$$2\phi CHO + 2NO \rightarrow 2\phi CO_2H + N_2$$
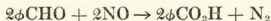
A mechanism has been proposed which accounts for the catalytic effects of nitrogen dioxide and the inhibiting action of various additives. Nitrogen dioxide is formed as an intermediate and is found to react with benzaldehyde simultaneously with nitric oxide.

$$\phi CHO + NO_2 \rightarrow \phi CO_2H + NO$$
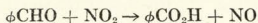
The kinetic data obtained support the reaction scheme to the best of their experimental validity.

A better understanding of the hydrogen-abstracting power of a nitrogen dioxide radical has been obtained and an approximate measure of this ability has been made. An explanation has been advanced for the greater reactivity of hydrogen abstracting radicals with aliphatic aldehydes than with aromatic aldehydes.

An apparent anomaly in the literature, the oxidation of benzyl alcohol to benzaldehyde in one case[19], and to benzoic acid in another[20], by dinitrogen tetroxide, has been explained. It was shown that minute traces of the reactant, benzyl alcohol, present in the former case, will retard oxidation of benzaldehyde to benzoic acid.
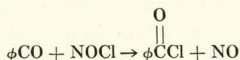
The transient existence of a nitroso benzoyl structure,

$$\phi C \overset{\overset{\displaystyle O}{\|}}{} - N = O,$$
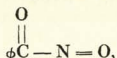
has been proposed with kinetic evidence suggesting its reaction with nitric oxide to form benzoyl diazonium nitrate.

$$\phi - \overset{\overset{\displaystyle O}{\|}}{C} - N = N - ONO_2$$
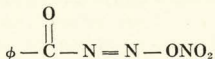
The transient existence of benzoyl radicals has been indicated by reaction with NOCL to form benzoyl chloride.

$$\phi CO + NOCl \rightarrow \phi \overset{\overset{\displaystyle O}{\|}}{C} Cl + NO$$

Kinetic data and the effects of additives also point to its existence. Substantial evidence has been presented to show that the benzoyl radical is the chain carrier in a radical chain reaction with a chain length of about 0.5.

It has been further indicated that benzaldehyde may catalyze the disproportionation of nitric oxide to a mixture of nitrogen and nitrogen dioxide, in small yields.

INTERFACIAL RESISTANCE IN GAS ABSORPTION

L. Edward Scriven II, Chemical Engineering

That phase equilibrium exists at the gas-liquid interface during gas absorption has commonly been assumed in the analysis and design of absorption equipment. It is concluded from the experimental results reported by the author and other investigators that equilibrium exists after a few thousandths of a second at a freshly-formed, clean water surface which is absorbing carbon dioxide gas; no data are available from which to draw a conclusion regarding younger surfaces. There is evidence that an accumulation of minute amounts of surface-active materials at the interface sometimes may seriously reduce the rate of gas absorption, perhaps by offering resistance to the transfer of solute molecules across the interface. Several mathematical models of interfacial resistance are presented,

and for each of them the effect of an interfacial resistance on transient absorption rates is derived. These analyses should provide a starting point for the interpretation of results as the additional data which are needed concerning the influence of absorbed layers on gas absorption become available.

Measurements of the absorption rates at 25° C. of pure carbon dioxide into short water jets, in which the liquid was in laminar flow, are reported. The jets issued from circular nozzles of about 1.5 mm. diameter, flowed intact downward at average velocities of from 75 to 550 cm./sec. over a distance of 1 to 15 cm., and were collected in a receiver slightly larger in diameter than the nozzles. An analysis is presented of the flow situation near the jet surface, based on theoretical fluid dynamics and measurements of the jet profiles. Making use of this analysis, absorption rates are predicted from unsteady-state diffusion theory, assuming interfacial equilibrium. The agreement of experiment with theory is excellent over the entire range of nominal contact time of liquid with gas, which was 0.0035 to 0.04 seconds.

New measurements of the diffusion coefficient of carbon dioxide in water at 25° C., which is required for theoretical predictions of absorption rates, are also reported. The data were obtained by the sintered-glass diaphragm cell method, and are in general agreement with the determinations of previous investigators.

THE STRUCTURE AND CONSTITUTION OF MUCUS

Victor Ezra Shashoua, Chemistry

Mucus from the large marine snail, Busycon Canaliculatum (Linnaeus), was studied in an effort to determine its structure and constitution. The mucus was extracted from the hypobranchial gland of the snail with 0.5N NaCl to give a concentration of 0.3% solids. A study of the ease of extraction showed that mucus was secreted only in the presence of salts of monovalent cations and that a maximum evolution of mucus took place at its isoelectric point of pH 7.7.

The polyelectrolyte nature of mucus was established by viscosity, light scattering, U.V. spectra, and titration experiments. The viscosity measurements showed a close resemblance to model syn-

thetic polyelectrolytes with a dependence upon the type of ions, pH, and the ionic strength of the solvent. The intrinsic viscosity (1.73 in 0.5M $CaCl_2$) indicated a high molecular weight structure. Light scattering measurements by the turbidity method confirmed this observation and gave a weight average molecular weight of 2.5–3.5×10^7 g. with a particle diameter of about 200Å. A comparison of this result with the measurements of the particle volume by the angular dissymmetry method (light scattering) showed that the particles were swollen as much as a thousand fold in solution, thus providing some explanation for the high degree of hydration of mucus. The U.V. spectral studies showed the presence of an absorption band which varied with pH in a similar manner to model polyelectrolytes such as polyvinyl pyrridine and desoxyribonucleic acid. The titration experiments confirmed the general ionic nature of mucus with an isoelectric point at pH 7.7.

The chemical composition of mucus was determined by fractionation into its component mucopolysaccharide, mucoprotein, and inorganic fragments. A study of the mucopolysaccharide and mucoprotein hydrolyzates with paper chromatography and ion exchange chromatography revealed the hexoseamine nature of the polysaccharide together with the seventeen amino acid constituents of the protein. The ratio of the acidic amino acids (glutamic acid and aspartic acid) to the basic amino acids (arginine, lysine, histidine and ornithine) was found to be 2.96, indicating the predominant acidic nature of the protein.

It was found that the properties of mucus could be accounted for by a structure consisting of a mucopolysaccharide based on a hexoseamine sulfate linked to the mucoprotein with calcium ions through the carboxyl groups of glutamic and aspartic acids. The essential points of the structure: namely an acid polysaccharide fraction, a calcium atom and an acidic protein, were found to be applicable to other mucus materials such as Ovomucin, Human Plasam Mucoprotein MPl, and bone mucus, indicating the possible generality of this concept. A number of synthetic analogues of mucus were prepared to test the hypothesis.

KINETIC STUDY OF THE CANNIZZARO REACTION

Richard N. Smith, Chemistry

The homogeneous Cannizzaro reaction with benzaldehyde has been examined kinetically using the Polarograph to follow the rate of disappearance of benzaldehyde in aqueous solutions. Rate studies were made at five concentrations of lithium hydroxide (1.5015, 1.737, 1.825, 1.90 and 2.122 M/L) and at three temperatures, i. e., 16 deg., 25 and 35 $\pm$ one degree centigrade.

Interpretation of the data according to the classical collision theory showed that the reaction was second order, as generally conceded, with respect to the benzaldehyde. However, our data leads to the conclusion (classical theory) that, in the concentration range studied here, the order with respect to the alkali concentration is two and one-half. Activation energies in the range of 8260 cal/mol were calculated. Through the addition of lithium chloride, a positive salt effect (which could not be accounted for as a simple primary salt effect) on reaction velocity was observed. A sharp controversy exists in the literature, in that some workers claim the reaction to be first order with respect to the alkali concentration while others claim second order.

Reconsideration of the effect of alkali (OH⁻), as well as the salt effect, in the light of the Theory of Absolute Reaction Rates for reactions between ions and neutral molecules, would account for the observed variation in the rate constant with alkali concentration and similarly would account for the positive salt effect observed. Hence, we may assume that the reaction is catalyzed by hydroxyl ion and that the process is third order over-all (first order with respect to the alkali). The reliable, although controversial, data from the literature on the Cannizzaro reaction has been reexamined in this light and the results are all consistent with this theory.

A MECHANISTIC STUDY OF THE
CARBOXYLIC ACID–NITRILE REACTION

Eugene L. Stogryn, Chemistry

The present investigation was undertaken to gain information on the mode or modes of the reaction between a carboxylic acid and a nitrile.

The accumulation of data from experimentation and the chemical literature has resulted in the proposal of a mechanism for the carboxylic acid-nitrile reaction.

The mechanism that best correlates the observations involves the formation of an O-acyl amide intermediate by a reaction path that does not require the formation of a free acyl carbonium ion. The O-acyl amide rearranges intramolecularly, by a four-membered cyclic transition state, to an N-acyl amide, i. e., a diamide. The reversibility of the rearrangement was demonstrated by the thermal conversion of a pure diamide to acids and nitriles.

Because of the importance of the O-acyl amide to the establishment of the mechanism, considerable experimentation was performed in an attempt to isolate the intermediate. Although the isolation of the O-acyl amide was unsuccessful the experimental evidence pointing to its formation is too numerous and conclusive to deny its transitory existence.

PREPARATION AND REACTIONS OF
VICINALLY–SUBSTITUTED HYDROXAMIC ACIDS

Marvin A. Stolberg, Chemistry

The hydroxamic acids were prepared by standard procedures from the corresponding esters or acid chlorides and hydroxylamine. Compounds which have not been previously reported in the literature are: o-nitrobenzohydroxamic, o-methoxybenzohydroxamic, o-dimethylaminobenzohydroxamic, cis-hexahydrophthalohydroxamic and exo-cis-3,6-endoxohexahydrophthalohydroxamic acids. The pKa's of the hydroxamic acids as well as other compounds prepared and isolated are reported.

Cis-N-hydroxyhexahydrophthalimide and *endo-cis*-N-hydroxy-3, 6-endomethylene-Δ⁴-tetrahydrophthalimide were prepared by the reaction of the corresponding anhydrides with hydroxylamine. Their infrared spectra were similar to the spectrum of N-hydroxyphthalimide. The structural assignment of " phthaloxime " as N-hydroxyphthalimide is corroborated.

The half-time of hydrolysis, pseudo-monomolecular rate constants and the specific rate constants for the reaction of certain *ortho*-substituted benzohydroxamic and vicinal dihydroxamic acids with Sarin are reported. A plot of the log of the specific rate constants versus the pKa's of the hydroxamic acids coincided with that previously established for *para*-substituted benzohydroxamic acids. Thus, there is no marked acceleration of the rates of reaction of hydroxamic acids with Sarin due to vicinal substitution and no alteration in the nature of the reacting group by these substituents. The most probable reactive form of the hydroxamate ion is postulated.

The reaction of Sarin with *o*-hydroxybenzohydroxamic and *o*-aminobenzohydroxamic acids yielded benzoxazol-2-one and benzimidazol-2-one respectively. The same products were obtained with benzenesulfonyl chloride in slightly reduced yields.

Cis-Hexahydrophthalohydroxamic acid and Sarin reacted to yield *cis*-3-hydroxy-1H-hexahydroquinazolinedione whereas benzenesulfonyl chloride produced *cis*-3-benzenesulfonoxy-1H-hexahydroquinazolinedione.

The reaction of *cis*-3-hydroxy-1H-hexahydroquinazolinedione with benzenesulfonyl chloride to produce *cis*-3-benzenesulfonoxy-1H-hexahydroquinazolinedione was faster than that of *cis*-hexahydrophthalohydroxamic acid. Therefore, the reaction mechanism proposed in the chemical literature for disodium phthalohydroxamate and benzenesulfonyl chloride is supported.

HEAT TRANSFER TO NON–NEWTONIAN FLUIDS

Robert D. Vaughn, Chemical Engineering

A theoretical analysis and an experimental study were made of the variables controlling heat transfer to non-Newtonian fluids in the streamline flow region.

The theoretical analysis was based upon solutions of the unsteady state heat conduction equation for the two limiting cases of non-Newtonian behavior. These analyses, together with the known relationships for the intermediate case of Newtonian behavior, permitted the development of methods applicable to all non-Newtonian fluids. As in the case of the recommended equations for heat transfer to Newtonian fluids, the theoretical analysis does not allow for distortions of the velocity profile caused by the temperature gradient in the fluid. The usual empirical correction factor for Newtonian fluids satisfactorily accounted for these deviations for the non-Newtonian fluids studied.

The proposed correlating equation, which was found to correlate the experimental data with a mean deviation of 13.5 percent, is:

$$\frac{h_{\Delta M} D}{k} = 1.75 \, \Delta^{\frac{1}{3}} \left(\frac{w \, Cp}{k \, L} \right)^{\frac{1}{3}} \left(\frac{\gamma}{\gamma_w} \right)^{0.14}.$$

Where

  h = heat transfer coefficient
  D = diameter of tube
  k = fluid thermal conductivity
  $\Delta^{\frac{1}{3}}$ = theoretical factor which accounts for difference in the flow behavior of fluids (e. g. Newtonian vs. non-Newtonian)
  w = weight rate of flow
  Cp = fluid heat capacity
  L = length of the tube
  γ = fluid consistency analogous to the viscosity of a Newtonian fluid—evaluated at the average bulk temperature
  γ_w = the above quality evaluated at the wall temperature

It was suggested that the methods applied to the solution of this problem be extended to the more complex and only slightly less important problems of heat transfer to non-Newtonian fluids outside the streamline flow region.

BETA AMINO ACID DERIVATIVES OF D–GLUCOSAMINE

Hans R. Voelkl, Chemistry

Derivatives of D-glucosamine with three different β-amino acids and with one β-amino acid dipeptide have been synthesized by two different methods. By coupling 1,3,4,6-tetraacetyl-β-D-glucosamine with acylamino acid chlorides in the presence of pyridine in an anhydrous solvent or by coupling the amine with amino acids in the presence of N,N'-dicyclohexyl carbodiimide the following compounds were prepared: N-(Carbobenzoxy-β-alanyl)-1,3,4,6-tetraacetyl-β-D-glucosamine, N-(Carbobenzoxy-β-phenyl-β-alanyl)-1,3,4,6-tetraacetyl-β-D-glucosamine, N-[Carbobenzoxy-β-(p-methoxyphenyl)-β-alanyl]-1,3,4,6-tetraacetyl-β-D-glucosamine and N-(Carbobenzoxy-β-alanyl-β-phenyl-β-alanyl)-1,3,4,6-tetraacetyl-β-D-glucosamine. These carbobenzoxy glucopeptide acetates gave the corresponding crystalline carbobenzoxy glucopeptides on deacetylation with sodium methoxide. Hydrogenolysis of the deacetylated compounds in the presence of palladium black and acetic acid gave uncrystallizable syrups which reduced Fehling's solution and gave positive biuret tests.

NORBORNYLENE DIOLS AND RELATED COMPOUNDS

William G. Vosburgh, Chemistry

The three vicinal diols of bicyclo[2.2.1]heptane have been prepared. The *cis-exo*-bicyclo[2.2.1]hepta-2,3-diol was synthesized by the oxidation of bicyclo[2.2.1]heptene-2 with cold, dilute, aqueous potassium permanganate. The *cis-endo*-bicyclo[2.2.1]hepta-2,3-diol was prepared by reduction of the Diels-Alder adduct of cyclopentadiene and vinylene carbonate, followed by either alkaline or acid hydrolysis of the carbonate to the diol. The *trans*-bicyclo[2.2.1]hepta-2,3-diol was obtained upon the stepwise reduction of bicyclo[2.2.1]hepta-2,3-dione. The dione was first reduced to the *endo*-acyloin with zinc and acetic acid and the acyloin then reduced to the *trans*-diol with sodium and alcohol.

A fourth diol in this series, namely 2-*exo*-7-*cis*-dihydroxynorcam-

phane, was prepared. When bicyclo[2.2.1]-heptene-2 was reacted with hydrogen peroxide in formic acid, an excellent yield of the 2,7-diol was obtained. The same diol resulted from the acid rearrangement of the *exo*-bicyclo[2.2.1]-2,3-epoxyheptane.

The structural assignments given to the four diols were based on the periodic test, infrared spectra, analysis, mixed melting point depression, methods of synthesis and intramolecular hydrogen bonding measurements.

It was determined that when norcamphor or *α*-substituted norcamphors were reduced with $LiAlH_4$ the *endo*-alcohols were produced. For example, norcamphor quinone yielded the *endo*-bicyclo [2.2.1]hepta-3-one-2-ol upon reduction with one equivalent of $LiAlH_4$ and the *cis-endo*-bicyclo-[2.2.1]hepta-2,3-diol was produced with an excess of the reducing agent. Likewise, *endo*-bicyclo[2.2.1]-3-bromohepta-2-one yielded the *cis-endo*-bicyclo[2.2.1]-3-bromohepta-2-ol on reduction with $LiAlH_4$.

Reduction of norcamphor quinone with zinc and acetic acid also yielded the *endo*-bicyclo[2.2.1]hepta-3-one-2-ol.

When *endo*-bicyclo[2.2.1]hepta-3-one-2-ol was reduced with sodium and alcohol the reduction went *exo* and *trans*-bicyclo[2.2.1]hepta-2, 3-diol was produced.

It was noted that neither *cis-exo-* nor *cis-endo*-bicyclo[2.2.1]hepta-2,3-diol would undergo rearrangement even under severe acid conditions. Also no epimerization of the glycols could be noted upon treatment with sodium and fluorenone. No attempt was made to either rearrange or epimerize the *trans*-bicyclo[2.2.1]hepta-2,3-diol.

When *endo*-bicyclo[2.2.1]-3-bromohepta-2-ol was treated with alkali no *endo*-epoxide was produced but the bromohydrin did dehydrohalogenate and the parent ketone, norcamphor, was obtained. The structures of *cis-endo*-bicyclo[2.2.1]-3-bromohepta-2-ol and *endo*-bicyclo[2.2.1]-3-bromohepta-2-one were established.

Evidence was deduced from the intramolecular hydrogen bonding measurements of the diols and the shift of the carbonyl frequency of *endo*-bicyclo[2.2.1]-3-bromohepta-2-one confirming the fact that the cyclopentane ring system in norcamphane is puckered.

SEVERAL ASPECTS OF ACID CATALYZED REACTIONS: KINETICS AND MECHANISM

Lewis B. Weisfeld, Chemistry

Two divergent types of acid catalyzed reactions have been investigated: one, illustrating features of general acid catalysis; the other, " specific oxonium " catalyzed or " lyonium ion activity controlled."

The isomerization of 5-alpha,6-beta-dibromocholestane to 5-beta, 6-alpha-dibromocoprostane in benzene solution at 44° shows correspondence with the general acid catalytic theory of Brønsted. The mechanistic implications of this are herein considered and it is concluded that the breaking of the carbon-bromine (5) bond is rate-determining. The observed acid catalysis is correlated with acid molecularity, and in this respect new evidence is brought forth on the nature of acid catalysis in non-aqueous media.

It is demonstrated that the rate of racemization of optically active 3-p-menthene is equal to the rate of saturation of the double bond in highly acidic aqueous alcoholic media. These results exclude a reaction sequence in which a carbonium ion of classical designation is formed in a preliminary reversible protonic equilibrium. The rates of hydration are correlated with the Hammett acidity function as well as the Grunwald activity postulate to establish a reaction mechanism whereby a pi-complex is formed in a preliminary equilibrium, followed by rate-determining transition to a carbonium ion, with the exclusion of solvent from the rate-determining transition state. The acidity function and the activity postulate have been combined and extrapolated to give greater scope of interpretation to several other reactions of similar mechanism in ethanol-water systems.

THE KINETICS OF NITROGEN DIOXIDE
ABSORPTION IN WATER

Martin M. Wendel, Chemical Engineering

An investigation of the absorption of nitrogen dioxide-nitrogen tetroxide gas mixtures into water was made to determine that rate-controlling step in the process. Equilibrium mixtures of NO_2 and N_2O_4 were absorbed from a nitrogen carrier into water in very short wetted-wall columns which were used to give known flow conditions in both the gas and liquid phases. The penetration theory, or unsteady-state absorption plus reaction theory, was used to interpret the results.

The controlling mechanism in the absorption was found to be the homogeneous, liquid-phase reaction of dissolved nitrogen tetroxide with water. Rate constants for this pseudo-first-order hydrolysis of 294 sec.$^{-1}$ at 25° C. and 1342 sec.$^{-1}$ at 40° C. were obtained. The solubility of dissolved but unreacted N_2O_4 in water was also derived from the absorption rate data and was found to be about thirty times the solubility of carbon dioxide at the same temperature.

No effect of gas rate was found, indicating that diffusional resistance in the gas film was negligible. Changes in contact time between gas and liquid had no influence on the absorption, showing that the concentration distribution of absorbed material reached steady-state during the time of exposure of the liquid to the gas and that diffusion and chemical reaction rates are of equal importance in the mass transfer rate. The absorption rate was directly proportional to the interfacial partial pressure of nitrogen tetroxide, showing that this was the compound being absorbed rather than nitrogen dioxide. An increase in temperature from 25 to 40° C. caused a slight decrease in absorption rate owing to the decrease in solubility of N_2O_4.

A qualitative study of the fluid dynamics in short columns showed that two kinds of waves occurred on the liquid surface in the column near the exit liquid slot. They are capillary waves, which were caused by surface tension effects and had no influence on mass transfer, and stagnant waves, which were a result of surface

contamination by impurities in the liquid and which caused the surface downstream of them to be partially inactive during absorption.

REACTIVITY OF CELLULOSE TOWARD ACETYLATION

Harry D. Williams, Chemistry

The reactivity of cellulose toward acetylation was measured by a new method which involved measuring the rate of temperature rise during perchloric acid catalyzed acetylation of water-pretreated cellulose in the presence of an inert diluent, 2,2'-dichlorodiethyl ether. The rate of temperature rise correlated well with actual substitution obtained and with moisture regain values of the starting cellulose.

Cellulose, in which approximately one half the primary hydroxyl groups had been oxidized by nitrogen dioxide, was much less reactive than the starting cellulose. On the other hand, cellulose which had been acetylated to about the same extent on the secondary hydroxyls was as reactive as the starting cellulose for the first half of the reaction.

Highly polar liquids such as dimethylformamide were as effective as water in pretreating cellulose. Less polar liquids such as n-octyl alcohol or acetic acid were much less effective.

Heating cellulose in organic liquids decreased its reactivity with accompanying decreased molecular weight and moisture regain. Grinding cellulose, on the other hand, increased its reactivity toward acetylation.

Sulfuric acid-catalyzed acetylation of unpretreated cellulose gave the same relative reactivity as perchloric acid-catalyzed acetylation; temperature rise and substitution effects were much smaller, however.