Physical Chemistry

Construction of 300KV electron microscope and its electronmicroscopy. Keinosuke Kobayashi, Hatsujiro Hashimoto, Eiji Suito, Shinichi Shimadzu and Masaya Iwanaga. *Japan. J. Appl. Phys.*, **2**, 47 (1963).—The three stage voltage supply and three stage electron gun for a 300 KV electron microscope are described. Each stage of the high voltage supply is operated at 100 KV with a ripple stability of about 1×10^{-4} and is connected to corresponding electrode of the gun. 300 KV is applied to the top electrode directly through an insulated cable whose exterior surface is kept at 200 KV so that 300 KV is not exposed to the air. The stability when operated at about 300 KV is within 4×10^{-4}/min. The resolving power of the electron microscope measured at 300 KV is 20 Å. Transmissive powers of electron waves accelerated at 100 KV, 200 KV and 300 KV have been estimated for an aluminium single crystal from the contrast of the electron micrographs. Energy dependence of inelastic scattering in organic specimens is also shown. Electron micrographs of MgO smoke crystals, stainless steel and polyoxymethylene single crystals taken at 300 KV are presented.

Transformation and growth of copper-phthalocyanine crystal in organic suspension. Eiji Suito and Natsu Uyeda. *Kolloid-Z.*, **193**, 97 (1963).—Processes of dimorphic transformation of copper - phthalocyanine, which took place in various organic suspension media, were traced by means of the electron microscopy and the X-ray diffractometry. It has been revealed that the preliminary growth of metastable crystals preceeds the actual transition into stable crystals. The preliminary growth has been found also in the case of thin crystalline films of the metastable form vacuum-condensed onto glass plates or cleavage faces of mica, both giving rise to very large slender lamellae of the metastable form. Outward appearances as well as lattice orientations in the crystals themselves are in close resemblance to each other for those kinds of slender lamellae of metastable and stable crystals. Two crystal habits are assumed by each of the crystal form. In parallel to the longitudinal principal zone axis, two lattice spacings ranging from 9 to 13 Å exist, while perpendicular to this axis, a lattice spacing of about 4 Å exists, again for each crystal form. The mechanism of the nucleation of stable crystals in suspension is also discussed on the basis of the similarity of outward appearance as well as lattice structure of two crystal forms.

Crystal growth and dimorphic transformation of organometallic compounds. Eiji Suito. "5th International Congress of Electron Microscopy" (Philadelphia), H-2 (1963).—The fine precipitates of some organometallic compounds, originally produced as metastable form, often grow to larger crystals of stable one in suspension system, being accompanied by transformation. The electron microscopy as well as electron and X-ray diffraction on the mechanism of these phenomena regarding two organometallic compounds, copper phthalocyanine and copper oxinate, were studied.

Auto-recording centrifugal instrument for particle size determination. Eiji Suito, Masafumi Arakawa, Tatsunosuke Masuda, Shuzo Miwa and Masakazu Sase.

Oyo Butsuri, **32,** 823 (1963), in Japanese. — For particle size determination, an automatic recording centrifugal instrument consisng of a balancing machine and a special rotor has been devised. The rotor has one sedimentation cell instead of the usual two, which makes the center of gravity of the rotor change as the particles precipitate toward the bottom of the cell. The curve of sedimentation of powder is automatically recorded by the detection of the change of center of gravity with time. With a rotor weigihng ca. 500 g and a sample of 1g (s. g. ca. 4), the change of center of gravity was about 20 micronms which is far greater than the sensitivity 0.05 microns/div. of the used balancing machine. A theoretical formula is derived by which the particle size distribution can be calulated from the sedimentation curve obtained by this method. Some sampes were measured with sufficient accuracy, the results agreeigng with those obtained by other methods.

Differential thermal analysis of hydrogen peroxide decomposition by various evaporated metal films. Kazo Umeda, Kimio Tarama and Eiji Suito. *Nippon Kagaku Zasshi,* 84, 553 (1963), in Japanese.—The kinetics of the decomposition of hydrogen peroxide solution on evaporated metal films was studied. The reaction rates were measured by the differential thermal analysis method, and they were found to be proportional to the weight of films. The activation energies decreased linearly with increasing pH. Activities of the film catalysts decrease in the following order ; Pd, Pt, Fe, Au, Ni, Ag, Cr, Cu, Al, which is the order found in the case of sol catalysts.

Electric properties and catalytic activities of evaporated metal film. Kazuo Umeda, Kimio Tarama and Eiji Suito. *Nippon Kagaku Zasshi,* 84, 553 (1963), in Japanese.—In the decomposition of hydrogen peroxide by the evaporated palladium film, relationship of the electric properties of the film and the catalytic activity was studied and the reaction mechanism was discussed. The experimental results were obtained as follows. (1) The electric resistance of the film increased in the course of the reaction. (2) The reaction was accelerated it the film was charged negatively. (3) In the pH range where the reaction rate was large, the capacity and the charge of double layer were also large. Therefore, it was assumed in the reaction mechanism that the process of the electron transfer from catalyst to hydrogen peroxide molecule was rate-determining.

Structure and catalytic activity of evaporated metal film. Kazuo Umeda, Natsu Uyeda, Kimio Tarama and Eiji Suito. *Nippon Kagaku Zasshi,* 84, 557 (1963), in Japanese.—The relationship between the structure and the catalytic activity was studied with palladium film as catalyst for the decomposition of aquecus hydrogen peroxide. The state of Pd films of various thickness was observed by means of an electron microscope. The change in strucure of films by heat treatment was studied by the X-ray diffraction method. These observation led to the conclusion that the change in the catalytic activity caused by heat treatment can be related to the change in the crystal structure such as decrease of spacing, increase of crystal size and decrease in the degree of distortion and disorder of the crystal.

Simple apparatus for density measurements of liquids under high pressure. Yoshimasa Takezaki, *Koatsugasu Kyokai Shi* **27,** 16 (1963), in Japanese.

Infrared studies of some complex between montmorillonite and octadecylamine or steramide. Eiji Suito, Masafumi Arakawa and Mitsuji Kondo. *Kogyo Kagaku Zasshi,* **66,** 1618 (1963), in Japanese.—No information concerning the interaction between bentonite and nonionic organic compounds has been obtained yet, although the interaction between bentonite and organic cation has been studied in most detail. The structures of octadecylamine~bentonite and stearamide-octadecylamine complex ~ bentonite were studied by X-ray diffraction and infrared absorption spectrum. The relation between the organic content and the separation of the crystal layer of montmorillonite was measured by X-ray diffraction. The basal specing of octadecylamine ~ bentonite was expanded stepwise, in increments of 4 Å with the quantity of organic compound, while, stearamide bentonite was expanded to about 22 Å with the smallest amount of organic compound. These results and infrared spectra suggest that the octadecylamine bentonite was prepared by cation exchange adsorption as usually considered. On the other hand, in infrared spectra of stearamide bentonite, significant changes of absorption occur in the amine I and II frequencies as well as in the NH- and the OH-stretching bands. These results suggest that the steramide molecule is chemically bonded as hydrogen bond with crystal layer lattice of montmorillonite.

Infrared studies of the interaction between rubber and filler. Eiji Suito and Masafumi Arakawa. *Kogyo Kagaku Zasshi,* **66,** 1614 (1963), in Japanese.— The interaction between rubber and filler was studied by infrared absorption spectrum. A microtome cooled at low temperature was employed for the preparation thin sections of cured rubber compounded with filler, which were used as samples for infrared spectrum measurements. This microtome technique was applied to the rubber analysis as to the identification of the filler contained in rubber. As seen from the absorption spectra measured by this method, the characteristic absorption in each rubber and filler was not influenced by the procedure of compounding with fillers and vulcanization. On examination of other absorptions, however, several changes were observed, which were conceivable caused by these treatments. In the case of hard clay, it was observed that only $3,700 \, cm^{-1}$ for the OH stretching band of the kaolinite changed when it was compounded in rubber. Since this absorption is due to the OH on the lateral surface of the plate-like crystal of kaolinite, the fact suggests that the effect of reinforcement by hard clay is due to the interaction between OH radical on the lateral surface of kaolinite crystal and rubber molecules.

Infrared absorption spectra of some monovalent metal salts of fatty acids. Rempei Gotoh and Tohru Takenaka. *Nippon Kagaku Zasshi,* **84,** 392 (1963), in Japanese.—See, this Bulletin, **41,** 219 (1963).

On the coagulation theory of colloids and the coalescence of mercury droplets aqueous solutions. Rempei Gotoh and Akira Watanabe. *Nippon Kagaku Zasshi,* **84,** 480 (1963), in Japanese.—See, this Bulletin, **41,** 219 (1963).

On the theory of coagulation and the coalescence of mercury droplets in aqueous solutions. Akira Watanabe and Rempei Gotoh. *Kolloid-Z*, 191, 36 (1963). The potential ranges of polarization of a pair of dropping mercury electrodes, over which the two mercury droplets coalesced, were measured as functions of ionic concentrations for various electrolytes. In the case of simple inorganic electrolytes the condition of coalescence obtained was proved be in quantitative aggreement with the Verwey-Overbeek theory of coagulation of lyophobic sols, thus indicating that the interaction between sub-microscopic particles of hydrophobic sols is essentially the same as that between macroscopic mercury droplets. While, in the case of sodium citrate solutions two kinds of marked deviations from the theory were observed, which appeared to be due to the specific adsorption of citrate ions and to the formation of protective interfacial films.

Chromatographic investigation of the interaction between dyestuffs and surfactants. Rempei Gotoh and Naomi Hayama. *Nippon Kagaku Zasshi*, 84, 104 (1963). Developing power, R_f, of the aqueous solution of surfactants has been observed for the spots of dyestuffs placed on the chromatographic paper. It has been found that non-ionic surfactants increase remarkably the developing power with increasing concentration, while anionic and cationic ones decrease it. This promotive action of the non-ionic surfactants has been investigated with respect to the species of dyestuffs, length of the ethylene oxide chain of the surfactants, pH, temperature as well as the effect of inorganic electrolytes. The relation between R_f and the concentration of the surfactants is theoretically discussed on the assumption of complex formation between the dyestuff and the surfactant.

Theory of capillary analysis. Naomi Hayama. *Nippon Kagaku Zasshi*, 84, 943 (1963), in Japanese.—The capillary analysis, which was usually carried out in the open system, was investigated in the closed system. Attempts were made to relate the ratio of heights of the substance and the solvent front (R_h) to the partition or absorption coefficient (K), and the following expression was derived:

$$\alpha K = \frac{1 - \ln 2}{R_h - \ln (1 - R_h)} - 1,$$

where α is the ratio of volumes of the non-mobile and the mobile phases. This equation was applied to the interaction between dyestuffs and organic polar substances as well as on the association of solute in aqueous solutions. The equlibrium constant of complex formation between Orange II and Polyvinylpyrrolidone (PVP) obtained by the capillary analysis was in good agreement with that obtained by dialysis. However, the eqilibrium constant of complex formation between Benzopurpurine 4 B and PVP obtained by the present method lay in between the scattered data in literatures. The degrees of association of various dye molecules in the aqueous solution was in agreement with the lowest values in literatures.

Interaction between dyes and non-ionic surfactants. Naomi Hayama. *Nippon Kagaku Zasshi*, 84, 948 (1963), in Japanese.—The interaction of dyes (Benzopurpurine 4 B, Orange II and Crystal Violet) with non-ionic surfactants has been investigated

by the capillay analysis. The combination of dye with non-ionic surfactants in solution results in a marked increase in the migration ratios of dyes, R_h (the ratio of heights of dye and solvent front on the chromatographic paper). This is compared with the case of polyvinylpyrrolidone. The relation between R_h and the concentration of non-ionic surfactants is theoretically discussed on the assumption that the complex is formed between the dye and the surfactants. The equilibrium constant of complex formation (K_2) and the order of the complex - formation reaction (m) are obtained. It appears that the value of m for Crystal Violet and some non-ionic surfactants in lower concentrations of surfactant is larger than in higher concetrations.

The interaction between dyes and deoxyribonucleic acid. Naomi Hayama. *Nippon Kagaku Zasshi*, **84,** 953 (1963), in Japanese.—The interaction of several dyes with sodium deoxyribonuclate (DNA) has been investigated by the capillary analysis and by the infra-red spectroscopy. The migration ratio (R_h: the ratio of heights of dye and the solvent front on the chromatographic paper) of cationic dyes increases with increasing DNA concentrations, while R_h of anionic ones decreases. The relation between R_h and the concentration of the DNA is theoretically discussed on the assumption that the complex is formed between the dyes and DNA. The binding force of the dye to DNA is related to the structure of the dye. Therefore, the infra-red absorption of the hydrogen-bonded base-pairs (1680 cm^{-1}) decreases by the addition of the dye which strongly combines with DNA. It is inferred that two dye molecules are intercalated between adjacent three purine bases of a DNA moleculer chain to form such a compound, and the base - pair formation is inhibited by binding of dye.

The dielectric behaviour of emulsions. Tetsuya Hanai, Naokazu Koizumi and Rempei Gotoh. "Emulsion Rheology" Pergamon Press, Oxford (1963) p. 91.—Dielectric constants and electrical conductivities of Nujol-in-water (o/w) and water-in-Nujol emulsions at rest, and under shear (about 40 sec^{-1} in the mean rate of shear), were measured over wide ranges of concentration (0-85 per cent) and measuring frequency (20 c/s-5 Mc/s). Results obtained were as follows : (a) The o/w emulsions show very different dielectric behaviour from that of the w/o emulsions with the same volume fraction of the oil. (b) Dielectric constants and conductivities of the o/w emulsions show no dielectric dispersion due to the interfacial polarization, their dependence on concentration being expressed better by the equations of the Bruggeman type rather than by those of the Wiener type. (c) The w/o emulsions show striking dielectric dispersions due to the interfacial polarization at high frequencies above 100 kc/s, the limiting dielectric constants at high frequencies being expressed better by Bruggeman's equation rather than by Wiener's. (d) The o/w emulsions show no appreciable change in dielectric constant and conductivity on agitation or on application of shearing stress. In the case of the w/o emulsions remarkable changes in dielectric properties are observed on agitation : both the limiting dielectric constants at low frequencies and the limiting conductivites at high frequencies decrease under shearing flow, the limiting dielectric constants at high frequencies being subjected to no shearing effect. In order to

interpret the dielectric behaviour of emulsions, theories of interfacial polarization are discussed with reference to a spherical dispersion system. The general solutions of the Wagner theory are discussed, being found to be insufficient quantitatively for the experimental results. A new theory applicable to a concentrated dispersion is developed on the assumption that the Wagner equation holds for an infinitesimally increasing process in concentration of disperse phase. Experimental results are interpreted quantitatively by this new theory. It is suggested by the new theory that, if the dielectric constant of oil phase is much larger, dielectric dispersion may be observed even in emulsions of o/w type. Such a suggestion was verified by dielectric measurements for nitrobenzene-in-water (n/w) emulsions. The shearing effect found in w/o emulsions may be caused by breaking up partice agglomerates.

Polymer Chemistry

Application of the Archibald ultracentrifugal method for the study of dilute polymer solutions. II. Examination of two solution systems near the Flory temperature. Hiroshi Inagaki, Shuji Kawai and Atsushi Nakazawa. *J. Polymer Sci.*, **A1,** 3305 (1963).—To test the validity of the generalized Archibald method developed previously, sedimentation experiments were made for two systems, polystyrene-cyclohexane and polymethyl methacrylate-n-butyl chloride, near the Flory temperature relevant to each. It was found that the slope of the resulting plot between the reciprocal of the apparent molecular weight M_{app} (extrapolated back to zero centrifugation time) and the concentration tends to zero at the Flory temperature, while this slope shows positive or negative values, depending on whether the temperature is higher or lower than the characteristic one. Thus the present method gives just the same information for dilute polymer solutions as does the the light scattering. A further study was carried out to elucidate the time-dependent nature of M_{app} (t), calculated at each centrifugation time, in terms of the thermodynamic nonideality of solution and of the fractionating action of the ultracentrifuge on a polydisperse solute.

Einige Bemerkungen über die Molekulargewichtsbestimmung nach dem Archibald-Verfahren unter besonderer Berücksichtigung der Arbeit von W. Scholtan und H. Marzolph. Hiroshi Inagaki. *Makromol. Chem.*, **64,** 215 (1963).—The apparent molecular weight M_a is determined from sedimentation data. The slope of the sedimentation diagram is discussed. The curve obtained by plotting $1/M_a$ (0) vs. polymer concentration c, where $1/M_a$ (0) is the value of $1/M_a$ (t) extraporated to the time t = 0, is discussed with regard to the cause of its curvature. The bending, for a given system, increases with better solvents. Also, for a given system, the bending of the curve increases with increasing molecular weight of the solute. Thus, the author interprets the molecular weight dependence on the second virial coefficient A_2, namely the fact that the value of A_2 increases anomalously with increasing molecular weight, differently than was observed by Scholtan and Marzolph (Makromol. Chem. **57,** 52 (1962)).