THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF (I) REACTION KINETICS. (II) THEORY OF LIQUIDS, AND (III) OPTICAL ROTATION

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The list of publications 79 titles. Methods of pressure calibrations of high pressure are developed. The decomposition and electrical conduction of a variety of compounds have been studied over a wide range of temperatures and pressures. The "region of indifference" to a phase change with pressure in camphor has been found to decrease markedly with purification. Mini
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batteries have been studied with the purpose of using them as sensors for high pressures. The enzyme lysozyme has been studied under changing pressures and ionic strengths and the results explained theoretically.

The conformation of many biological molecules is critical for their physiological effectiveness. Because of this we have entered into an extensive study of the adsorption spectra and circular dichroism (CD) supplemented by quantum mechanics. These considerations are widely applicable and are reported, in part, here. Besides experimental measurements the quantum mechanical basis of C. D. has been extensively studied and reported. Magnetic circular dichroism (M. C. D.) is less sensitive to conformation change than C. D. but is a valuable supplement to adsorption spectra in determining the electronic structure of molecules. The fact that some bands have negative and some positive M. C. D. permits the resolution of many problems raised by adsorption spectra. We have made extensive use of M. C. D. in studying molecular studies and some results are reported here. Reaction rates have long been a special concern of the principal investigator and the measurements and theoretical explanations for a variety of systems are reported. Because chromatography is a dynamic separation depending on the distribution between the stationary and flowing phase, it is important to know the theoretical plate height of a chromatographic column. This matter is treated here.

Electrochemistry is important for batteries, for corrosion and for revealing information about the properties of surfaces, such as their catalytic properties. These questions are studied and treated in the report. A particularly important result is the development of a theoretical equation to predict the rate of atmospheric corrosion of galvanized surfaces. This is a widely applicable result.

Theoretical and Experimental Investigations of (I) Reaction Kinetics (II) Theory of Liquids and (III) Optical Rotation

Final Report

Henry Eyring, Principal Investigator

F bruary 14, 1975

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DA-ARO-D-31-124-72-G15

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Table of Contents

Final Twelve Year Report of Grant DA-ARO-D-21-124-G298, DA-31-124-ARO-D-408 DA-ARO-D-31-124-G1051, DA-ARO-D-31-124-G1110, DA-ARO-D-31-124-71-G5 and DA-ARO-D-31-124-72-G15 of the Army

by Henry Eyring

Some measure of what was accomplished is given by the list of seventy-nine titles of publications credited all or in part to Army support. The titles and authors follow together with the number of the paper in the authors list of publications which will be used to identify the paper hereafter in this report.

LIST OF PUBLICATIONS

I. High Pressure

399. "The Melting and Pyrolysis of Teflon and the Melting of Silver Chloride and Iodine under High Pressure", by M. Tamayama, T. N. Andersen and H. Eyring, Proc. Natl. Acad. Sci., 57 3, 554-561, (1967).

345. "On the Region of Indifference for High Pressure Transitions in d-Camphor (II-III) and Phosphorus (I-II)", by A. F. Gabrysh, A. Vanhook and H. Eyring, J. Phys. Chem. Solids, 25, 129-133, (1964).

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410. "Study of Pressure Calibration and Pressure Distribution in a Piston-Cylinder High Pressure Press", by M. Tamayama and H. Eyring, Rev. Sci. Instru., 38, 8, 1009-1018, (1967).

416. "Some Techniques for High Pressure Experiments", by M. Tamayama and H. Eyring, Rev. Sci. Instru., 38, 11, 1666-1667, (1967).

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II. Spectroscopy Excluding Magnetic Circular Dichroism

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VI. Liquid Structure

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VII. Electrochemistry

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VIII. Reaction Rates - Applied

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510. "Atmospheric Corrosion", by B. Robertson, C. C. Chu, T. N. Andersen and H. Eyring, Proc. Natl. Acad. Sci., 71, 2, 245-247, (1974).

506. "A Molecular Mechanism of General Anesthesia", by J. W. Woodbury and J. S. D'Arrigo, Anesthesiology, 38, 415-424, (1973).

Summary Results

The next thing that might be done to give an indication of the results of the research would be to give all seventy-nine abstracts of the papers but this is too long so even these abstracts need to be abbreviated.

Consequently certain highlights will be indicated which can readily be amplified by the interested reader by consulting the literature. Many substantial efforts will of necessity not be mentioned in this summary report.

I. High Pressure:

In paper (383), the electrical conductivities of protoporphyrin, hematoporphyrin free base, hematoporphyrin dihydrochloride, copper protoporphyrin, hemin, hematin, etroporphyrin and vandyl etroporphyrin are reported at static pressures of 1-90 kilobars and at temperatures of 25 to 100°C. The study was made in a Bridgman anvil press. A resistivity reduction of as great as five orders of magnitude was observed for the bridged compounds (hemin, hematin and vandyl etroporphyrin) over the pressure range, and a corresponding activation energy decrease by more than half was observed in the same pressure range. The resistivity versus pressure curves for these compounds showed a change in slope, and the activation energies of the nonbridged compounds were essentially pressure independent. A hole-conduction mechanism independent of pressure for the nonbridged porphyrins accounts for the observed results. A conduction mechanism for the bridged compounds is proposed which involves passage of the electron from one chelated cation to the next through the bridging anion. Two rate determining processes in series are required to explain the electron mobility.

In paper (389) the electrical resistances of several polyaromatic-halogen intermolcular charge complexes (pyrene with varying concentrations of bromine, coronene with iodine, and perylene with bromine) were measured at pressures up to 80 kilobars. Activation energies as a function of composition were measured for the pyrene. XBr_2 samples, as were Seebeck coefficients and activation energies at varying pressures for one of the complexes. The resistance decreases with increasing pressure is interpreted as due to an increase in concentration of charge carriers. Possible states in which the charge carriers exist are discussed.

In paper (389) artificial coalification of high volatile bituminous coal was experimentally effected by heating the coal at temperatures up to 850°C at pressures of 30 kilobars. Such samples were compared with coal heated at atmospheric pressure and also with standard coal samples of various ranks, by means of ultimate analysis, X-ray spectroscopy, Infra-red spectroscopy and electrical resistivity. The above tests indicate that heat breaks off fragments "volatiles" of the coal structure, and drives them off as gases, while high pressure causes retention of many of these products through retardation of bond breakage or through reactions which condense them onto the coal structure. The structure of coal subjected to elevated temperatures and pressures, tends toward that of higher rank coals, while the product of low pressure heating tends toward coke.

In paper (345) report is made of the effect of pressure on the transformation in d-camphor and phosphorus. The so-called "region of indifference" reported as approximately .38 kilobars in phosphorus, was found to be less than .14 kilobars

and .16 kilobars respectively. Rates of transformation between phases showed strong dependence on the purity of the material, and it is suggested that for sufficiently high purity the region of indifference may become vanishingly small.

In paper (392) a large amount of data is reported for the transmission of light in sapphire both radiation damaged and undamaged in the ultraviolet, visible and infra-red regions as well as in the Shuman region of the ultraviolet. The crystals had been previously subjected to 30 kilobars of pressure which induced slips on the basal (0001) and (1210) planes. The color centers were induced by Co^{60} γ-radiation and bleached with radiation from a mercury lamp. Gratinglike slip bands were prominent features of the compressed crystals. In paper (399), teflon (polytetrafluoroethylene), was investigated up to 30 kilobars and the decomposition temperatures, and the melting temperatures of silver chloride and iodine were determined up to thirty kilobars and 20 kilobars respectively. In paper (403) the plastic deformation of marble is interpreted as arising from two sets of slip planes. In one there is dislocation movement along grain boundaries and in the other through crystal grains. The experimental results of Dr. H. C. Heard find a satisfactory explanation using this model. In paper (405) a study is made of the thermal decomposition of β-cholestanyl S-methyl Xanthate at temperature of 176-236°C and pressures from 1-12,000 atmospheres. Decomposition is retarded by pressure. The results are systematized using **Absolute** Reaction Rate Theory. In paper (406) the electrical resistances of β-rhombohedral and tetragonal polycrystalline boron were measured at temperatures from 25°C to 300°C and pressures from 1 atmosphere to 60 kilobars. The thermoelectric power was measured up to 13 kilobars. With increasing temperature the resistance, R, continually decreased and the thermoelectric power, Q, at first increased and then levelled off. The log R vs. 1/T and Q vs. T curves indicate intrinsic conduction at high temperatures becoming extrinsic at the lowest temperatures studied. In the intrinsic region an increase in pressure causes a reduction in the resistance, energy gap and thermoelectric power of boron. For the low-temperature extrinsic region pressure lowers the resistance and hardly affects the thermoelectric power. These effects are discussed further in the paper. Paper (406) is a detailed study of pressure calibration and pressure distribution in a piston-cylinder high pressure press as the title indicates. Much detailed information is given and rules are developed for estimating pressure drops through materials under high pressure. Paper (416) gives helpful details for preparing samples and making measurements at high pressure.

Well behaved batteries are ideal instruments for measuring high pressures when appropriately protected and calibrated. With this in mind a study was made of the effect of high pressure on the voltage and current output of silver oxide-

zinc miniature batteries. Their emf varies with pressure in the manner expected based on the thermodynamics of the cell reactions. The results are elaborated in the paper.

As expected from significant structure theory the thermal conductivity of liquids, K_l, is well represented by the formula:

$$K_l = \frac{V_s}{V} K_s + (1-\frac{V_s}{V}) K_g$$

where V_s and V are the molar volumes of solid and liquid respectively and K_s and K_g are the thermal conductivities of the solid-like and vapor-like structures in the liquid. In paper (355) the behavior of argon and nitrogen were examined above and below the critical point and under pressure. The expected correlation with V_s/V which was found is a most gratifying result and of very general applicability for thermal conductivity of liquids not having metallic electrical conductance.

II Spectroscopy-Excluding Magnetic Circular Dichroism

In this section we will briefly characterize nine papers. In paper (438) the ultra-violet absorption, and in some cases, the optical rotatory dispersion and circular dichroism data of some sulfur-containing ribonucleosides are reported. Both the pH effect and the correlation of spectral data with the non-sulfur containing nucleosides show that the intense absorption bands in the 300 to 350 millimicron region are due to the $\pi \rightarrow \pi^*$ intramolecular charge-transfer transition by moving the charge from the sulfur-containing substituents to the purine ring. In paper (348) the variational principle is applied to the one electron theory of optical rotation of 3 methylcyclopentanone. The numerical results are compared with the results obtained by Kauzmann, Walter and Eyring. The variational method is better than the perturbation theory for the visible, where many excited states make appreciable contributions, since suitable eigenfunctions for excited states are hard to come by. The procedures employed should be widely applicable. Paper (356) is a review chapter written for the 1964 Annual Review of Physical Chemistry covering optical rotation. It treats optical rotatory dispersion and circular dichroism both theoretically and experimentally and is a useful introductory approach for workers in that field.

In paper (388) the Kerr Effect, the dispersion of electric birefringence, is treated quantum mechanically and is compared with the classical result. The determination of the direction of the transition moment for an electronic transition through the measurement of the dispersion of the Kerr constant is discussed. The numerical calculation of the Kerr constant is made for ethylene and acetone and is in satisfactory agreement with experiment.

Paper (470) a theoretical analysis of emission spectra of electronic transitions of molecules in dense media investigates the nature of band shapes of emission spectra and their relation to the rate of non-radiative processes. Two cases are discussed, one in which the Franck-Condon principle applies and the other in which the electronic transition is symmetry-forbidden but vibronic-allowed. The moment relations of emission spectra are derived and their application demonstrated. In paper (477) semiempirical quantum mechanical treatments are applied to the ethylenediamine di-cation, mono-cation, and neutral molecule by the use of the extended Huckel theory. The minimum energies of conformations of molecules for rotation about the CH_2-CH_2 axis is found. The theoretical predictions for the conformation with minimum energy are in good agreement with the experimental values. The importance of the ethylenediamine conformations are discussed. In paper (492) the optical and conformational properties of certain 7-ribosyl purines have been studied using several experimental and theoretical methods. The CD, MCD and absorption spectra of the 7-ribosyl purines and their cations have been determined experimentally with some solvent effects being noted. Theoretically we have used the SCF-CI and CNDO molecular orbital calculations to determine the optical properties of the bases. On the basis of these calculations, we concluded that the oxy derivatives and the amino derivatives are predominately in the "extreme anti" conformation and "standard anti" conformation, respectively. However, the conclusions are tentative since at the present time the band assignments are not unequivocal. At least one $n\rightarrow\pi^*$ transition has been identified in the spectra which is not notably sensitive to pH and solvent effects. Several implications of this observation are discussed. In paper (496) we develop the systematics in the electronic spectra of nucleoside derivatives. With the exception of adenine-like chromophores, a strong intuitive approach has been quite fruitful in explaining the fundamental nature of the major nucleoside chromophores. The most practical way of estimating the chromophore properties is via the semi-empirical SCF method, but it is not clear how accurate these calculations are, especially with regard to higher energy states. The mutual agreement of the two methods we have explored here speaks well for the Adams-Miller program and also for Simpson's independent system approach to spectroscopy. Paper (516) is a molecular orbital study of the conformation of Formycin. The proposition that the biological activity of formycin is a consequence of its ability to readily adopt either the anti or syn conformations is an attractive one. However, due to the recent report (Prusiner, Brennan and Sundaralingam, 1973) that formycin monohydrate is neither syn nor anti in the crystalline state, this proposition needs further consideration. Against this

background we have made molecular orbital calculations using the Iterative Extended Huckel Theory on lone gaseous formycin and adenosine molecules in order to compare the conformational energy curves of these two compounds. The paper should be consulted for the results of the calculation.

III. Magnetic Circular Diameter Studies of Molecular Structure

In paper (365)the Faraday rotations of certain tetrahedral and octahedral transition-metal complexes are examined by using Kramer's equation from the view-point of the crystal-field theory. Paper (473) is a chapter in the Annual Reviews of Physical Chemistry in 1971 on Magnetic Circular Dichroism. It considers both the theory and applications. In summary, the most common use of MCD appears to be in deciding whether the excited state of a transition has threefold or higher symmetry on the basis of whether the MCD shows an A or a B term. However, Stephens has reversed this procedure and, upon observing an A term in the spectrum of sulfur dissolved in oleum, he has postulated the existence of square planar S_4^{2+} in analogy with the well-characterized species Te_4^{2+} and Se_4^{2+}. This is claimed to be the first use of MCD in the identification of a new chemical species. In paper (488) the MCD spectra of the d-d transitions of ferrocene and some substituted ferrocenes are measured and found to fall into two distinct categories: one group of compounds giving absorption-like peaks and the other giving S shaped curves. It is found that the lowering of symmetry of the molecule is responsible for the difference. In paper (489) the theory of the magnetic circular dichroism of molecules in dense media is treated. The magnetic circular dichroism (MCD) of molecules dissolved in dense media has been investigated for the case in which the Franck-Condon principle applies and for the case in which the electronic transition is symmetry-forbidden but vibronic-allowed. In the adiabatic approximation and the approximation that the effect of the static magnetic field on the energy and wave function of nuclear motion is negligible, we have shown that the band shape of MCD is mainly determined by nuclear motion, while the electronic portion of the system is responsible for the strength of MCD. MCD and absorption coefficient are compared. It is found that for non-degenerate systems, for a particular electronic transition in which the Franck-Condon principle applies, the band shapes of MCD and absorption spectra are identical. The moment relations of MCD are also discussed. As an application we study the MCD for the $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ and $n\rightarrow\sigma^*$ transitions of the formaldehyde molecule. In paper (503) a general method for correlating data from CD and MCD spectra is formulated. The origin dependence of the MCD terms is resolved by minimization of appropriate terms in the Lagrangian density expression. Approximate summation techniques are developed for magnetic and natural optical activity. The salient

features of the MCD spectra of benzene derivatives are analyzed. The observed opposite signed magnetic rotational strengths of (o, p)- and m-directors is accounted for by a variation calculation which includes electron donor and acceptor wavefunctions based on occupied and unoccupied substituent orbitals. The uniqueness of the alternating signed benzene spectrum as compared with most hexasubstituted derivatives of D_{6h} symmetry is rationalized on the basis of the vibrational modes of E_{2g} symmetry for carbon-carbon bond stretching and bending. The importance of comparable vibronic and electronic effects is emphasized in the anomalous behavior of the B_{2u} and B_{1u} bands for low symmetry derivatives. A continuation of our study of substituted benzenes is reported in (505). The magnetic circular dichroism (MCD) of benzene and 27 derivatives through the absorption region 1850-3000 Å have been measured. Two different electronic transitions in the region 2000-2300 Å (generally assigned to benzene $^1B_{1u}$ upper state) were observed in some of the compounds. The theory developed by Sklar, Platt and Petruska for predicting the intensity of the benzene $^1A_{1g} \rightarrow {}^1B_{1u}$ electronic transition is adapted to correlate the sign and intensity of the substituted benzene MCD in this region. The method predicts the correct MCD sign and gives approximate estimates of the magnitude of the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition. We report in paper (508) that the isolation and characterization of several antibiotics and minor components of specific t-RNA's as nucleosides has generated a significant interest in the direct glycosylation and alkylation of purines and certain closely related derivatives. This prompted us to initiate a MCD study using the N-methyl purines since there does appear to be a significant change in electronic structure for this series of compounds. The MCD and absorption spectra of 1-, 3-, 7- and 9- methylpurine (5-7) were determined with the essential information from the MCD spectra being summarized. Molecular orbital calculations of MCD spectra of benzene-indole sequence is reported in paper (509). The magnetic circular dichroism of benzene and indole derivatives was measured down to 190 nM. The following pairs of molecules have magnetic circular dichroisms of the opposite sign in the B_{2u} absorption region: aniline and benzonitrile, indene and indoline, indole and 4-aminoindole and 4-aminoindole and 5-aminoindole. The sign and magnitude of the magnetic circular dichroisms observed are in good agreement with those calculated by the semiempirical self-consistent field with configuration interaction Pariser-Parr-Pople method with incorporation of variable π-electronegativity and σ-polarization. The energy dominator in the magnetic rotational strength expression serves to limit the important contributions to a few terms only. The purpose of paper (511) has been to study the effect of chemical substitution

on the magnetic circular dichroism and absorption spectra for the parent molecule which has the C_{2v} symmetry. Four electronic transitions, $A_1 \rightarrow A_1$, $A_1 \rightarrow B_1$, $A_1 \rightarrow B_2$ and $A_1 \rightarrow A_2$ have been considered. In each case, the intensity changes in magnetic circular dichroism and absorption spectra due to substitution have been expressed in terms of number of substituents and positions of substitution.

IV. Reaction Rates

Paper (347) the Absolute Reaction Rate Theory and the Law of Mass Action was an invited paper honoring Guldberg and Waage. Absolute Reaction Rate Theory is developed and used to discuss the uses and limitations of Mass Action in actual chemical reactions. Paper (395) is the text of the presidential address, delivered by Henry Eyring retiring president of A.A.A.S., on December 28, 1966 at the Washington meeting. It is concerned chiefly with membrane permeability and nerve action. Paper (409) and (417) carry the matter further especially with respect to the chemical senses. Models in Research (440) is an invited address delivered to a Quantum Chemistry Symposium at Sanibel Island honoring the author. It recounts centain research developments originating in the speakers laboratory which illustrate the utility of scientific models. Paper (457) reports that some optically active (L-amino acidato) triethylene-tetraminecobalt iodides (abbreviated cis-β_2-(Co(Trien)-(L-AA))I_2) have been prepared, and the loss of optical rotation of aqueous solutions containing these compounds has been studied. Possible structural changes which occur in the overall racemization may include (a) change in relative configuration of the triethylenetetramine ligand about the cobalt atom with respect to the amino acid ligand, (b) racemization of the asymmetric secondary planar amino in the trien group, (c) displacement of various ligands about the Co by water or hydroxyl ions, and (d) racemization of the asymmetric carbon atom in the amino acid. The kinetics of the racemization have been studied by measuring the optical rotation, ellipticity (CD) and absorption spectra as a function of time and by studying the influence on these racemization vs. time curves of pH, charcoal, and the variation of the type of amino acid in the initial reactant. From these measurements a mechanism for racemization is proposed and the relative rates of the various steps in the mechanism are deduced for the various conditions.

An important environmental problem is the accumulation of pesticides in soils. Paper (463) addresses itself to this problem. A theoretical model for the accumulation of pesticides in soil has been proposed and discussed from the viewpoint of heterogeneous reaction kinetics with a basic aim to understand the complex nature of soil processes relating to the environmental pollution.

In the bulk of soil, the pesticide disappears by diffusion and a chemical reaction; the rate processes considered on the surface of soil are diffusion, chemical reaction, vaporization and regular pesticide application. The differential equations involved have been solved analytically by the Laplace-transform method. A formulation of reaction rates in term of quantum mechanics is given in paper (471). We first use the time-dependent Schrödinger Equation to treat rate processes. An exact procedure would lead to serious difficulties, but it is possible to formulate the problem and so get a feeling for the nature of the difficulties. Having done this, we develop the equilibrium theory of reaction rates which has been successfully applied in a wide variety of cases. This involves treating the system at the transition state as an activated complex, like other molecules, except that it has a fourth translation corresponding to motion along the reaction coordinate. The equilibrium rate of crossing the barrier must then be corrected for non-equilibrium conditions and for quantum effects. This correction is formally lumped into a mean, κ. It is a matter of considerable interest to relate absolute reaction rates and chemical reaction cross sections. This is done in paper (474). Detailed specific rate constants of bimolecular reactions have been derived from the viewpoint of the absolute reaction rate theory, and the corresponding reaction cross sections have been obtained. The energy dependence of the reaction cross sections of the absolute reaction rate theory in the high energy range has been discussed, and it has been shown that the cross sections of the absolute reaction rate theory converge as the energy approaches infinity, if the effect of the exclusion of the disallowed states is properly taken into account. Paper (376) presents a useful method of estimating the reaction rates important in mass spectrography. The calculation of these rates was initiated in this laboratory. In paper (499) a general quantum mechanical approach for treating a great number of rate processes is developed and the temperature dependence of the rate constants is discussed. The purpose of paper (507) is to show how to apply the singular perturbation method to the rate equations in reaction kinetics that involve different time scales. The Lindemann scheme has been chosen for illustration, and the steady-state and equilibrium approximations used in the Lindemann scheme are discussed. In paper (513) the composition and formation constants of molecular complexes are investigated. The theoretical results have been verified experimentally on the weak interaction between naphthalene and methyl iodide. The purpose of paper (521) has been to develop a systematic approach for classifying and distinguishing the relative orders of approximation of various types of couplings like the vibronic (Herzberg-Teller) couplings and

Born-Oppenheimer couplings, and for studying the importance of the anharmonicity in the quantitative calculation of the spectral intensity and electronic relaxation. It will be shown that the perturbation parameter introduced by Born and Oppenheimer in separating the electronic and nuclear motion involved in the molecular Schrödinger equation, $\lambda = (m/M)^{1/4}$, can be used for this purpose by expanding wavefunctions and energies in power series of λ. Paper (522) is a study of the Frank-Condon and Herzberg-Teller quantum mechanical approxmations. Using the Born-Oppenheimer parameter $\lambda = (m/M)^{1/4}$ as a perturbation parameter, we find that for allowed transitions, the zeroth order approximation of the spectral intensity gives rise to the Condon approximation, the first order vibronic coupling and anharmonic effect appear in the first order approximation of the spectral intensity, which gives us the non-Condon scheme, and only the intensity of the transition of totally-symmetric modes with nonvanishing normal coordinate displacements is affected by the inclusion of the first order vibronic coupling and anharmonic effect. For symmetry-forbidden but vibronic-allowed transitions, the first nonvanishing term of the spectral intensity is second order with respect to λ and the B-O couplings do not appear in the calculation of the spectral intensity until the fourth order approximation with respect to λ; in this case, other high order vibronic couplings and anharmonic effect are competing with the B-O couplings.

V. Chemical Analysis

Paper (350) is a calculation of the contribution of interfacial resistance to theoretical plate height in gas chromotography. An investigation has been made into the magnitude of the interfacial resistance to the plate height of gas-liquid chromatographic columns. It is found that this contribution depends on the value of the accommodation coefficient or the sticking probability for solute molecules hitting a liquid surface of different chemical composition. The Mortensen-Eyring theory has been extended to account for the accommodation coefficient in a system of unlike molecules. The results agree quite well, in general, with the experimental literature. The combined theoretical and experimental evidence strongly suggests that the plate-height contribution of interfacial resistance is negligible in practical laboratory columns. In paper (377) Eyring discusses isotopes in analysis in an address at the Welch Foundation in Houston where he was chairman in 1963 of a symposium devoted to "Modern Developments in Analytical Chemistry".

VI. Liquid Structure

Paper (352) deals with stress-relaxation and recovery time for grease and polymer system. When stress is applied to a grease system, the fibers tend to become disentangled and flow is increased. When allowed to rest, the systems show a tendency to return to the original state. These effects, termed stress-relaxation and recovery time, were studied in these experiments. The experimental differences and their significance are discussed in relationship to the composition of the samples. Eyring's theory of flow was applied to the flow curves obtained, and the results are explained in terms of models based on photomicrographs of the substances. The statistical mechanics of liquid mixtures is treated in paper (357) using carbon tetrachloride and cyclohexane as an example. The thermodynamic properties are calculated with gratifying agreement with experiment. In paper (425) our significant structure model of the liquid state is used to calculate the thermodynamic properties of CO_2, COS and CS with good results. Our liquid theory is used as the equation of state for the shock compression of argon in paper (432). Again the agreement with experiment is good. In paper (452) the significant structure theory of liquids has been extended to the supercooled region and to the prediction of glass transition temperatures. The constants A and B fitted from Barlow's experimental data of viscosities and densities of alkylbenzenes are in good agreement with those calculated from significant structure theory. In calculating B we used the same constant $a' = 0.0085$ for all substances. The a' value is larger than the parameter a in significant structure theory since the activation energy for flow, involving a', should be equal to or greater than the energy, involving a, required by a molecule to deny a neighboring vacancy to the other neighbors. We used significant structure theory to treat the viscosity in the non-Arrhenius region. The theory also automatically predicts the occurrence of a temperature, T_k, near the melting point, at which log η plotted against $(1000/T)^3$ shows a break. If the fact that the solid-like microstructure should shrink near the melting point, due to a shift to more dense conformers, is taken into account, this effect should become more conspicuous. The glass transition temperature, T_g, can be calculated from the viscosity equation by defining it as $\eta_g \approx 10^{13}$ P. Alternatively, T_g can be calculated from a viscosity equation derived from significant structure theory by expressing it as a ratio of viscosities at two temperatures. The free volume fractions obtained in this work are smaller than the WLF "iso-free volume fraction" of 0.025. The average value found is 0.013, which is closer to the values of Barlow, et. al. In fact there is not an exact iso-free volume fraction. The glass point is well characterized as

the point where the viscosity reaches about 10^{13} P. This is a more reproducible criterion than specifying the ratio of free volume to total volume at the glass transition. The exciting result is that significant structure theory yields both the thermodynamic and transport properties of liquids down to the glassy region. The theory connects the disappearance of entropy upon supercooling with the disappearance of fluidity in a single all-embracing theory. Paper (472) is written as a chapter in the 1971 Annual Reviews of Physical Chemistry giving the status of significant structure at that time. It gave a picture of the successes of the theory up to that time. Paper (480) is a successful application of significant structuresto a variety of hydrocarbons. In paper (481) the theory of solubility of gases in liquids proposed by Jhon and Kihara has been tested and extended to aqueous solutions of gases. In the present paper, the theory is discussed in terms of the significant structure model of liquid water developed by Jhon and Eyring. Besides the usual Kihara potential, the inductive interaction potential is used in the solute-water interaction terms. The calculated values of the solubility and its temperature dependence for the gases Ar, Kr, Xe, Ne, O_2, N_2 and C_2H_4 show good agreement with experiment. Papers (483), (485), (486), (487) and (502) use significant structure theory to calculate the thermodynamic and transport properties of the liquid alkali metals with gratifying success. In paper (490) the significant structure theory of quantum liquids such as hydrogen, deuterium and helium has been applied to the physical adsorption occurring in the submonolayer region. The partition function for the two-dimensional adsorbed fluid has been derived. The properties of isothermal and isosteric heat show good agreement with the available data from the literature. Paper (494) develops numerical methods useful in applications of the significant structure theory of liquids. This involves an iterative method for finding a common tangent at two points on a complex surface. Also, a generalization of Gauss regula falsi method is developed to solve sets of nonlinear equations. In paper (501) the liquid properties of the halobenzenes are treated. In paper (520) the significant structure theory of liquids has been applied to amorphous and crystalline polyethylene. In this theory the amorphous state, like liquids in general, is assumed to have solid-like structure, gas-like structure and positional degeneracy which arises from the motion of kinetic segments and from the libration of CH_2 units. This concept leads to a partition function giving the Helmholtz free energy in terms of volume, temperature and composition. Thermodynamic and transport properties are calculated for amorphous polyethylene. The thermodynamic properties are also calculated for the crystalline solid. The calculated results are in reasonable agreement with the experimental values.

No such detailed calculation of polymer properties from a partition function, depending on both volume and temperature, have been previously attempted.

VII. Electrochemistry

In paper (419) reduction of alkali chloride and alkali carbonate aqueous solutions containing CO_2, N_2 and H_2 was carried out on lead cathodes in the acidic and neutral pH range. Steady state polarization curves from the rest potential up to -2.1 volts (vs. the N.H.E.) showed five regions with increasing current: (i) a region in which impurities controlled the kinetics; (ii) a region in which reduction of H_3O^+ ions is the rate controlling step, and in which mostly H_2 and a small percentage of formic acid are the products; (iii) a limiting current region for H_3O^+ ions; (iv) a region in which water and carbon dioxide are reduced, and in which the current efficiency for production of HCOOH is greater than 50 per cent; (v) another limiting current region in which OH^- transport away from and CO_2 transport to the electrode influence the kinetics of region (iv). Possible reaction paths and mechanisms are postulated for the cathodic reduction of CO_2. Paper (429) studies the reactions at fresh metal electrodes which are immersed in a wide variety of electrolytes. Electrochemical phenomena on bare metal surfaces were studied by measuring the potentials of wire electrodes as their surfaces were scraped off in various aqueous solutions. The scrape potentials were found to be determined by (1) the adsorption of the various species from solution for systems in which the faradaic currents are sufficiently slow and (2) the rates of the various faradaic reactions when the latter are rapid compared to the scraping process. It was found that noble metals conform to case (1) over at least part of the pH range, and in that case the scrape potential can be identified with the potential of zero charge. Over at least part of the pH range for the noble metals studied, solvent reduction is rapid enough that the scrape potentials are described by case (2). All the base metals studied reacted rapidly with the electrolyte over the entire pH range. In paper (436) the surfaces of 24 different elemental metal electrodes were removed by scraping up to 500 times/sec and the fresh surface potentials were recorded. From the scrape potentials obtained in the solutions of varying pH and anion type and from the nature of the potential decays at the cessation of scraping it was concluded that the scrape potentials fit into one of two categories: (1) faradaic reactions charged the freshly formed surface so slowly that the scrape potential yielded the potential of zero charge; or (2) faradaic reactions occurred so rapidly on the fresh surface that the scrape potential was shifted, in some cases positively and sometimes negatively, away from the zero charge potential. On several of the electrodes the faradaic reactions were found to establish the potential faster than would have been predicted from kinetic data.

The use of dimethylsulfoxide instead of water apparently diminished but did not eliminate the rapid oxidation of the reactive metals by the solvent. For the nonreactive metals the pzc was used to deduce the relative adsorbabilities of halide ions on the various metals. These adsorbabilities showed no simple relationship to the covalent metal-halogen bond strengths. Kinetic studies of the electrolyte reduction of carbon dioxide on the mercury electrode are reported in paper (441). The reduction of CO_2 to HCOOH has been studied for the Hg electrode in neutral and acidic aqueous solutions in the potential range between -0.8 and -1.9 V(sce). In the neutral pH range all the current is consumed in the production of formic acid, while in acid solutions both HCOOH and H_2 are produced. Steady-state polarization curves, catholic galvanostatic charging curves, current-efficiency measurements, reaction orders with respect to CO_2 partial pressure, and double-layer variation have been used to determine possible reaction pathways. In neutral solutions the mechanism may be described by a direct reduction of CO_2 in which two consecutive charge-transfer steps occur. In acidic solutions the above process occurs in parallel with the reduction of H_3O^+ ions. The H atoms formed react in a branching mechanism either with H_3O^+ ions and electrons to yield H_2, or with CO_2 to yield eventually HCOOH. Paper (454) derives the kinetic parameters for electrode processes by the method of mixed potentials. A steady-state titrational procedure has been developed leading to the direct determination of the transfer coefficients of both the Ce^{3+}/Ce^{4+} and Fe^{2+}/Fe^{3+} couples in one experiment. The results are derived from the dependence of mixed potentials on the concentrations of the various reactants. The success of the above method is attributed to the recognition of the optimum experimental conditions for obtaining directly linear Tafel regions, and thus avoiding mass-transport corrections. In addition, the titrational procedure has led to the discovery of the significant effect that platinum oxide has on the Ce^{3+}/Ce^{4+} transfer coefficient. In paper (460) the structure of the electrical double layer between mercury and dimethylsulfoxide in the presence of chloride ions is studied. The adsorption of the chloride ion on a mercury electrode from solutions of lithium chloride in dimethyl sulfoxide (DMSO) has been studied by measuring the interfacial tension of the electrode as a function of potential and concentration at 25°. The adsorption could be described by a virial isotherm in which the free energy of adsorption varied linearly with electrode charge, and in which the second virial coefficient (ion-ion repulsion term) is large. Specific adsorption of chloride ions is stronger from DMSO than from water. The inner layer capacity is analyzed into its components and the relative distances from the surface to the inner and outer

Helmholtz planes (x_1 and x_2, respectively) are deduced. $(x_2-x_1)/x_2$ is larger for adsorption of Cl^- ions from DMSO than from water. In paper (498) the electrolytic reduction of CO_2 in neutral, aqueous solution at a mercury pool cathode has been studied to establish the mechanism and to obtain the kinetic parameters by the steady-state galvanostatic method. The log current vs. potential curves show two Tafel regions of different slope which is indicative that different, i.e., consecutive, steps are rate determining in the two regions. The most plausible steps considered are (1) $CO_2 + H_2O + e \rightleftarrows HCO_2.(ads) + OH^-$ and (2) HCO_2 . (ads) + $e \rightarrow HCO_2^-$. Reaction orders with respect to the partial pressure of the CO_2 and the Tafel slopes are considered as the criteria for the proposed mechanism. The Langmuir and Temkin conditions for the adsorption of the reaction intermediate are considered and compared. The experimental results show that the Temkin condition is the more suitable and hence there is an appreciable change in the heat of adsorption with the surface coverage of the reaction intermediate. In paper (514) a comparison of the immersion and open-circuit scrape methods for determining the potential of zero charge of metal electrodes is made. Open-circuit potentials were measured for freshly immersed metal surfaces and for metal surfaces renewed abrasively (scraped-off) in situ in aqueous electrolytes. Electrode materials included Au, Ag, Cu, Pt, Ga, In, Bi and Sn and the electrolytes included alkali halides and alkali sulfates in acid, neutral, and alkaline solutions. The fresh-surface potentials for Au, Ga, In, Bi and Sn were approximately the same following either immersion or scraping in solution and yielded the potential of zero charge at certain pH conditions. For Ag, Cu, and Pt the immersion potentials were several hundred millivolts more positive than the scrape potentials. This is attributed to the presence of adsorbed oxygen on these metals at the instant of immersing them in solution. For Ag, Cu and Pt the scrape potentials are interpreted as the potential of zero charge for the bare metal while the immersion potentials reflect a superimposed dipolar effect or faradaic reduction of the oxygen.

VIII. Reaction Rates - Applied

Paper (500) shows how the autocatalytic equation $S = (1 + \exp k(t-\tau))^{-1}$ applies to survival of homogeneous populations of living things as well as persistance, rust free, of changing fractions, S, of a galvanized surface. This has been followed by the development in paper (510) of the effective predicting of the rate of atmospheric corrosion in many regions. Finally paper (506) is the initial study in what has developed into an extensive studied of anesthesia in this laboratory.