

Abstracts of the Papers Published by the
Staff Members of the Institute from
July 1978 to June 1979

Nuclear Chemistry

Relationship between Shakeoff Probabilities. T. Mukoyama. *Acta Physica Hungar.*, **44**, 187 (1978).—The prediction of CARLSON et al for relationship between electron shakeoff probability in beta decay and those accompanying other processes has been proved for *K*- and *L*-shell electron ejection by using the nonrelativistic hydrogenic wave functions. It is shown also that this relationship holds for the differential probability (energy spectrum of the ejected electrons) as well as for the total shakeoff probability.

Electronic Relativistic Effects in *K*-Shell Ionization by Charged-Particle Impact. T. Mukoyama and L. Sarkadi. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 33 (1979).—The *K*-shell ionization cross sections by heavy charged-particle impact are evaluated in the plane-wave Born approximation, using relativistic Dirac functions for the atomic electrons. The effect of binding-energy increase due to the projectile is estimated by the use of relativistic wave functions for *K*-shell electron and the Coulomb-deflection effect is also taken into account. Numerical results are compared with the corresponding values of the nonrelativistic plane-wave Born approximation and the relativistic semiclassical approximation as well as the experimental data.

Superconducting and Magnetic Properties of Dilute Tc-(Fe) Alloys. T. Takabatake and H. Mazaki. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 45 (1979).—The superconducting transition temperature T_0 , the upper critical field H_{c2} , and the hyperfine field have been measured for dilute Tc-Fe alloys. The samples prepared by electrodeposition and reduction have an almost dirty limit structure. The linear decrease in $\ln T_0$ with respect to the impurity concentration is consistent with the theoretical prediction for the localized spin fluctuation system. Observed curves of $H_{c2}(T)$ and the small negative value of the saturation hyperfine field indicate that Fe impurities in Tc do not have well defined magnetic moment, and that there exist localized spin fluctuations in the Tc-Fe system. This conclusion is not consistent with the previous results found for arc-melted Tc-Fe alloys.

Complex Susceptibility Measurements of Superconducting Transition of Electrodeposited Technetium. T. Ishida and H. Mazaki. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 55 (1979).—The superconducting transition of electrodeposited Tc films was studied by measuring the complex susceptibility of specimens. The electrodeposition was carried out under several different conditions and the preparation of metallic Tc by this method was established. For the measurement of complex sus-

ceptibility, a Hartshorn-type mutual inductance bridge was constructed. The measuring system involving the bridge was examined by using Sn and Pb films, and was found to have the sensitivity of $0.05 \mu\text{H}$. It has been revealed that the structural situation of specimens is well reflected in the observed complex susceptibility and that the information on dislocation and homogeneity in the sample can be obtained from the measurement. Some attempts to prepare Re samples were also performed by means of electrodeposition.

Excitation of Nuclear Isomers by γ Rays from ^{60}Co . Y. Watanabe and T. Mukoyama. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 72 (1979).—Long-lived isomeric states in stable nuclei ^{111}Cd and ^{115}In have been excited by the Compton-scattered γ rays from ^{60}Co . The flux of the scattered photons at resonance has been calculated in the single-scattering approximation. Using the observed γ activities of $^{111\text{m}}\text{Cd}$ and $^{115\text{m}}\text{In}$ and the calculated photon flux, the integral cross sections for the isomer production by photoexcitation of ^{111}Cd and ^{115}In have been evaluated to be $(3.5 \pm 0.4) \times 10^{-25} \text{ cm}^2\text{-eV}$ and $(1.9 \pm 0.1) \times 10^{-25} \text{ cm}^2\text{-eV}$, respectively.

A Study on Electron Irradiation Effects in Hydrated Cobalt Ferricyanide Using Mössbauer Spectroscopy. K. Fukumura, T. Kobayashi, and Y. Nakayama. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 164 (1979).—Recent works on irradiation experiments with complexes have reported that low-spin Fe^{III} is reduced to Fe^{II} after the irradiation. The same effect has been obtained by heating the sample. In this report we give Mössbauer spectroscopic measurements with hydrated cobalt ferricyanide irradiated by electron beams.

Compositional Analysis with Inner-Shell Ionization by Radioisotopic Beta Rays. T. Ishida and H. Mazaki. *J. Phys. E: Sci. Instrum.*, **12**, 549 (1979).—Compositional analysis of specimens with inner-shell ionisation by β rays has been investigated. By uniform mixing of β -ray emitters (about 0.5 MBq or less) in a sample and observation of characteristic K X-rays with a solid state detector, the relative amount of each component ($Z > 15$) can be conveniently determined within experimental errors of only a few per cent. The minimum amount of component which can be distinguished depends on the atomic number, the β -ray energy, and the energy resolution of the X-ray detector, but the typical detection threshold found in the experiment is 50 ppm for elements around $Z = 40$. The shake-off process accompanying β decay, by which determinations of the relative amounts of components in different samples can be made, is also discussed.

Many-Electron Effect on the K -Shell Internal Ionisation Accompanying Beta Decay. T. Mukoyama and S. Shimizu. *J. Phys. G; Nucl. Phys.*, **4**, 1509 (1978).—The K -shell internal ionisation during beta decay has been treated relativistically on the basis of the wavefunction proposed by Greenland and Irvine. The total ionisation probabilities are calculated and compared with those from the hydrogenic wavefunctions. Comparison with experimental data indicates that a discrepancy still remains between theory and experiment. A possible reason for this discrepancy is discussed.

Mössbauer Studies on Dilute Tc-(Fe) Alloys. T. Takabatake, H. Mazaki, and T. Shinjo. *Joul. de Physique, Colloque No. 2, C2*, 172 (1979).—The quadrupole splitting and the isomer shift of a dilute Tc-Fe alloy have been determined as -0.13 ± 0.02 mm/s and -0.020 ± 0.006 mm/s (relative to α -Fe), respectively. The hyperfine field measurement in the external magnetic field of 30 and 50 kOe for $1.5 < T < 4.2$ K shows that the saturation field for 50 kOe is -7.4×1 kOe and the local susceptibility is -0.145 ± 0.009 . These results and the previous study on the superconductivity of Tc-Fe alloy indicate the existence of localized spin fluctuation in this system.

A Double Ionization Chamber for the Differential Method. S. Kakiuchi, H. Mazaki, R. Katano, S. Shimizu, and R. Sellam. *Nucl. Inst. Methods*, **158**, 435 (1979).—A double ionization chamber for the differential method has been constructed, by which a minute difference in intensities (1 part in 10^5) of two γ -ray sources can be measured with the aid of a conventional sampling method. By the use of this chamber, the effect of superconductivity on the nuclear decay rate λ of ^{99m}Tc has been measured, but no effect was found within an experimental error $\Delta\lambda/\lambda = (0.2 \pm 0.5) \times 10^{-4}$. This result is consistent with our previous result, but is in essential disagreement with that of Byers and Stump. Another application of the device for determination of a long half-life is also demonstrated. The half-life of ^{60}Co was determined in a 10 d measurement as $T_{1/2} = (5.27 \pm 0.07)\text{y}$, which is in excellent agreement with the current value.

Double Internal Bremsstrahlung in the Electron-Capture Decay of ^{55}Fe . A. Ljubičić, T. Nakayama, Y. Isozumi, and S. Shimizu. *Nucl. Phys.*, **A320**, 289 (1979).—The energy distribution of photons emitted in double internal bremsstrahlung accompanying the electron-capture decay of ^{55}Fe has been investigated. For sum photon energies in the range of 44–230 keV and at an emission angle of 90° , the ratio of transition probabilities of double to single internal bremsstrahlung processes has been found to be $(5.6 \pm 0.5) \times 10^{-5}$. The experimental data are compared with the existing theoretical predictions.

Effect of Iron Impurities on the Superconductivity in Granular Technetium. T. Takabatake and H. Mazaki. *Phys. Rev.*, **B**, **19**, 189 (1979).—The effect of Fe impurities on the superconductivity of Tc has been investigated with almost dirty-limit samples prepared by electrodeposition and reduction. Upper-critical-field curves show, as expected from the Mössbauer study, the existence of an exchange field due to the impurity. The observed transition-temperature depression by Fe impurities indicates that there is localized spin fluctuation in the Tc-Fe alloy. This conclusion is not consistent with the previous results found for arc-melted Tc-Fe alloys.

Superconducting Transition of Electrodeposited Technetium. T. Ishida and H. Mazaki. *Phys. Rev.*, **B**, **20**, 131 (1979).—Complex-susceptibility measurements of the superconducting transition of Tc films prepared by electrodeposition and reduction (heat treatment) have been performed. In order to find the optimum experimental conditions for preparation of metallic Tc by the present method, several different conditions have been attempted. For the measurement of the complex susceptibility, a Hartshorn-type mutual-inductance bridge was constructed. The whole performance

of the measuring system was examined by using Sn and Pb films. It has been revealed that the structural details (dislocation or homogeneity) of the samples are well reflected on the observed complex susceptibility and that the mean energy dissipation in the temperature region of the superconducting transition is a good probe for structural examination of the samples.

Nuclear Excitation of ^{115}In by Positron Annihilation with K -Shell Electrons. Y. Watanabe, T. Mukoyama, and S. Shimizu. *Phys. Rev., C*, **19**, 32 (1979).—When a positron annihilates with a K -shell electron, the excess energy liberated may be given to the nucleus involved. In the case when this energy is just the right energy for any excited state within its level width of a fraction of an electron volt, nuclear excitation can be expected, and if the excited level cascades down to an isomeric state with appreciable lifetime we can confirm the occurrence of this annihilation mode by observing γ transitions or conversion electrons from this isomeric level. In the present work we observed γ rays from $^{115}\text{In}^m$ after irradiation of natural indium foils by positrons from the β^+ decay of ^{64}Cu . Using the observed induced γ activity of $^{115}\text{In}^m$ and assuming this phenomenon to be the two-step process, we have evaluated the cross sections of nuclear excitation by positron annihilation for 1078- and 1464-keV levels of ^{115}In ; $(3.9 \pm 1.4) \times 10^{-24} \text{ cm}^2$ and $(1.4 \pm 0.5) \times 10^{-22} \text{ cm}^2$, respectively.

Positrons from 1.4-GeV Uranium-Atom Collisions. C. Kozhuharov, P. Kienle, E. Berdermann, H. Bokemeyer, J. S. Greenberg, Y. Nakayama, P. Vincent, H. Backe, L. Handschug, and E. Kankeleit. *Phys. Rev. Lett.*, **42**, 376 (1979).—A large fraction of the number of positrons observed in collisions of $^{238}\text{U} + ^{238}\text{U}$, $^{238}\text{U} + ^{208}\text{Pb}$, and $^{208}\text{Pb} + ^{208}\text{Pb}$ at relative velocities $v/c=0.11$ and for distance of closest approach $R_{\min} < 40 \text{ fm}$ can be assigned to pair creation of nonnuclear origin, induced by the time-varying Coulomb fields of the projectile and target charges. An order-of-magnitude increase in the positron yield is observed by increasing the united-atom charge from 164 to 184.

K_β/K_α Intensity Ratios for X-Ray Production by Heavy Ions. T. Mukoyama, L. Sarkadi, D. Berényi, and E. Koltay. *Phys. Lett.*, **67A**, 180 (1978).—The K_β/K_α intensity ratios for low-energy proton (2 MeV) and N-ion (2.8 MeV) bombardments have been measured for several targets. The experimental results indicate the relative importance of K - and M -shell simultaneous ionization. In the paper a qualitative interpretation is given.

Relative Intensities and Energy Shifts of K X-Rays Produced in Heavy Charged-Particle Collisions. T. Mukoyama, L. Sarkadi, D. Berényi, and E. Koltay. *Abst. 6th Int. Conf. on Atomic Physics*, ed. by E. Anderson et al., Riga, 1978, p. 377.—Relative intensities and energy shifts of K X-rays produced by 2.8-MeV ^{14}N -ion bombardments have been measured for several targets from Ti to Ge. The K_β/K_α intensity ratios are expressed as the relative ratios to the 2.0-MeV proton impact on the same target and the energy shifts are determined from the K X-ray energies obtained from photo-ionization. The change in the K_β/K_α ratios and the existence of the

K_β-ray energy shifts suggest the simultaneous K- plus L- and M-shell ionization. The decrease in the K_β/K_α ratio from the value for the single K-ionized atom indicates that the M-shell vacancies produced together with K-shell vacancy play a dominant role for the change of the ratio in the energy region studied.

Nuclear Processes and Electronic Structures. T. Mukoyama. *Proc. Symposium on "Wechselwirkung ionisierender Strahlung," Gera, 19–23. 9. (1977), Zfi-Mitteilungen, Nr. 14, Akademie der Wissenschaften der DDR, Leipzig, 1978, p. 175.*—Internal ionization processes accompanying nuclear decay have been reviewed. The existing theories are compared with the recent experimental results and the further works are suggested. For the K-shell ionization in β decay, it is pointed out that there exists a serious disagreement between theory and experiment and the importance of the direct-collision process is discussed. In the case of K-electron ejection during K-electron capture and K-shell internal conversion, the measured values are in fairly good agreement with the calculated values. However, in both cases the number of reliable experimental data is too small and further accurate experiments are urgently needed.

Efficiency Calculation and Measurement of Large NE213 Neutron Counter. T. Higo, S. Matsuki, Y. Iwashita, A. Okihana, N. Fujiwara, and T. Yanabu. *Bull. Inst. Chem. Res., Kyoto Univ., 57, 13 (1979).*—A 14 cm diameter and 19 cm depth counter with liquid scintillator (NE213) was constructed for the fast neutron detection. Design, performance and efficiency calibration are described. Calculated efficiency and experimental efficiency are compared at low energy region. They agree within about 20%.

Three-Particle Relativistic Kinematics. S. Kakigi, K. Fukunaga, T. Oh-sawa, and S. Tanaka. *Bull. Inst. Chem. Res., Kyoto Univ., 57, 83 (1979).*—For reactions leading to three particles in the final state, five independent variables are assigned to the polar and azimuthal angles of two particles and the kinetic energy of one of them. Formulas are given for calculations of other variables from these five. Formulas are also given for transformations of polar and azimuthal angles from the laboratory system to the rest frames of two-particle systems. A FORTRAN programme using these formulas is included in an appendix.

Computer Program for Three Body Break Up Reaction. K. Fukunaga and S. Kakigi. *Bull. Inst. Chem. Res., Kyoto Univ., 57, 92 (1979).*—A FORTRAN program is developed to calculate the energy spectrum for three body break up reaction at intermediate energy. Energy spectra are calculated on the basis of AGS (Alt, Grassberger and Sandhas) formalism assuming quasi free scattering with final state interaction. The calculated curves reproduced well energy spectra of ^3He in coincidence with protons for $^3\text{He}(\tau, p)$ reaction and deuterons for $^3\text{He}(\tau, \tau d)$ reaction at 120 MeV.

Fast Neutron Fields Produced by Kyoto University Cyclotron. J. Miyajima, T. Nishidai, and H. Takekoshi. *Bull. Inst. Chem. Res., Kyoto Univ., 57, 147 (1979).*—Beams of fast neutrons were produced by Kyoto University Cyclotron, using the $^9\text{Be}(d, n)^{10}\text{B}$ reaction.

A number of physical properties of fast neutron fields have been measured for the purpose of radiobiological experiments. These include the effectiveness of neutron collimator, the neutron energy distributions, and the estimation of the neutron component and γ -ray component of absorbed dose in tissue.

Breakup Reaction of ^3He by ^3He at 120 MeV. K. Fukunaga, N. Fujiwara, S. Kakigi, T. Ohsawa, H. Nakamura-Yokota, S. Tanaka, A. Okihana, T. Sekioka, T. Higo, and T. Miyanaga. *J. Phys. Soc. Japan*, **45**, 1783 (1978).—Kinematically complete experiments for $^3\text{He}(\tau, \tau p)d, d^*$ reaction and the $^3\text{He}(\tau, \tau d)p$ reaction were performed at 120 MeV. In the coincident energy spectra, large peaks corresponding to the quasi-free scattering were observed and bumps were also observed at higher part in the ^3He energy. The energy spectra were compared with the curves calculated on the basis of the Alt, Grassberger and Sandhas (AGS) formalism and the bump was reproduced well with the curve for the τ - d quasi-free scattering followed by the p - d final state interaction. Any evidence for the excited state of ^3He nucleus was not found.

The $D(d, d)D$, $D(d, p)T$ and $D(d, ^3\text{He})n$ Reactions at 13.2 MeV. A. Okihana, N. Fujiwara, H. Nakamura-Yokota, T. Yanabu, K. Fukunaga, T. Ohsawa, and S. Tanaka. *J. Phys. Soc. Japan*, **46**, 707 (1979).—The differential cross sections for the $D(d, d)D$, $D(d, p)T$ and $D(d, ^3\text{He})n$ reactions were measured at 13.2 MeV. The angular distributions of the differential cross sections were obtained from 12° to 90° in the c.m. system for the elastic scattering, from 3.6° to 90° for (d, p) and from 6.0° to 90° for $(d, ^3\text{He})$. The differential cross sections for the (d, n) reaction, deduced from the data on the $(d, ^3\text{He})$ reaction, coincide with those for the (d, p) reaction over the whole experimental angles.

Analyses were made with the DWBA theory. The differential cross sections for the elastic scattering were well reproduced by using the optical model potential with the Majorana exchange term.

A Study of a Large Plastic Scintillation Fast Neutron Detector. Y. Deschamps, E. Hourany, S. Kakigi, F. Reide, and T. Yuasa. *Nucl. Instrum. & Methods*, **155**, 135 (1978).—For the purpose of studying some nuclear reactions in few-nucleon systems in the hundred MeV region, a large plastic scintillation detector ($50\text{ cm} \times 10\text{ cm} \times 10\text{ cm}$) equipped with two photomultipliers and a system of hodoscopes was constructed. Its principal characteristics and the neutron detection efficiency at about 20 MeV have been studied with neutrons produced by the $^2\text{H}(d, n)^3\text{He}$ reaction for which the energy E_n and the scattering angle θ_n have been precisely defined by those of ^3He in coincidence. The efficiency is about $25\% \pm 2\%$ with the threshold energy of 1 MeV (UEQ). The discrimination n - γ was made by the difference of their times of flight. The reduced time of flight resolution is in the order of 0.8 ns in which the fluctuation of the correlated ^3He time of flight is included.

The 2_2^+ and 4_1^+ States of the Even Isotopes $^{78-86}\text{Kr}$ Excited in the Inelastic Scattering of 51.9 MeV Protons. N. Sakamoto, S. Matsuki, K. Ogino, Y. Kadota, T. Tanabe, and Y. Okuma. *Phys. Lett.*, **83B**, 39 (1979).—The 2_2^+ and 4_1^+ states of the even isotopes $^{78-86}\text{Kr}$ have been studied by the inelastic scattering of protons. The

$B(E2; O_g^+ \rightarrow 2_2^+)$ values of these isotopes are roughly equal, whereas the $B(E4; O_g^+ \rightarrow 4_1^+)$ values decrease to a minimum at ^{82}Kr and then increase with neutron number. Comparison of the experimental results with current theoretical models implies an abrupt change of structure between $^{78-82}\text{Kr}$ and $^{84-86}\text{Kr}$.

Energy Spectra of Neutrons Induced by 0.75 GeV/c Negative Pions on Complex Nuclei. S. Matsuki, T. Higo, Y. Iwashita, T. Sekioka, T. Yanabu H. Itoh, T. Maki, A. Yoshimura, H. Yoshinaga, T. Cho, and S. Uehara. *Phys. Lett.*, **84B**, 67 (1979).—Energy spectra of neutrons ($3 < E_n < 100$ MeV) induced by 0.75 GeV/c negative pion bombardment on Al, Fe, Cd and Pb were measured. The low energy part ($3 < E_n < 8$ MeV) of the spectra in heavier targets can be reasonably well understood by the intranuclear-cascade (INC)/evaporation model, while the cross section and its target mass dependence of higher energy neutrons ($E_n > 20$ MeV) are in disagreement with the INC prediction.

Effects of Kyoto Univ.-Cyclotron-Induced Fast Neutrons on a Mouse Tumor. T. Nishidai, M. Abe, Y. Yukawa, S. Suyama, J. Miyajima, and H. Takekoshi. *J. Jap. Soc. Cancer Ther.*, **14**, 10 (1979), in Japanese.—Effects of Kyoto Univ.-Cyclotron-induced fast neutron beams on a spontaneous C3H/He mouse mammary carcinoma were studied in vivo. Relative effectiveness of fast neutron beams (5~6 rads/min) vs ^{60}Co γ rays, ^{137}Cs γ rays and 32 MeV electron beams on 1 to 20 growth delay-days were changed with the growth delay-time and the dose rates of compared radiations.

The values were reduced continuously from 5.0 to 3.0 as compared with ^{137}Cs γ rays (15 rads/min) and from 4.2 to 2.7 as compared with 32 MeV electron beams (1,500 rads/min). However, the values as compared with ^{60}Co γ rays (150 rads/min) were smaller than those compared with 32 MeV electron beams on 1 to 6 growth delay-days, and were similar to those for ^{137}Cs γ rays on 8 to 20 growth delay-days.

Analytical Chemistry

EPR Studies of the Cobalt (II)-(N_2S_2)-Schiff Base Complex with Lewis Bases and CO. M. Sakurada, Y. Sasaki, M. Matsui, and T. Shigematsu. *Bull. Chem. Soc. Japan*, **52**, 1861 (1979).—The EPR and optical spectra of N,N' -bis(3-thioxo-1-methylbutylidene)ethylenediaminocobalt (II) in the presence of Lewis bases and CO were measured. The cobalt (II) complex formed five-coordinate adducts with Lewis bases and CO, which had a rhombic symmetry with a $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ ground configuration.

Forced-Flow Chromatography of Metal Ions with the Eluent Containing a Color Forming Reagent. T. Aoki, M. Matsui, N. Tanahashi, T. Kumagai, and T. Shigematsu. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 255 (1978).—Copper (II), cobalt (II), and zinc (II) are separated with ion exchange chromatography using the eluent containing xylene orange and ammonium acetate. These eluted ions are detected continuously with spectrophotometric absorption at 580 nm. The separation of zinc

(II) and cadmium (II) are also carried out by using the eluent containing xylenol orange, sodium chloride, and hexamine. Copper, cobalt, and zinc ions of 0.2 to 1 μg level can be determined with the peak height calibration curves. A linear relationship between the peak area and the amounts of ions is obtained over the range 0.2 to 4 μg . Cadmium (II) of 0.5 to 5 μg can be determined with the peak height or peak area calibration curves.

Some Studies on Atomic Absorption Spectrometry Using Ultrahigh-Frequency Plasma as Atomizer. M. Matsui, O. Fujino, H. Natsuume, J. Tôei, and T. Shigematsu. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 263 (1978).—Some preliminary works were performed in the use of ultrahigh-frequency plasma as an atomizer for atomic absorption spectrometry. The plasma flame was set at the position of the burner of a conventional atomic absorption spectrometer. As sodium chloride was added, the absorbance of the atom lines for magnesium and calcium considerably increased and that of the ion lines for them increased rapidly at first and reduced until near nil absorbance. This may be caused by the fact that the thermodynamic equilibrium between atom and ion or between ions changes with the variation of sodium chloride concentration in plasma flame. The detection limit (1% absorption) in the presence of moderate amounts of sodium chloride was 0.04 ppm (2852.1 Å atom line) for magnesium and 0.03 ppm (4226 Å atom line) and 0.003 ppm (3968.5 Å ion line) for calcium. The detection limits for some other elements were also determined.

Determination of Cadmium in Individual Organs and Divided Shells of Sea Water Clam by Atomic Absorption Spectrometry with a Carbon Tube Atomizer. T. Nagahiro, O. Fujino, M. Matsui, and T. Shigematsu. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 274 (1978).—Cadmium contents in individual organs and divided shells of sea water clam were estimated by atomic absorption with a carbon tube atomizer. After samples were digested with nitric acid, cadmium was separated from the interfering sample matrices by extracting it into diisobutyl ketone as diethyl-dithiocarbamate. By this method, 0.06~0.75 ppb of cadmium was found in the divided shells. In the shellfish, cadmium was enriched to a very high extent in the kidney, to some degree in the organ of Keber.

Coprecipitation of Manganese with Calcium Carbonate. T. Kumagai. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 280 (1978).—The distribution behavior of manganese with calcium carbonate, calcite and aragonite was studied at 25°C. Precipitates of calcite and aragonite were made from calcium bicarbonate solution by the homogeneous precipitation method. Five point seven was obtained as the logarithmic distribution coefficient of manganese with calcite, and 0.058 was obtained as that of manganese with aragonite. The reason why the distribution coefficient of manganese with calcite is about one hundred times as large as that with aragonite is considered to be the distortion energy in the aragonite crystals which comes from the difference of free energy of ideal solid solution and that of real solid solution.

Coprecipitation of Rare Earth Elements with Hydroxyapatite. O. Fujino. *Radioisotopes*, **28**, 9 (1979).—The distribution behavior of trace rare earth elements

between an aqueous phase and hydroxyapatite crystals was investigated. The apatite prepared by adding phosphate ion extremely slowly to an aqueous solution containing calcium, rare earth elements, ethylenediamine and nitrilotriacetate ion at 80°C.

Apparently the coprecipitation reaction seems to be anomalous, because the apparent distribution coefficient did not have a constant value through the reaction. But when the true distribution coefficient was calculated by using the thermodynamic data at 80°C, it was revealed that rare earth ions were coprecipitated obeying logarithmic distribution law. The true distribution coefficient values of trivalent yttrium, scandium, europium and cerium ions were about $10^{7.3}$, $10^{9.8}$, $10^{7.4}$ and $10^{6.5}$, respectively.

Atomic Absorption Spectrometry of Trace Metals in Natural Water. On the Separation and Concentration by DDTC-DIBK Extraction Method. O. Fujino, M. Matsui, and T. Shigematsu. *Mizushori Gijutsu (Water Purification and Liquid Wastes Treatment)*, **20**, 201 (1979), in Japanese.—A method of solvent extraction was investigated for selectively concentrating manganese, iron, cobalt, nickel, copper, zinc, cadmium, and lead ions from natural water prior to analysis by atomic absorption spectrometry. In the present work, diisobutyl ketone (DIBK) was used as an extractant because of its extremely low solubility in water. Quantitative extraction from an aqueous solution into DIBK was possible, using 1 per cent DDTC in the pH range of 8–9 for a total of eight metals.

Cobalt, nickel, copper, cadmium, and lead complexes in the DIBK were stable for a whole day. However, after five hours, manganese, iron, and zinc complexes started to break down.

By this procedure, eight metal ions in an aqueous solution can be concentrated from tens to hundreds fold by extracting them into DIBK. Therefore, these metals in natural water at ppb and ppt levels can be determined with flame and flameless atomic absorption spectrometry.

Chemical Analysis of Trace Elements in Seawater. T. Shigematsu. *Nippon Kaisui Gakkai-shi (Bulletin of the Society of Sea Water Science, Japan)* **32**, 150 (1978), in Japanese.—Review.

Physical Chemistry

Numerical Table of Complex Permittivities for the Williams-Watts Type of Dielectric Relaxation. N. Koizumi and Y. Kita. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 300 (1978).—Numerical values of normalized complex permittivities for the Williams-Watts type of relaxation have been tabulated in the ranges of the logarithm of reduced frequency, $\log \omega\tau$, of -3.0 to 3.0 with increments of 0.1 and of the distribution parameter β of 1.0 to 0.3 with increments of 0.01 .

Complex permittivities and reduced frequencies at dielectric loss maxima are also shown with respective values of β since the loss maximum takes place at a different frequency from the reciprocal of relaxation time except for $\beta=1$.

All numerical values are given in floating numbers with six significant digits.

Membranes and Ions—Theories and Calculi of Membrane Transport of Substances. T. Hanai. Published by Kagaku Doujin, Kyoto (1978), in Japanese.

—This textbook is intended to be an introduction to physico-chemical aspects of membrane transport phenomena. Ion transport through membranes comprises a train of fundamental processes of physical chemistry. In order to understand each of these physico-chemical processes in biological membranes as well as in artificial high-polymer films, it is essential to understand the basic principles of thermodynamics, theory of solutions, electrostatics and electrochemistry. The author's emphasis throughout the book is consistently placed on the readable and comprehensible interpretation of the physico-chemical bases so that students and investigators in special fields not only of chemistry but also of chemical engineering, biology and agriculture may be readily led to an understanding of the basic principles concerned.

The movement of electrically neutral particles inside the membrane phase can be interpreted as a simple diffusion process. On the other hand, the movement of charged particles such as ions gives rise to electric field or potential gradient, which reflects some electrical constraint upon the succeeding ions, physico-chemical interpretation of such a process being explained in the first three chapters in detail.

In Chapter 1 the movement of an ion subjected to an external electric field is expressed in terms of ionic mobility, which is related to electrical conductivity showing the measure of the migration of the ions. Chapter 2 is concerned mainly with a diffusion process of neutral solute, the diffusion coefficient as the measure of the drift of solute particles being related to molar mobility of the particle. The driving force acting on the particles in this diffusion process is shown to be derived from thermodynamic origin. Some elementary interpretations are also given of the electric field arising when the ions move on in the membrane phase by the diffusion process. In Chapter 3, particular attention to the derivation and the interpretation of an analytical expression of ion flux is paid to highlight the mechanism of generation of electric field caused by ion migration due to diffusion. Solutions of the analytical expressions of ion flux are explained in detail in Chapter 4 for general cases of electrolyte solutions. Chapter 5 introduces some systematic knowledge of thermodynamics and of theory of solution essential to understand the formulation of ion migration in a solution-membrane-solution system. In Chapter 6, detailed interpretation of theories is introduced for some typical systems which include fixed charges such as Donnan equilibrium system, fixed charges on a solid surface, fixed charges in a phase bounding on another phase, and a membrane with fixed charges. On observation of membrane phenomena, care must be taken for the characteristics of electrodes used. Basic knowledge of electrodes necessary for the membrane experimentation is introduced in Chapter 7.

Crystal and Molecular Structures of Bisphthalocyaninatothorium (IV).

T. Kobayashi. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 204 (1978).—Bisphthalocyaninatothorium (IV), $(C_{32}N_8H_{16})_2Th$, structure was studied by three dimensional X-ray analysis. The crystal belongs to a space group $C2/c$ with the cell dimensions $a=18.92$, $b=18.81$, $c=15.92$, and $\beta=116^\circ$. Two Phthalocyanine ligands are linked by one thorium ion to form a sandwich-like molecule.

The parallel mean planes of the ligands are separated by 3.59Å. The thorium ion is displaced 1.49Å from the plane of pyrrol nitrogens.

Preparation and Properties of Alumina Supermicrogrid. Y. Fujiyoshi and N. Uyeda. *Proc. Ninth Int. Congr. on Electron Microscopy, Toronto, 1*, 108 (1978).—It is often required in high resolution electron microscopy to use very thin supporting films for the reduction of random noise. When the specimen is crystalline film, it is also desirable that the thickness is controlled to be less than a hundred angstroms so that the specimen can be dealt with as a thin phase object. In both cases, a suitable supporting technique is necessary to secure the stability and mechanical strength of these very thin films and perhaps very small fragments of a few hundred angstroms in size. The present work was undertaken to prepare rigid supporting films by means of chemical thinning of alumina films produced by the anodic oxidation of aluminium plate.

Atomic Resolution from 500 kV Electron Micrographs by Computer Image Processing. N. Uyeda, E. Kirkland, Y. Fujiyoshi, and B. Siegel. *Proc. Ninth Int. Congr. on Electron Microscopy, Toronto, 1*, 220 (1978).—The method suggested by P. Schiske for optimally combining several micrographs of different defocus values have been applied successfully to images of a crystalline specimens of hexadecachlorophthalocyanine-copper taken on 500 K HVEM (HAREM). The resulting image shows increased resolution and the S/N ratio of the images.

Discrimination of Individual Atoms in the Molecular Images of Chlorinated Copper Phthalocyanine. N. Uyeda, Y. Fujiyoshi, and T. Kobayashi, *Proc. Ninth Int. Congr. on Electron Microscopy, Toronto, 1*, 242 (1978).—For the establishment of solid approaches to the target of discriminating individual atoms in molecular images, it still seems to be necessary to deal with radiation resistant compounds with known structures. The 500 kV electron microscope constructed by Kobayashi *et al.* has the capability of achieving the ultimate resolution of 1.5 Å, and played the principal role in the present attempt to reach the atomic resolution. The specimen used here is the thin epitaxial crystallite of chlorinated copperphthalocyanine (hexadecachlorophthalocyanatocopper) prepared by vacuum-condensation on KCl cleavage face. Various images, reproduced after the random noises were averaged by multiple exposure technique with 10 to 15 periodic translations along the b-axis were given. As predicted by Uyeda and Ishizuka, on the basis of computer simulation, the images dramatically change their appearance.

Effect of Radiation Damage on the Molecular Image of Th-Phthalocyanine T. Kobayashi and N. Uyeda. *Proc. Ninth Int. Congr. on Electron Microscopy, Toronto, 1*, 300 (1978).—The sensitivity of Th-Pc against the electron irradiation was measured as the dose necessary for destroying the diffraction spots. The dosage needed to destroy the 600 diffraction spots, which correspond to the resolution limit (3.2 Å) given by Scherzer equation for 100 kV electrons, was about 0.3 C/cm². The total dose necessary to destroy all of the diffraction was more than 30.0 C/cm². It is concluded that thorium atom sandwiched between two phthalocyanine ligands through eight coordinated bonds could not displace much when the bond breakage has occurred following the ionisation by electron and the surrounding light atoms gathered around the thorium atom to form clusters or they made some other bondings with neighboring molecules.

Anisotropic Radiation Damage of Potassium Tetracyano Platinite (KCP). N. Uyeda, E. J. Kirkland, and B. M. Siegel. *Proc. Ninth Int. Congr. on Electron Microscopy, Toronto*, **1**, 392 (1978).—The radiation damage of potassium tetracyano-platinite [$\text{K}_2(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}:\text{KCP}$] was dealt with on the basis two dimensional observation of fading rates of diffraction spots. KCP is known as an ionic crystal which possesses “one dimensional” electronic properties and it would be of great interest to know if radiation damage proceeds in a strongly asymmetric manner. The apparent anisotropy of fading rate indicates that the damage process has a close connection to the original configuration of the crystal lattice.

Studies of Radiation Damage Mechanism—by Optical Diffraction Analysis and High Resolution Image. Y. Murata. *Proc. Ninth Int. Congr. on Electron Microscopy, Toronto*, **3**, 49 (1978).—The mechanism of radiation damage was studied down to molecular level, by means of optical diffractometer. The gradual damage with electron dose was denied quite clearly by observing the high-resolution image and comparing the optical diffraction patterns from both non-damaged area and damaged area. Mechanism of the damage was very drastic at the vicinity of initially damaged molecule and further approach must be put forth before final conclusions.

Particle Size Measurement by Monoparticulate Film Method. M. Nishino and M. Arakawa. *Zairyo (J. of the Society of Materials Science, Japan)*, **27**, 696 (1978), in Japanese.—The particulate film method was investigated for practical particle size measurement. Powder was spread on a trembling water surface and was compressed to form a monoparticulate film. The mean particle size perpendicular to the water surface can be determined by measuring the area and packing fraction of the particulate film. The packing fraction here was measured actually from the area occupied by particles in a photomicrograph of the particulate film. Powders were first treated with a flotation agent and then were used as the samples. The results agreed well with the particle size measured by the microscopic method.

As a conclusion, the particulate film method was found to provide simple and practical measurement of the particle dimension, especially such as the thickness of thin flake-like materials and the specific surface area of large particles.

Cohesion Mechanism of Powder at Normal Atmosphere. M. Arakawa. *J. of the Society of Powder Technology, Japan*, **16**, 305 (1979), in Japanese.—Review.

Resonance Raman Spectra of Insoluble Monolayers Spread on a Water Surface. T. Takenaka and H. Fukuzaki. *J. Raman Spectroscopy*, **8**, 151 (1979).—Resonance Raman spectra of insoluble (or spread) monolayers of cetyl orange on a water surface have been obtained by the use of a total reflection method previously proposed. The spectra of the monolayers resemble that of solid cetyl orange rather than that of the chloroform solution, suggesting that the structure of cetyl orange in the monolayer is similar to that in the solid state. From polarization measurements of the spectra, the molecular orientation in the monolayers has been examined at various surface pressures. The molecules in the insoluble monolayers show a higher orientation with respect to the vertical axis as compared with those in soluble (or adsorbed)

monolayers. The degree of molecular orientation rises with an increase in surface pressure of the monolayers but decreases considerable upon collapse.

Spectroscopic Studies of Interfacial Membranes. T. Takenaka. *Makugaku Nyumon* (Introduction to Membrane Science) pp, 21–40, edited by M. Nakagaki, Kitami Shobō (1978), in Japanese.—This is a review article dealing with application of infrared and Raman spectra to studies of interfacial membranes. Contents of the article are as follows.

Introduction

1. Studies by Infrared Spectroscopy

- 1.1 Interaction between Monolayers and Metal Ions
- 1.2 Conformation of Polypeptides in Monolayers
- 1.3 Molecular Orientation in Monolayers of Fatty Acids
- 1.4 Molecular Orientation in Adsorbed Layers at the Solid-Liquid Interface

2. Studies by Raman Spectroscopy

- 2.1 Adsorption at the Solid-Gas Interface
- 2.2 Adsorption at Electrode Surfaces (the Solid-Liquid Interface)
- 2.3 Surface Thin Layers of Solid
- 2.4 Adsorbed Monolayers at the Liquid-Liquid Interface

Concluding Remarks

References

Raman Spectral Studies of Ionic Motion and Ionic Interaction in Aqueous Nitrate Solutions. T. Kato, J. Umemura, and T. Takenaka. *Molecular Phys.*, **36**, 621 (1978).—The Raman spectra of the totally symmetric $\nu_1(A_1')$ mode of an NO_3^- ion have been recorded in aqueous LiNO_3 , NaNO_3 , KNO_3 and NH_4NO_3 solutions at various concentrations. The vibrational and rotational correlation functions have been calculated from the Fourier transform of the Raman profiles. Reorientation of the symmetry axis of an NO_3^- ion in the aqueous solutions may be represented by the inertial motion for short times ($t \leq 0.15$ ps, jump angle 17°), and by the rotational diffusion for longer times ($t \geq 0.3$ ps). An effective moment of inertia for short times has been found to be $I_\perp = 20 \times 10^{-39}$ g cm², which suggests, as compared with the free NO_3^- value $I_\perp^\circ = 6 \times 10^{-39}$ g cm², some association with the surrounding water molecules or cations. The mean-square torque acting on an NO_3^- ion from the moment analysis has been found to increase linearly with nitrate concentration. The torque on an NO_3^- ion in concentrated nitrate solutions is predominantly from other ions, while the contribution from an NO_3^- -water interaction is small. It is concluded that the vibrational band width of $6\text{--}13$ cm⁻¹ in these nitrate solutions is to be attributed to the pure vibrational dephasing, due to an NO_3^- -water interaction in dilute solutions, and due to NO_3^- -water and increased NO_3^- -cation interactions in concentrated solutions. The contribution from the induced dipole-induced dipole resonance vibrational energy transfer has been found to be negligible.

Raman Study of Vibrational Dephasing Process in Aqueous Nitrate Solutions. T. Katō and T. Takenaka. *Chem. Phys. Letters*, **62**, 77 (1979).—The observed vibrational correlation functions of the $\nu_1(A_1')$ mode of NO_3^- in some aqueous

nitrate solutions are interpreted by Kubo's stochastic line-shape theory. The results indicate that the modulation is fast. The increase in the vibrational width with increasing concentration is interpreted by a broadening of the distribution of environments and by a slight increase in the modulation time τ_c (0.25 ps \rightarrow 0.3 ps).

Vibrational Spectra of Rare Earth Bromate Nonahydrate Crystals. Y. Kato, K. Okada, H. Fukuzaki, and T. Takenaka. *J. Molecular Structure*, **49**, 57 (1978).—Polarized Raman spectra of lanthanum and neodymium bromate nonahydrate crystals and IR spectra in a powdered sample have been observed from 30–4000 cm^{-1} . Observed Raman bands are experimentally classified into three active symmetry species. The vibrational assignment is made by comparing the spectra of these nonahydrates with those of the corresponding nonadeuterates and similar crystals containing various rare earth ions. From a comparison of the Br-O stretching and lattice vibrations, the binding character between the rare earth ions and ligands is discussed. This consideration is consistent with the result supposed from the lanthanide contraction.

Intensity of Laser-Excited Fluorescence of Erbium Ethylsulfate. Y. Kato, K. Okada, S. Hayashi, and T. Takenaka. *Chem. Phys. Letters*, **61**, 266 (1979).—The fluorescence spectrum for the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition of the erbium ethylsulfate crystal has been observed at 87 K by using the 488.0 nm line of an Ar⁺ laser. According to the Judd-Ofelt theory for spectral intensity, the relative intensities of 10 σ transitions and 5 π transitions between the manifolds have been evaluated using wavefunctions obtained from a crystal-field calculation including configuration interaction. The calculated intensities are in fair agreement with experiment. A discussion is given of the approximations employed.

Adhesion and Dispersion Energies. M. Matsumoto. *Ganryo (Pigments)*, **23**, 13 (1979), in Japanese.—The adhesion between two bodies in contact has been reviewed in terms of surface and interfacial energies being of dispersion and polar components. Both the components are obtained experimentally by the measurement of contact angle between two bodies, and the dispersion component in the both components has been indicated to be estimated theoretically with using a Lifshitz theory.

Substituent Effects upon Dissociation and Migration Reactions of Five-Coordinate Platinum (II) Carbonyl Complexes. N. Sugita, J. V. Minkiewicz, and R. F. Heck. *Inorg. Chem.*, **17**, 2809 (1978).—A series of five iodobis (triphenylphosphine)arylplatinum (II) complexes was prepared and rates of carbonylation in the presence and absence of excess triphenylphosphine were measured. Four related palladium (II) complexes were compared with the platinum complexes. The results are interpreted in terms of a five-coordinated carbonyl intermediate which forms the acylmetal product by two reaction paths—a migratory route and a dissociative route. The migratory reaction is much more sensitive to changes in the electronic character of the migrating group than the dissociative reaction is. The results show that carbon monoxide insertion is not rate limiting in the catalytic carbonylation of aryl halides.

Nonrandom Isomerization of *cis*-3-Methyl-1,3-Pentadiene-1,2- d_2 . Internal Energy Relaxation. T. Ibuki and S. Sugita. *J. Chem. Phys.*, **70**, 3989

(1979).—The unimolecular isomerization via 1,5-H atom shift of *cis*-3-methyl-1,3-pentadiene-1,2- d_2 (*c*-3MP-1,2- d_2) was studied in the gas phase. *c*-3MP-1,2- d_2 was produced by the cross combination of $\text{CH}_3\text{CH}=\text{CCH}_3$ and $\text{CD}=\text{CHD}$ radicals and chemically excited at 25°C to 122 kcal/mol on the average. Nonrandomization of internal energy was observed. An effective intramolecular energy relaxation time of $(3.97 \pm 0.14) \times 10^{-11}$ sec was obtained by the application of RRKM theory to the isomerization reaction. The experimentally determined rate constant for the unimolecular isomerization of *c*-3MP-1,2- d_2 with randomized energy was found to be $5.0 \times 10^9 \text{ sec}^{-1}$.

Inorganic Chemistry

Unidirectionally Solidified Transparent Ceramics in the System $\text{NaNbO}_3\text{-BaTiO}_3$. S. Ito, T. Kokubo, and M. Tashiro. *Am. Ceram. Soc. Bull.*, **58**, 591 (1979).—An ingot consisting of elongated columnar grains of a perovskite-type solid solution was produced from a melt of the congruently melting composition $70\text{NaNbO}_3\cdot 30\text{BaTiO}_3$ using the directional solidification method. A pore-free ingot consisting of columnar grains aligned along the $\langle 110 \rangle$ direction was obtained when the melt was solidified at 1 mm/h under a thermal gradient of 70°C/cm. The as-solidified ingot was dark blue but lightened easily by annealing in air. Transverse thin sections, 0.1 mm thick and cut from the lower part of the ingot, showed a quadratic electrooptic effect with a Kerr constant of $8 \times 10^{-10} \text{ (m/v}^2\text{)}$.

Formation of Stable $\gamma\text{-6Bi}_2\text{O}_3\cdot\text{SiO}_2$ Crystal from Its Supercooled Melt and Metastable Crystal Induced by Their Surface-Contamination. S. Ito, T. Kokubo, and M. Tashiro. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 286 (1978).—A $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ melt, when naturally cooled in a platinum crucible to room temperature, precipitated only the metastable δ -phase. When a tip of platinum wire once touched by a finger of the worker of the present experiment was brought in contact with the surface of the supercooled $6\text{Bi}_2\text{O}_3\cdot\text{SiO}_2$ melt or its δ -phase during their cooling, they transformed into the stable γ -phase instantaneously. A trace of the $\gamma\text{-6Bi}_2\text{O}_3\cdot\text{SiO}_2$ and $\gamma\text{-Bi}_2\text{O}_3$ crystals contaminating the sweat of the worker were concluded to be most probable nucleating agents for the formation of the $\gamma\text{-6Bi}_2\text{O}_3\cdot\text{SiO}_2$. These contaminants could not be removed completely from the skin of the worker by a simple washing with soap.

Effect of pH of $\text{Ti}(\text{SO}_4)_2$ Solution on Properties of Hydrous Ti(IV) Oxide Precipitated from the Solution. T. Maki. *Nippon Kagaku Kaishi (Journal of the Chemical Society of Japan, Chemistry and Industrial Chemistry)*, 945 (1978), in Japanese.—Hydrous Ti(IV) oxides were prepared, at room temperature, by adding aqueous ammonia to concentrated or diluted $\text{Ti}(\text{SO}_4)_2$ solutions until pH of the solutions were raised to 3.0, 4.5, 6.0 and 8.0, respectively. Chemical, thermal, IR absorption spectrum and X-ray diffraction analyses were made of these hydrous oxides. Their specific surface areas and adsorption capacities of $\text{UO}_2(\text{CO}_3)_3^{4-}$ ions in alkaline solutions were also measured. The results obtained can be summarized as follows:

1) The crystallinity of the hydrous Ti(IV) oxide decreased linearly with increasing pH of the mother solution; the crystallinity of the hydrous oxide prepared at pH 8.0 was about one fifth of that of the hydrous oxide prepared at pH 3.0 (Fig. 6).

2) The specific surface area of the hydrous oxide increased linearly and markedly with increasing pH of the mother solution (Fig. 7). The adsorption capacity of the oxides showed a remarkable increase with increasing pH of the mother solution (Fig. 8). The oxides with maximum adsorption capacity were prepared from the solution of pH 6.0 for the concentrated $\text{Ti}(\text{SO}_4)_2$ solution, and from the solution of pH 4.5 for the diluted $\text{Ti}(\text{SO}_4)_2$ solution.

3) The chemical composition of the hydrous oxide was greatly dependent on the concentration of $\text{Ti}(\text{SO}_4)_2$ in the mother solution (Table 1 and Table 2). The result revealed that the chemical composition had close relationship to the hydrolytic mechanism in $\text{Ti}(\text{SO}_4)_2$ solution.

4) The dependencies of the crystallinity and the adsorption capacity etc. on pH of the mother solution were explained in terms of the hydrolytic mechanism, the growth and aggregation model of hydrous Ti(IV) oxide polymers, and the constitutional formulas of the hydrous oxides after heated at 50°C (Fig. 12, 13 and Table 3).

Effect of Added Oxides on the Microstructure of Unidirectionally Solidified $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ Ceramics. M. Arioka, T. Kokubo, and M. Tashiro. *Nippon Kagaku Kaishi (Journal of the Chemical Society of Japan, Chemistry and Industrial Chemistry)*, 1357 (1978), in Japanese.—Melts of the compositions $100\text{Li}_2\text{O}\cdot 200\text{SiO}_2\cdot 3\text{R}_m\text{O}_n$, where R_mO_n is B_2O_3 , Na_2O , MgO , Al_2O_3 , SiO_2 or P_2O_5 , were unidirectionally solidified at a rate of 1.3 mm/h with a temperature gradient of 80°C/cm in a clay crucible. A thin glass-ceramic layer of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ previously formed on the inner surface of the bottom of the crucible was used as the seed crystals. All the ingots made were mainly of columnar $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ crystals with their c -axes parallel to the direction of their elongation. The diameter of the columnar crystals was in the range 170–400 μm for all the ingots containing R_mO_n whereas it was 560 μm for the ingot containing no R_mO_n . The total porosities of the ingots containing Na_2O , B_2O_3 , P_2O_5 and Al_2O_3 were 1.1, 1.7, 7.6 and 9.1%, respectively, whereas the total porosity of the ingot containing no R_mO_n was 3.4%. The lower porosity of the ingots containing Na_2O or B_2O_3 as compared with that of the R_mO_n -free ingots was attributed to the formation of a glassy matrix (5–7 wt%) at the boundaries of the columnar crystal; Viscous flow formed in the presence of the glassy matrix probably relaxed thermal stresses induced in the ingots after solidification, thus suppressing the formation of microcracks.

Porosities of Unidirectionally Solidified $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ Ceramics. M. Arioka, T. Kokubo, and M. Tashiro. *Yogyo-Kyokai-Shi (Journal of the Ceramic Association, Japan)*, 86, 368 (1978), in Japanese.—A $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ melt was unidirectionally solidified in a clay crucible at rates, R , of 0.7, 1.3, 3.3, 6.7 and 13 mm/h with a temperature gradient of 80°C/cm. The ingots solidified at rates $R \geq 3.3$ mm/h had cylindrical pores resulted from a big difference in solubility of gases in the melt and crystal. Their porosities were all larger than 4%, increasing with their solidification rate. The ingots solidified at rates $R \leq 1.3$ mm/h had no cylindrical pore but many microcracks were found present at the grain boundary of the columnar $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ crystals, which were

oriented with *c*-axis parallel to their crystal elongation direction. The formation of microcracks was attributed to a big difference in thermal shrinkage between the *a*- and *b*-crystallographic axes of the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ crystal.

Bubble Formation during Unidirectional Solidification of a $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ Melt. M. Arioka, T. Kokubo, and M. Tashiro. *Yogyo-Kyokai-Shi (Journal of the Ceramic Association, Japan)*, **86**, 512 (1978), in Japanese.—When a $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ melt was unidirectionally solidified in a crucible at rates higher than 3 mm/h with a temperature gradient of $80^\circ\text{C}/\text{cm}$, many bubbles were found to form in the melt near the solid-melt interface. Mass spectroscopic analysis of the bubbles and infrared spectroscopic analyses of the quenched melt and the ingot indicated that the bubbles were formed of the H_2O gas expelled from the melt on its solidification. Mathematical analysis of the distribution of H_2O in the solidifying melt indicated that the bubbles were formed in the melt near the solid-melt interface when the H_2O concentration of the melt reached a value about 15 times the equilibrium saturated H_2O concentration of the melt.

Thermal and Mechanical Properties of Unidirectionally Solidified $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ Ceramics. M. Arioka, T. Kokubo, and M. Tashiro. *Yogyo-Kyokai-Shi (Journal of the Ceramic Association, Japan)*, **87**, 182 (1979), in Japanese.—Melts of the compositions of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ and $100(\text{Li}_2\text{O}\cdot 2\text{SiO}_2)\cdot 3\text{R}_x\text{O}_y$, where R_xO_y is B_2O_3 , Na_2O , MgO , Al_2O_3 , SiO_2 or P_2O_5 , were unidirectionally solidified. Thermal expansions of the solidified ingots in the direction of their crystal elongation agreed with that of the *c*-axis of a $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ single crystal whereas those in the direction perpendicular to their crystal elongation varied markedly, depending on their compositions and solidification rates. Anisotropy was also found in their compressive strength as well as in the propagation rate of a 12 MHz longitudinal sound wave in them. These anisotropic properties were interpreted in terms of their microstructures.

Effect of pH values on the Formation and Solubility of Zinc Compounds. T. Takada, M. Kiyama, H. Torii, T. Asai, M. Takano, and N. Nakanishi. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 242 (1978).—Aqueous suspensions, prepared by mixing the solution of NaOH and that of zinc sulfate, chloride or nitrate, were subjected to aging at 25, 50, and 70°C . Examination of the products by X-ray powder diffraction showed that zinc oxide, basic zinc sulfate, chloride and nitrate are formed depending mainly on the pH. Their solubilities in the suspension media with different pH values were determined at 25°C .

Formation and Solubility of Lead (II) Compounds at Various pH Values in Aqueous Suspensions Containing Acetate Ions. H. Torii, M. Kiyama, and T. Takada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 247 (1978).—When aqueous suspensions containing NaOH and $\text{Pb}(\text{OAc})_2$ in various mol ratios were subjected to aging at 25, 50, and 80°C , formation of $\text{Pb}(\text{OAc})_2\cdot 2\text{Pb}(\text{OH})_2$, $\text{PbO}\cdot 2/5\text{H}_2\text{O}$, orthorhombic PbO , or tetragonal PbO took place, depending on the pH, temperature, and acetate ion concentration. Their solubilities in the suspension media with various pH values at 25°C were determined.

Hydrolysis Products of Tungstates. H. Torii, M. Kiyama, and T. Takada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 251 (1978).—Aqueous suspensions, 0.2 M ammonium or sodium tungstate and different amounts of one of HCl, HNO₃, or H₂SO₄, were subjected to aging at room temperature. The resulting products were examined by means of X-ray powder diffraction. The formation of 5(NH₄)₂O·12WO₃·11H₂O and hydrates of tungstic oxide takes place, depending mainly on the pH. The presence of sulfate was found to hinder the crystal growth of hydrates of tungstic oxide except for that of H₂WO₄·H₂O.

The Stability of Evaporated Fe Films Sandwiched with Various Materials; A Mössbauer Study. S. Hine, T. Shinjo, and T. Takada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 130 (1979).—Multilayer Fe films sandwiched with Rh, B, Sn, Sb, and MgF₂ were prepared by the alternate deposition in UHV deposition system. The compounds formed at the interface layer of Fe film coated with some materials were determined by the Mössbauer spectroscopy. Some compounds were found at the interface between Fe films and coating Rh or B. In the Fe-Sn multilayer film, all of Fe atoms are in the state of some intermetallic compounds like FeSn and FeSn₂. The Sb-coated Fe films as-deposited are stable up to 370K, but all of Fe atoms transformed to FeSb₂ at 490K. Fe films coated by MgF₂ are also stable, but the grain growth of Fe film occurs after the thermal treatment at 480K in vacuum for twenty days. In this paper, the mechanism of the compound formation at the interface layer is also discussed.

Surface and Interface Magnetism by Mössbauer Spectroscopy. T. Shinjo. *Journal de Physique*, **40**, C2-63 (1979).—Magnetic behaviors near a surface, or an interface, of a magnetically ordered crystal are of great interest. Local magnetic moment of a surface atom, temperature dependence of surface magnetization and surface anisotropy are studied from ⁵⁷Fe Mössbauer measurements. The results obtained by complementary means are briefly reviewed. The advantages and also limits of the Mössbauer spectroscopy as a tool for surface magnetic studies are discussed.

Interface Magnetism of Epitaxial Fe Films on Sb by Mössbauer Effect. S. Hine, T. Shigematsu, T. Shinjo, and T. Takada. *Journal de Physique*, **40**, C2-84 (1979).—Mössbauer spectra of epitaxial thin Fe(III) films (48, 32, 24, 16, and 8Å) sandwiched with Sb(0001) layers are obtained at 4.2K and 300K. The hyperfine fields at 4.2K are reduced with the decrease of the film thickness and their distribution is increased. The average hyperfine field of the Fe surface layers is about 320K kOe at 4.2K. The intensity ratio of 3:4:1:1:4:3 independent of the film thickness at 4.2K suggests that the magnetic moments in an Fe(III) plane are completely oriented surface parallel. There is no paramagnetic peak at 4.2K in the spectra, which means that the magnetically "dead layers" do not exist in the Fe(III) plane.

Mössbauer Spectra of Ultrathin Fe Films Coated by MgO. T. Shinjo, S. Hine, and T. Takada. *Journal de Physique*, **40**, C2-86 (1979).—Mössbauer spectra of thin Fe films (24, 16 and 8Å) sandwiched with MgO layers showed that the hyperfine field at 4.2K increased with the decrease of the film thickness. From the computer

fitting results with the least squares method the hyperfine field at the surface layers of the MgO-coated Fe film is nearly 380 kOe. The spectrum at 4.2K of the 8Å film sandwiched with MgO shows the intensity ratio of 3:1:1:1:1:3, which means that the magnetization of the 8Å Fe film was preferentially perpendicular to the surface due to the surface anisotropy.

Mössbauer Study on Intercalation Compounds of Graphite with FeCl_{3-x} . K. Ohhashi, T. Shinjo, T. Takada, and I. Tsujikawa. *Journal de Physique*, **40**, C2-269 (1979).—A Mössbauer study on intercalation compounds of graphite with iron chloride, G-FeCl_{3-x} ($0 \leq x \leq 1$) was reported. The use of Grafoil sheets as host graphite led to a surface effect to be more important than the use of bulk graphite, *i.e.* the appearance of an additional Fe^{2+} form. It was found that the Néel temperature regarded as for G-FeCl_3 became higher with increase of Fe^{2+} concentration.

Mössbauer Effect of SrLnFeO_4 ($\text{Ln}=\text{La, Pr, Nd}$). M. Shimada, M. Koizumi, M. Takano, T. Shinjo, and T. Takada. *Journal de Physique*, **40**, C2-272 (1979).—The Mössbauer effect has been studied in SrLaFeO_4 , SrPrFeO_4 and SrNdFeO_4 with K_2NiF_4 structure in the temperature range between 4K and 640K. The results of the combined magnetic and quadrupole interactions indicated that SrPrFeO_4 and SrNdFeO_4 exhibited spin re-orientation phenomena at about 77K. On the other hand, no spin reorientation was found in SrLaFeO_4 .

Metallic Antiferromagnetism of $(\text{V}_{1-x}\text{Ti}_x)_2\text{O}_3$ ($0.06 \leq x \leq 0.30$). Y. Ueda, K. Kosuge, S. Kachi, and T. Takada. *Journal de Physique*, **40**, C2-275 (1979).—Mössbauer effect measurement of ^{57}Fe doped in $(\text{V}_{1-x}\text{Ti}_x)_2\text{O}_3$ ($x \geq 0.06$), which shows a metallic conductivity down to absolute zero, confirmed the metallic antiferromagnetism of the system.

Mass Spectrometric Study on Chemical Transport OF VO_2 . Y. Bando, M. Kyoto, T. Takada, and S. Muranaka. *J. of Crystal Growth*, **45**, 20 (1978).—The analysis of gas in the chemical transport reaction of VO_2 using TeCl_4 as a transport agent was carried out with a quadrupole mass spectrometer. In the transport reaction from 600 to 500°C, it was found that the oxygen and vanadium of VO_2 were transported in the form of VOCl_3 and TeOCl_2 gases; the transport reaction was $\text{VO}_2 + 3/2\text{TeCl}_4 = \text{VOCl}_3 + \text{TeOCl}_2 + 1/2\text{TeCl}_2$. The transport reaction from 900°C to 800°C was assumed to be $\text{VO}_2 + 3/2\text{TeCl}_2 = \text{VOCl}_3 + 1/2\text{O}_2 + 3/4\text{Te}_2$. In the transport at high temperature, the oxygen partial pressure estimated from the mass spectrum was considerably higher than that in equilibrium with VO_2 phase. In this paper a study of the chemical transport of the system $\text{VO}_2\text{-TeCl}_4$ is presented.

Additive Element and Lattice Defect in Semiconductive Ceramics. Y. Bando. *Kagaku Kogyo (Chemical Industry)*, **29**, 64 (1978), in Japanese.—Valence control principle, and the roll of grain boundary in ZnO , BaTiO_3 and ferrite were reviewed in connection with electric conductivity.

Organic Chemistry

Facile Synthesis of Chiral 18-Crown-6 Derivatives from L-Tartaric acid.

N. Ando, Y. Yamamoto, J. Oda, and Y. Inouye. *Synthesis*, 688 (1978).—Starting from L-tartaric acid, (*S:S*)-1,2-bis[benzyloxymethyl]-, (*S:S*)-1,2-bis[acetoxymethyl]-, (*S:S*)-1,2-bis[benzyloxymethyl]-5,16-dioxo-6,15-diaza-, and (*S:S*)-1,2-bis[benzyloxymethyl]-6,15-diaza-18-crown-6, all of C_2 chirality and of potential interest in chiral recognition and asymmetric synthesis, were synthesized by a new simple procedure. This provides a facile access to chiral crown ethers in general and affords good yields.

Role of Hydroxyl Groups in the Stereochemistry of Hydrogen Transfer from Chiral NAD(P)H Model to Carbonyl.

T. Makino, T. Nunozawa, N. Baba, J. Oda, and Y. Inouye. *Tetrahedron Lett.*, 1683 (1979).—Asymmetric reduction of α -ketoester with a chiral dihydronicotinamide was significantly affected by chiral aromatic additives, capable of exerting an attractive interaction with dihydropyridine ring, which was further consolidated through the chelation of hydroxyl groups with magnesium.

The Wittig Rearrangement of Fluorenyl Ethers in Two-Phase System.

Y. Yamamoto, J. Oda, and Y. Inouye. *Tetrahedron Lett.*, 2411 (1979).—The Wittig rearrangement of fluorenyl ethers by the use of potassium hydroxide as base in solid phase was readily effected by crown ethers and onium salts, while diamines moderately catalyzed the reaction.

Stereochemical Studies on Azidation of β -Bromohydrins under Phase Transfer Condition.

Y. Nakajima, J. Oda, and Y. Inouye. *Tetrahedron Lett.*, 3107 (1978).—18-Crown-6 and (2,2,1)-cryptand-catalyzed azidation of diastereomeric β -hydroxy- β -phenyl-, and β -methoxy- β -phenyl- α -bromopropionates in solid-liquid system eventually afforded the mixtures of the corresponding amino acids in various ratios, which were greatly affected by the catalysts used. The reaction mechanism was discussed on the basis of the stereochemical outcome.

Asymmetric Reduction of Aryl Trifluoromethyl Ketones with an Achiral NADH Model Compound in a Chiral Hydrophobic Binding Site of Sodium Cholate Micelle, β -Cyclodextrin and Bovine Serum Albumin.

N. Baba, Y. Matsumura, and T. Sugimoto. *Tetrahedron Lett.*, 4281 (1978).—This communication deals with asymmetric reduction of phenyl, 1-naphthyl and 2-naphthyl trifluoromethyl ketones with an achiral NADH model compound, 1-n-propyl-1,4-dihydronicotinamide in chiral environments. Asymmetric induction in the alcohols was obtained with asymmetric bias ranging over 0.6–1.4% in sodium cholate micelle, 1–10% in β -cyclodextrin and 16–47% in bovine serum albumin. When the results were compared with those of sodium borohydride reduction under the same conditions, the enantiomeric excess were comparable, however, the configurations of the alcohol were dramatically reversed.

Lythraceous Alkaloids. X. Alkaloids of *Lagerstroemia subcostata* and *L. fauriei*: A Contribution to the Chemotaxonomy.

K. Fuji, T. Yamada, E.

Fujita, and H. Murata. *Chem. Pharm. Bull.*, **26**, 2515 (1978).—The basic components of *Lagerstroemia subcostata* collected on Amami-ohshima Island and two slightly different types of *Lagerstroemia fauriei* collected on Tanegashima Island were investigated. The two types of plants were distinguished by calling them *L. fauriei* and *L. fauriei* (*Tanegashima-type*). Four new alkaloids, lasubine-I,-II, subcosine-I, and -II, all of which belong to the abresoline type, were isolated from the former. From the latter two, however, lythrine, cryogenine, and lythridine were isolated.

L. fauriei has been classified as *L. subcostata* var. *fauriei* by S. Hatusima, but from the chemotaxonomic aspect, it shows prominent differences from *L. subcostata*. Thus their classification under species would be more appropriate.

Useful Dethioacetalization with Soft Acid Metal Salts: Thallium Trinitrate and Mercuric Perchlorate. E. Fujita, Y. Nagao, and K. Kaneko. *Chem. Pharm. Bull.*, **26**, 3743 (1978).—Dethioacetalization with thallium trinitrate (TTN) was tried on thioacetals and good results were obtained. Then, the utility of co-solvents to be used with methanol was checked, and a wide range of co-solvents were shown to be available. The mechanism was also discussed.

Subsequently, dethioacetalization with mercuric perchlorate was found to be another excellent method. This procedure provided a great success for the dethioacetalization of some compounds which was not successful by the TTN procedure.

Oxidation of Organic Selenides to Selenoxides with Thallium (III) Salts. E. Fujita and M. Ochiai. *J. Indian Chem. Soc.*, **55**, 1226 (1978).—Thallium trinitrate oxidized diaryl- and aryl alkyl-selenides to their corresponding selenoxides in good yields. Oxidation with thallium tris(trifluoroacetate) was also discussed.

Dethioacetalization with Isoamyl Nitrite. K. Fuji, K. Ichikawa, and E. Fujita. *Tetrahedron Lett.*, 3561 (1978).—A new method of dethioacetalization with isoamyl nitrite is described. A typical experimental procedure is as follows: To a solution of dithioacetal of aldehyde or ketone in dichloromethane was added isoamyl nitrite (1 equiv.) and the mixture was stirred for 15 min. at room temperature. To the resulting red solution was added water and stirring was kept for an additional 15 min. Usual work-up of the reaction mixture gave the corresponding aldehyde or ketone in high yield.

New Reactions of Organic Sulfur Compounds with Thallium Trinitrate: A Synthesis of α -Oxodimethylketals. Y. Nagao, K. Kaneko, and E. Fujita. *Tetrahedron Lett.*, 4115 (1978).—The authors reported the conversions of β -oxosulfides into the corresponding α -oxodimethylacetals by treatment with thallium trinitrate in methanol. This reaction was now extended to a general synthesis of the α -oxodimethylketal, which is reported in this communication.

A New General Synthesis of α -Oxodimethylketals and α -Diketones: An Improved Bissulfenylation of α -Oxomethylenes. Y. Nagao, K. Kaneko, K. Kawabata, and E. Fujita. *Tetrahedron Lett.*, 5021 (1978).—A new bissulfenylation reagent was exploited by the authors. It is unsymmetrical disulfide, e.g. methyl 2-

nitrophenyl disulfide. By this reagent, the active methylene group at the α -position to a carbonyl group is subject to disulfenylation to give an α -oxodimethylthioacetal. The selective conversion of α -oxodimethylthioacetals into α -oxodimethylketals by thallium trinitrate in methanol and into α -diketones by mercuric perchlorate in THF is achieved.

Dealkylation of Esters and Cleavage of Alcoholic Carbon-Oxygen Bond of Lactones with Aluminium Halide-Thiol System. M. Node, K. Nishide, M. Sai, and E. Fujita. *Tetrahedron Lett.*, 5211 (1978).—Aluminium halide-thiol system had been proved by the authors to be very effective demethylation agent for aliphatic as well as aromatic methyl ethers. Now, this reagent system was applied to dealkylation of esters, and to the cleavage of alcoholic carbon-oxygen bond of lactones. Many examples are shown. Thus, a new efficient reagent system for conversions of esters into carboxylic acid by dealkylation and of lactones into ω -ethylthio-carboxylic acid by the C-O bond cleavage is exploited.

The Chemistry on Diterpenoids in 1977. Part-II. E. Fujita, K. Fuji, Y. Nagao, and M. Node. *Bull. Inst. Chem. Res., Kyoto Univ.*, 56, 356 (1978).—This is one of a series of the annual reviews on diterpenoids chemistry. This review covers the literatures published between July and December 1977 and also omissions in Part I.

The Chemistry on Diterpenoids in 1978. Part-I. E. Fujita, K. Fuji, Y. Nagao, and M. Node. *Bull. Inst. Chem. Res., Kyoto Univ.*, 57, 260 (1979).—This is one of a series of the annual reviews on diterpenoids chemistry. This review covers the literatures published between January and June 1978 and also omissions in 1977.

Aluminium Halide-Thiol System: A Useful Reagent for Demethylation of Aliphatic and Aromatic Methyl Ethers and Demethylenation of Methylenedioxy Compounds. M. Node, K. Nishide, M. Sai, K. Ichikawa, K. Fuji, and E. Fujita. *Chemistry Lett.*, 97 (1979).—A new efficient procedure for demethylation of methyl ethers and demethylenation of methylenedioxy compounds under mild conditions has been exploited by the use of aluminium halide-thiol system.

Total Synthesis of a Cyclophane Alkaloid, (\pm)-Lythranidine. K. Fuji, K. Ichikawa, and E. Fujita. *Tetrahedron Lett.*, 361 (1979).—The first total synthesis of lythranidine, a cyclophane alkaloid isolated from *Lythrum anceps* Makino, is described. Synthesis of a seventeen-membered ring using the Wittig reaction, epimerization of 2,6-*cis*-disubstituted pyridine into its *trans* isomer, and partial demethylation of *O,O'*-dimethoxybiphenyl moiety are involved as the key steps in this total synthesis.

Biosynthesis of Natural Products. Part 2. Syntheses of ^{14}C - or ^3H -Labelled *ent*-Kaur-16-ene Derivatives Oxygenated at C-7 or at C-7 and C-15, from Epicandicandiol. T. Fujita, S. Takao, and E. Fujita. *J. Chem. Soc. Perkin Trans. I*, 910 (1979).—*ent*-Kaur-16-en-7 α -ol, *ent*-kaur-16-en-7-one, *ent*-kaur-16-en-7 β -ol, *ent*-kaur-16-en-15-on-7 α -ol, and *ent*-kaur-16-ene-7,15-dione, and their labelled com-

pounds, which are required for the investigation on the biosynthetic route from *ent*-kaur-16-ene into enmein and oridonin, were synthesised from epicandicandiol.

Biosynthesis of Natural Products. Part 3. Syntheses of *ent*-[17-¹⁴C]-Kaur-16-en-20-ol from Enmein and of *ent*-[17-¹⁴C]Kaur-16-ene Derivatives Oxygenated at C-3 from *ent*-Kaur-16-ene-3 β ,19-diol. T. Fujita, I. Masuda, S. Takao, and E. Fujita. *J. Chem. Soc. Perkin Trans. I*, 915 (1979).—*ent*-[17-¹⁴C]Kaur-16-en-20-ol was synthesised from enmein, and *ent*-[17-¹⁴C]kaur-16-en-3 β -ol, *ent*-[17-¹⁴C]kaur-16-en-3-one, and *ent*-[17-¹⁴C]kaur-16-en-3 α -ol were synthesised from *ent*-kaur-16-ene-3 β ,19-diol. These labelled compounds were required for the investigation on the biosynthetic route from *ent*-kaur-16-ene into enmein and oridonin.

Hard Acid and Soft Nucleophile System. New Efficient Method for Removal of Benzyl Protecting Group. K. Fuji, K. Ichikawa, M. Node, and E. Fujita. *J. Org. Chem.*, **44**, 1661 (1979).—Aliphatic and aromatic benzyl ethers were easily cleaved on treatment with a hard acid, boron trifluoride etherate, and a soft nucleophile, EtSH or ethanedithiol, to give parent alcohols and phenols, respectively. Competitive debenzylation experiments demonstrated that the coordination of a hard acid (pulling factor) is more important than the nucleophilic attack of a soft nucleophile to the carbon atom (pushing factor) in this reaction.

Photochemical Reduction of Di-*t*-butyl Thioketone. A. Ohno, M. Uohama, K. Nakamura, and S. Oka. *Bull. Chem. Soc. Japan*, **52**, 1521 (1979).—Photochemical reduction of the title compound has been studied and the result is compared with that from the reaction with thiobenzophenone, an aromatic thioketone.

Asymmetric Reduction of Methyl Benzoylformate with a Chiral NAD(P)-H-Model Compound. A. Ohno, M. Ikeguchi, T. Kimura, and S. Oka. *J. Chem. Soc. Chem. Commun.*, 328 (1978).—The title reaction with *N*-(*R*)- α -methylbenzyl-1-propyl-2-methyl-4-(*R*)-methyl-1,4-dihydronicotinamide or its 4-(*S*)-methyl isomer affords methyl mandelate in 97% optical yield and quantitative chemical yield.

Reduction by a Model of NAD(P)H. XXIV. Application of a Phase-transfer System. K. Nakamura, A. Ohno, S. Yasui, and S. Oka. *Tetrahedron Lett.*, 4815 (1978).—Thiopivalophenone has been reduced to the corresponding thiol in a two-phase system by 1-benzyl-1,4-dihydronicotinamide, a phase-transfer reagent. The catalytic cycle is 5–15.

The Chlorination of Nornornene and Cyclooctadienes with Sulfuryl Chloride and Phosphorus (V) Chloride. Ionic vs. Radical Chlorination with Each Reagent. S. Uemura, H. Okazaki, A. Onoe, and M. Okano. *Bull. Chem. Soc., Japan*, **51**, 3568 (1978).—The chlorination of norbornene and cyclooctadienes with sulfuryl chloride and phosphorus (V) chloride has been investigated mainly in carbon tetrachloride under various conditions. From the studies of the product distributions and the effect of radical scavengers, the following facts have been revealed for the first time in olefin chlorination: chlorination with sulfuryl chloride proceeds through an

ionic pathway at room temperature or in the presence of silica gel and that with phosphorus (V) chloride through a radical pathway at elevated temperature, and an ionic chlorination with phosphorus (V) chloride in nonpolar solvents does not seem to involve C-P bond formation through the reaction.

O-Methylation of Aromatic (*E*)-Oximes by Dimethylsulfonium Methylide S. Tanimoto, T. Yamadera, T. Sugimoto, and M. Okano. *Bull. Chem. Soc. Japan*, **52**, 627 (1979).—The reactions of dimethylsulfonium methylide with (*E*)-aldoximes and (*E*)-ketoximes proceeded smoothly at room temperature and gave moderately good yields of *O*-methyl (*E*)-aldoximes and *O*-methyl (*E*)-ketoximes, respectively. A possible scheme for the formation of *O*-methyl (*E*)-oximes has been discussed.

The Reaction of ω -Ethoxyalkyl Bromides with Silver (I) Cyanide and Nitrite. The Participation of an Oxonium Ion. N. Watanabe, S. Uemura, and M. Okano. *Bull. Chem. Soc. Japan*, **52**, 1975 (1979).—The reaction of ω -ethoxyalkyl bromides (C_n : $n=2-5$) with silver (I) cyanide or nitrite in less polar solvents to give the corresponding isocyanide or a mixture of the corresponding alkyl nitrite and nitroalkane respectively, proceeded with ease only when $n=4$. In the latter reaction, the ratios of O- and N-attack (O/N) were 16–18/82–84 and 31–46/54–69 when $n \neq 4$ and $n=4$ respectively. The facile reaction in both cases when $n=4$ and the increasing O-attack in the case of silver (I) nitrite may suggest that the reaction proceeds through the initial formation of a five-membered oxonium ion, the *O*-ethyltetrahydrofuranium ion, and a subsequent attack by CN^- and NO_2^- or their silver (I) bromide complex.

Sulfur Ylides Attached to Some Condensation Polymers. S. Tanimoto, Y. Imazu, T. Sugimoto, and M. Okano. *Bull. Inst. Chem. Res., Kyoto Univ.*, **56**, 345 (1978).—In the present paper the syntheses of polymer-bound sulfonium salts and oxosulfonium salt using a dichloromethyl derivative of methyl phenyl sulfide, 2,4-bis(chloromethyl)thioanisole, and the epoxidation reactions by use of polymeric sulfur ylides derived from them are described.

Asymmetric Reduction of Aromatic Ketones by Sodium Borohydride in the Presence of Bovine Serum Albumin. T. Sugimoto, Y. Matsumura, S. Tanimoto, and M. Okano. *J. Chem. Soc., Chem. Commun.*, 926 (1978).—Bovine serum albumin was used to provide a chiral template for asymmetric reduction of aromatic ketones by the achiral $NaBH_4$, and substantial (20–80%) enantiomeric excesses were obtained in the product alcohols.

Preparation of Optically Active Aromatic Sulfoxides of High Optical Purity by the Direct Oxidation of the Sulphides in the Presence of Bovine Serum Albumin. T. Sugimoto, T. Kokubo, J. Miyazaki, S. Tanimoto, and M. Okano. *J. Chem. Soc., Chem. Commun.*, 402 (1979).—Aromatic sulphides were oxidized with sodium metaperiodate in the presence of bovine serum albumin to give the corresponding sulfoxides of high optical purity (81% max.) in good chemical yields.

^{13}C Chemical Shifts and ^{13}C - ^{15}N and ^{13}C - ^{57}Fe Spin Coupling Constants as Structural Probes for Haem Environments. ^{13}C N.M.R. Study of the Binding

of ^{15}N and ^{13}C Labelled Alkyl Isocyanides to Myoglobin and Synthetic Porphyrins. I. Morishima, T. Hayashi, T. Inubushi, T. Yonezawa, and S. Uemura. *J. Chem. Soc. Chem. Commun.*, 483 (1979).—A ^{13}C n.m.r. study of ^{13}C and ^{15}N labelled alkyl isocyanides ($\text{R}^{15}\text{N}^{13}\text{C}$) bound to the haem iron (II) atom labelled with ^{57}Fe in natural myoglobin and synthetic tetraphenyl- and octaethyl-porphyrin iron (II) shows that the iron-bound isocyanide ^{13}C chemical shifts and ^{15}N - ^{13}C coupling constants are sensitive to variation of the R group and the presence of globin, while the one-bond ^{13}C - ^{57}Fe coupling constant is not susceptible to these structural factors.

Alkoxy- and Halogeno-Selenocyanation of Olefins with Copper (II) Chloride or Bromide and Potassium Selenocyanate. A. Toshimitsu, Y. Kozawa, S. Uemura, and M. Okano. *J. Chem. Soc. Perkin Trans. I*, 1273 (1978).—Treatment of olefinic hydrocarbons with copper (II) chloride or bromide and potassium selenocyanate in alcohols readily affords the corresponding vicinal alkoxy-selenocyanatoalkanes (A) in good yields, while in acetonitrile vicinal halogenoselenocyanatoalkanes (B) are formed in satisfactory yields. In the cases of cyclohexene and octenes, the formation of (B) together with (A) was observed in alcohol when the reaction was stopped after a short time, (B) being converted into (A) by prolonging the reaction. The reaction proceeds through oxidation of selenocyanate anion to the corresponding cation and its electrophilic attack on the olefin, followed by competitive addition of alcohol and complexed halide anion, such as Cu_2X_3^- . The route of the substitution of halogen in (B) by an alkoxy group giving (A) has also been elucidated. The conversion of (B) obtained from cyclohexene into (A) occurs with complete retention of configuration (*trans*→*trans*), suggesting the intervention of an episelenonium ion intermediate.

Stereochemistry of the Bromination of Acetylenes with Bromine and Copper (II) Bromide. S. Uemura, H. Okazaki, and M. Okano. *J. Chem. Soc. Perkin Trans. I*, 1278 (1978).—Reactions of acetylenes ($\text{RC}\equiv\text{CR}'$: R and/or $\text{R}'=\text{H}$, alkyl, or phenyl) (1) with molecular bromine in chloroform give a mixture of the corresponding *E*- and *Z*-dibromoalkenes in high yields, the *E*-isomer being predominant under kinetically controlled conditions except in the case of (1; $\text{R}=\text{Ph}$, $\text{R}'=\text{Bu}^t$) where the *Z*-isomer is the sole product. From the reaction with an excess of bromine or under u.v. irradiation a thermodynamic equilibrium mixture of both isomers was obtained, the same mixture being readily formed by u.v. irradiation of a solution of any mixture of isomers in chloroform. Reactions with copper (II) bromide in acetonitrile at 20–25°C also give the same products, the rates of reaction being much less and the isomerization of the products much slower, and the stereospecificity being much higher than for bromination with molecular bromine. The kinetically controlled product ratios between *E*- and *Z*-dihalogenoalkenes are obtained from the reactions of four alkyl-phenylacetylenes ($\text{R}=\text{Ph}$, $\text{R}'=\text{H}$, Me, Pr^t , or Bu^t) with iodine, iodine monochloride, bromine, and chlorine. The results are explained in terms of a cyclic iodonium ion intermediate for the former two reaction and an open vinyl cation intermediate for the last; for bromination, an open vinyl cation intermediate in which bromine may interact weakly with the benzylic cation is postulated.

Chlorination and Interhalogenation of Alkylphenylacetylenes with Antimony Pentachloride. S. Uemura, H. Okazaki, A. Onoe, and M. Okano. *J. Chem. Soc., Perkin Trans. I*, 548 (1979).—Reactions of alkylphenylacetylenes with antimony pentachloride in carbon tetrachloride give the corresponding dichloroalkenes in 20–55% yields, (*Z*)-addition predominating. In the presence of iodine or lead (*II*) thiocyanate, interhalogenation occurs to give the chloriodo- or chlorothiocyanato-alkenes respectively as the sole or the main products in fair to good yields, the (*E*)-isomer being predominant except the case of phenylacetylenes where the stereospecificity is low. A concerted or near-concerted molecular addition of antimony pentachloride or its dimer to triple bond is postulated for the chlorination with very high (*Z*)-stereospecificity, and the stepwise (*E*)-attack of iodine monochloride or chlorothiocyanogen activated by antimony pentachloride is proposed for the interhalogenation. Replacement of an iodine, a bromine, or a chlorine atom in *vic*-dihalogenoalkenes by a chlorine atom of antimony pentachloride has been shown to occur through a vinyl cation intermediate by product analysis as well as a study of the isomerization of the starting dihalogenoalkenes.

Intramolecular Oxselenation of Diolefins. A. Toshimitsu, S. Uemura, and M. Okano. *J. Chem. Soc., Perkin Trans. I*, 1206 (1979).—Reaction of *cis*, *cis*-cycloocta-1,5-diene, diallyl ether, or hexa-1,5-diene with copper (*II*) chloride and potassium selenocyanate in methanol gives smoothly 2,6-dimethoxy-9-selenabicyclo[3.3.1]nonane (1), an isomeric mixture of 3,5-bis(methoxymethyl)-1-oxa-4-selenan (2) and 3-methoxymethyl-6-methoxy-1,4-oxaselenepan (3), or an isomeric mixture of 2,5-bis(methoxymethyl)selenolan (4) and 2-methoxymethyl-5-methoxyselenan (5), respectively, in good yield. The ^{13}C n.m.r. spectra of (2)–(5) revealed the presence of nearly equal amounts of two isomers in each compound, probably *cis* and *trans* with respect to the two substituents on the ring. The reaction has been revealed to proceed through methoxyselenocyanation of one double bond, followed by *in situ* intramolecular oxselenation of the other in the resulting alkyl selenocyanates. Isomerizations between (2) and (3) and also between (4) and (5) were effected by hydrogen chloride in methanol through an episelenium ion intermediate, the ratios of (2):(3) and (4):(5) being 95:5 and 41:59 respectively at equilibrium.

Oxythallation of Norbornene Derivatives with Thallium(III) Acetate in Methanol. S. Uemura, H. Miyoshi, M. Okano, I. Morishima, and T. Inubushi. *J. Organometal. Chem.*, **165**, 9 (1979).—Treatment of norbornene, norbornadiene, benzonorbornadiene, and chloro- and methoxy-benzonorbornadiene with thallium (*III*) acetate in methanol affords only the corresponding *cis-exo*-acetoxythallation adducts in a sharp contrast to oxymercuration of such strained olefins where methoxymercuration prevails. In the cases of substituted benzonorbornadienes the products are obtained as the regioisomeric mixtures, the isomer ratio being determined by ^{13}C NMR. In the cases of 5-norbornene-2,3-dicarboxylic anhydride, 5-norbornene-2-methyl-2,3-dicarboxylic anhydride, and 5-norbornene-2-endo-carboxylic acid, lactonization occurs to give a *trans*-oxythallation adduct having a lactone ring, no introduction of either methoxy or acetoxy groups being observed. ^1H and/or ^{13}C NMR data for several new oxythallation adducts are provided. The alkaline sodium borohydride

reduction of adducts in methanol affords mainly the parent olefin together with 10–16% yields of the corresponding *exo*-alcohol.

Acetoxythallation and Acetoxymercuration of *endo*- and *exo*-Dicyclopentadienes and Bicyclo[3.2.1]octa-2,6-diene. S. Uemura, H. Miyoshi, M. Okano, I. Morishima, and T. Inubushi. *J. Organometal. Chem.*, **171**, 131 (1979).—Treatment of *endo*- and *exo*-dicyclopentadiene with thallium(III) acetate in methanol, chloroform or dichloromethane affords a regioisomeric mixture of the *cis-exo*-acetoxythallation adducts. The isomer ratios in the adducts were determined directly by ^{13}C NMR spectra of the crude products. Acetoxymercuration of the same dienes also affords the corresponding regioisomeric *cis-exo* adducts, the selectivity being lower compared with that of acetoxythallation. Acetoxythallation and acetoxymercuration of bicyclo[3.2.1]octa-2,6-diene in dichloromethane gives single *cis-exo* adducts, respectively.

Asymmetric Reactions in Hydrophobic Chiral Binding Sites of Molecular Aggregates, Inclusion Compounds and Proteins. T. Sugimoto. *Hyomen (Surface)*, **17**, 12 (1979), in Japanese.—This review deals with asymmetric reactions conducted in hydrophobic chiral binding sites of molecular aggregates (chiral micelles and bilayers), inclusion compounds (cyclodextrins) and proteins (avidin and bovine serum albumin).

Polymer Chemistry

Light Scattering Characterisation of Polymers. I. An Extension of the Zimm Plot. H. Suzuki. *British Polymer Journal*, **11**, 35 (1979).—A new method is proposed for extrapolating light-scattering data to the zero angle of scattering. Essentially the method consists of iterative extrapolations by use of the regression method as a subroutine, and it applies in general to the data obtained at low polymer concentrations and at low angles of scattering. Light-scattering results on high molecular weight linear polystyrene in benzene were successfully analyzed with the method. In comparison with other published methods, the strong points and limitations of the method are discussed.

Light Scattering Characterisation of Polymers. II. Analyses of High Molecular Weight Polystyrene. H. Suzuki. *British Polymer Journal*, **11**, 41 (1979).—For light scattering analysis of an extremely high molecular weight polymer with large size in solution, use of mixtures of a given polymer with its low molecular weight homologue is described to have great advantages. With such bimodal mixtures as test samples, one can alter the unknown form of the angular variations of scattered lights to a form to be expected and widen the range of the linearity with $\sin^2 (\theta/2)$, where θ is the scattering angle. According to the considerations, a sample of linear polystyrene was successfully analyzed on a commercial apparatus, Fica 50 to have the weight-average molecular weight of 27 million.

The Determination of Molecular Weights of *Streptomyces* Subtilisin Inhibitor and the Complex of *Streptomyces* Subtilisin Inhibitor and Subtilisin

BPN' by Sedimentation Equilibrium. K. Inouye, B. Tonomura, K. Hiromi, T. Kotaka, H. Inagaki, S. Sato, and S. Murao. *J. Biochem.*, **84**, 843 (1978).—The molecular weight of *Streptomyces* subtilisin inhibitor (SSI), a protein proteinase inhibitor, and that of the complex of SSI and subtilisin BPN'[EC 3.4.21.14] were determined by a sedimentation equilibrium method in 25 mM phosphate buffer, at pH 7.0, ionic strength 0.1 M (NaCl), 25.0°C. The molecular weight of SSI was found to be 23,000 over a wide concentration range, 0.01–10 mg/ml, the range used for inhibitory, spectrophotometric and kinetic measurements. Based on the amino acid sequence, the molecular weight of SSI has been calculated to be 11,500 (Ikenaka, T., *et al.* (1974) *J. Biochem.*, **76**, 1191–1209); therefore, the molecular weight of 23,000 obtained above suggests that SSI is in a dimeric form under usual conditions in the concentration range of $5 \times 10^{-7} - 5 \times 10^{-4}$ M.

The molecular weight of the subtilisin BPN'-SSI complex was determined to be 78,000 in the concentration range of 0.03–5.0 mg/ml by sedimentation equilibrium of the crystallized preparation and by that of a mixture of subtilisin BPN' and SSI treated as a multicomponent-polydisperse system. The molecular weight obtained here, combined with the results of binding stoichiometry (Inouye, K., *et al.* (1977) *J. Biochem.*, **82**, 961–967) that showed that one mol of SSI (molecular weight, 11,500) and one mol of the enzyme (molecular weight, 27,500) are tightly bound ($K_d < 1$ nM), demonstrate that one mol of dimeric SSI binds two mol of the enzyme to form a stable complex, E_2I_2 .

Conformation of Block Copolymers in Dilute Solution. 3. Determination of the Center-to-Center Distance between the Two Blocks by Light Scattering.

T. Tanaka, M. Omoto, and H. Inagaki. *Macromolecules*, **12**, 146 (1979).—The conformation of an AB diblock copolymer in dilute solution may be characterized by the mean-square radii $\langle S^2 \rangle_A$ and $\langle S^2 \rangle_B$ of the two blocks and the mean-square distance $\langle G^2 \rangle$ between the centers of mass of them. It was previously established that $\langle S^2 \rangle_K$ ($K=A$ or B) is almost identical with the radius $\langle S^2 \rangle_{H-K}$ of the equivalent K homopolymer, unless the A-B interactions are attractive. In such a situation, it is possible to determine $\langle G^2 \rangle$ by light scattering with a solvent having large refractive index increments for the two homopolymers. Experiments were conducted on polystyrene-poly (methyl methacrylate) diblock copolymers in 2-butanone. The parameter σ representing the extent of "segregation" of the two blocks, $\sigma = \langle G^2 \rangle / (2\langle S^2 \rangle_A + 2\langle S^2 \rangle_B)$, was evaluated with due regard to the sample heterogeneity. The influence of heterogeneity was found to be unexpectedly large even for a fairly homogeneous sample, say $M_w/M_n < 1.1$, and without adequate correction to this effect, the conclusion drawn from such an analysis could be misleading. It was found that σ lies very close to 1.2. This shows that the conformation of the block copolymer is almost the same as that of the homopolymers. Models like "segregated" and "core-in-shell" conformations are utterly at variance with reality.

Evidence for the Random-Coupling Structure of an Anionically Prepared Block Copolymer. M. Omoto, T. Tanaka, S. Kadokura, and H. Inagaki. *Polymer*, **20**, 129 (1979).—It was experimentally verified that a polystyrene (PS)-polybutadiene (PB) block copolymer of AB type, which was prepared anionically *via* a sequential

addition procedure, has a random-coupling structure, viz., a structure such that the molecular weights of the two blocks are uncorrelated with each other: Firstly, two living PB's of widely differing lengths were prepared separately. Secondly, they were mixed, and the second monomer styrene was introduced to form a PB-PS block copolymer, which was found to be a mixture of two copolymers largely different in composition, so that they could be easily separated from each other (the third step). In the fourth step, each fraction was subjected to selective degradation of the PB block. Finally, the two PS blocks thus recovered were compared by using gel permeation chromatography, and found to give an identical chromatogram.

Conformation of Polymer Chains as Revealed by Small Angle Neutron Scattering. T. Tanaka. *Kagaku no Ryoiki (J. Japanese Chemistry)*, **33**, 43 (1979), in Japanese.—Small angle neutron scattering (SANS) has made it possible to measure size and shape of macromolecules in bulk, in concentrated solution, in oriented polymeric solids, and in many other cases for which no other experimental techniques are available. It makes use of the large difference in the neutron scattering cross-section of hydrogen and deuterium. Following a brief description of the principles and instrumentation of SANS, recent experimental results are surveyed somewhat critically.

Sorption Mechanism of Mercuric Ions by Keratine Gels of Thiol-Type. T. Miyamoto, H. Ito, M. Sugitani, and H. Inagaki. *Sen-i Gakkaishi (Journal of the Society of Textile and Cellulose Industry, Japan)*, **34**, T-405 (1978).—Sorption behavior of Hg^{2+} by the keratine gel of thiol-type, which was prepared from wool keratin, was investigated. The behavior was discussed in relation to (i) the amphoteric nature, (ii) the chemical modification of side-chain polar groups, and (iii) the heat denaturation of keratine gels. It was found that the apparent isoelectric point of the keratine gel was closely related to the pH at which the Hg^{2+} uptake showed the minimum. The Hg^{2+} uptakes by modified keratine gels in acid media depended on their modification history. The results indicated that in acid media, the dominant binding modes of Hg^{2+} consist in chemisorption by the thiol as well as amino groups in the keratine gel and in chelation of Hg^{2+} through these groups. On the other hand, in neutral and alkaline media, very high Hg^{2+} uptakes were observed for all types of keratine gels independent of their modification history. Such high Hg^{2+} uptakes could be explained in terms of the cooperative interactions between electron negative atoms incorporated in the keratine gel, namely, sulphur, nitrogen, and oxygen rather than the ionization effect of the acidic groups present. The swelling volume of the heat-denatured keratine gels decreased considerably with increasing the treatment temperature, and a good relation was found between the rate of Hg^{2+} uptake and swelling volume of the gel: the rate of Hg^{2+} uptake decreased with decrease in the swelling volume.

Sorption Behavior of Heavy Metal Ions on S-Substituted Keratine Gels. T. Miyamoto, M. Sugitani, H. Ito, F. Taki, and H. Inagaki. *Sen-i Gakkaishi (Journal of the Society of Textile and Cellulose Industry, Japan)*, **34**, T-447 (1978).—Sorption behavior of heavy metal ions by various keratine gels, whose thiol groups were substituted with different groups, were investigated. For this purpose, the thiol groups of keratine gels were modified by (i) functional residues with chelate-forming or ion-binding

nature, (ii) residues with large group moments, and (iii) non-specific alkyl groups. In acid media, the sorption behavior of Hg^{2+} by these keratine gels depended strongly on the substituent introduced, although introduction of any substituent could cause no appreciable increase in the uptake. The results were discussed in relation to the chemical structure of keratine gels. On the other hand, prominent increases in the Hg^{2+} uptake were observed for all types of keratine gels independent of their substituent, when the pH of medium goes from neutral to alkaline. The sorption isotherms of Hg^{2+} observed at pH 9.0 for S-alkyl keratine gels were almost the same as that for the thiol-type gel. A series of experiments on Hg^{2+} desorption from the gel showed that the sorption characteristics of S-substituted keratine gels were more advantageous than that of the thiol-type gel from the standpoint of recovering Hg^{2+} once sorbed by the keratine gel. In addition, it was found that the sorption behavior of some metal ions, i.e., Cd^{2+} , Pb^{2+} , and Cu^{2+} , varied to some extent with the substituents introduced, although all types of keratine gels exhibited predominantly higher uptakes for Hg^{2+} than those for these metal ions.

Time-Dependent Flow Fields in a Coaxial Cylinder Rheometer. The Flow of a BKZ Fluid at the Start of Rotation. K. Osaki, K. Kajiwara, N. Bessho, and M. Kurata. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 169 (1979).—Numerical calculations were performed to study the flow of polymeric liquids at the start of rotation of a coaxial cylinder rheometer. The rheological behavior of polymeric liquids was assumed to be represented by a strain-dependent constitutive model of Bernstein, Kearsley, and Zapas (BKZ model) and the stress equation of motion was solved with an electronic computer. The distribution of rate of shear starts from that expected for the steady flow of a Newtonian liquid and approaches the distribution obtained for the steady flow of a power law liquid. The rate of shear at a fixed point varies monotonously at low rates of rotation where the phenomenon of stress-overshoot is not very marked. At high rates of rotation, the rate of shear passes over a maximum or a minimum, respectively, depending on whether the sample is located close to the inner wall or the outer wall. At a certain radius slightly smaller than the average of the inner and outer radii of the cylindrical gap, the rate of shear scarcely depends on time provided that the rotation velocity and the gap width are not too large. The use of coaxial cylinder rheometer to measure time-dependent shear stresses is justified under the same condition.

Transport and Equilibrium Phenomena of Gases in Styrene-Butadiene Block Copolymers. H. Odani, K. Taira, N. Nemoto, and M. Kurata. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 226 (1979).—The diffusion and solution behavior for a series of inert gases (helium, argon, nitrogen, krypton, and xenon) in films of styrene-butadiene block copolymers having different morphologies were studied by the static sorption method. The equilibrium solubility coefficients of gases in the copolymer films were described in terms of a model, in which additivity of volumes of both components was assumed. The temperature dependence of diffusion and solubility coefficients over the range from 25 to 75°C was represented by the Arrhenius-type equation with constant activation energy for diffusion and heat of solution, respectively. Thermody-

dynamic parameters were evaluated, and mechanisms of gaseous diffusion and solution in the block copolymer films were discussed.

Photon Correlation Spectroscopy of Particle Distributions. E. Gulari, E. Gulari, Y. Tsunashima, and B. Chu. *J. Chem. Phys.*, **70**, 3965 (1979).—A least-squares method for correlation function profile analysis using a histogram approximation is described. The method is completely general, especially for bimodal distributions, and compares favorably with the method of cumulants. The measured photoelectron time-correlation function yields a histogram of the linewidth distribution which can be related uniquely to the particle size. The analysis is tested using simulated data with unimodal and bimodal size distributions. In our verification of the method using aqueous suspensions of Dow latex spheres, we have shown that our method is not only consistent with the results from electron microscopy, but that it is more precise and truly measures the hydrodynamic size of particles suspended in fluids.

Polymer Diffusion in a Dilute Theta Solution: 1. Polystyrene in Cyclohexane. E. Gulari, E. Gulari, Y. Tsunashima, and B. Chu. *Polymer*, **20**, 347 (1979).—Translational diffusion coefficients of two narrow molecular weight distributions of polystyrene in cyclohexane under theta conditions have been studied using Rayleigh linewidth spectroscopy. Experimental evaluation of the time correlation function profiles according to the histogram approximation shows that the diffusion coefficient at zero concentration (D_0) and the concentration dependence of the first-order friction coefficient (K_f) can be determined by making only one measurement of the time correlation function of a polymer solution of known molecular weight (such as M_z , M_w or M_n) at one concentration and one scattering angle. By making photon correlation measurements at two different concentrations, we are able to make a definitive comparison of our experiments with the theoretical descriptions of Yamakawa, Imai, and Pyun and Fixman. In contrast to earlier findings of King, Knox, Lee and McAdam (*Polymer* 1973, **14**, 151), our results are in excellent agreement with the theoretical prediction of Pyun and Fixman at the theta temperature.

Rheology of Copolymer Solutions. IV. Nonlinear Viscoelasticity of Solutions of an SBS Block Copolymer. K. Osaki, B. S. Kim, and M. Kurata. *Polym. J.*, **11**, 33 (1979).—Nonlinear viscoelasticity was investigated for concentrated solutions of a styrene-butadiene block copolymer, having a 4-armed star-branched polybutadiene structure with a polystyrene block on each end. When the solvent was good for both polystyrene and polybutadiene, the viscoelastic behavior was similar to that of homopolymer solutions. In the case of 1-chlorohexadecane, a nonsolvent for polystyrene at temperatures below 25°C, the viscoelastic behavior of the solutions was quite different: the rate of shear-temperature and -concentration reduction rules were not applicable to the steady shear viscosity, the Cox-Merz empirical rule was not applicable, and the maximum relaxation time decreased with increasing rate of shear. It was inferred that the behavior of the copolymer solutions could be described by using the BKZ constitutive model. Model calculations performed for a solution in 1-chlorohexadecane revealed that the shear stresses for various flow histories were predicted well if the memory function was evaluated from the strain-dependent relax-

ation modulus. The characteristic behavior of the solutions in 1-chlorohexadecane was attributable to a strain-sensitive relaxation mode of a long relaxation time, presumably due to the molecular aggregate formed through temporary cross-links of precipitated polystyrene blocks.

Linear Viscoelasticity of Dilute Polymer Solutions. N. Nemoto. *J. Soc. Rheol. Japan*, 7, 3 (1979), in Japanese.—Recent progress in linear viscoelasticity of dilute polymer solutions is reviewed critically. Firstly, experimental results are summarized; (1) viscoelastic behavior of rigid rods can be described well by the Kirkwood-Auer theory with minor modification; (2) Stiff chains have three types of relaxation process related to the rotation of molecules as a whole, bending motions, and probably side chain motions. No theory can predict their frequency dependence satisfactorily; (3) In spite of the presence of the repulsive force between ions, which extends polyelectrolyte chains, they show the behavior quite similar to flexible coils at short times. At the long time end, however, another mode related to end-over end rotation appears. (4) The plateau value of intrinsic dynamic viscosity of flexible coils in a high frequency region, $[\eta']_{\infty}^E$, was found quite dependent on the detailed chemical structure of macromolecules. The second part describes two main progresses in theory, reformulation of viscoelastic theories based on the time-correlation function method, and the calculation of limiting high frequency viscosity, $[\eta']_{\infty}$, from real chains which have constraints on their motions. The former gives the same result as the general theory of Kirkwood to the linear term. Concerning $[\eta']_{\infty}$, values calculated are all lower than $[\eta']_{\infty}^E$ by about two orders. By taking into account of rotational potential properly, however, Fixman succeeded in predicting the frequency dependence of $[\eta']$ compatible with experiments.

Structural Changes of Polyethylene Single Crystal due to Electron Irradiation. A. Kawaguchi. *Bull. Inst. Chem. Res., Kyoto Univ.*, 57, 206 (1979).—The thickness of polyethylene single crystal mat decreases with the increase of electron irradiation while its width increases. The resultant macroscopic volume of mat decreases at the initial stage of irradiation and decreases with further irradiation. Being in line with the volume change, the observed macroscopic density increases at low radiation doses and decreases at high radiation doses. However, the crystalline density obtained from the X-ray measurement shows the monotonical decrease with irradiation. The wide angle X-ray diffraction pattern becomes blurry and broad with the increase of radiation dose and simultaneously the discrete small angle X-ray diffraction is less intense and disappears when the crystallinity of mat is lost. The annealing behavior of irradiated mats differs from one another depending on how they are damaged by radiation. The lattice spacing d_{200} and the half-value breadth, which increase with irradiation, increase further by annealing at rather low temperature and decrease at the temperature above a certain temperature. These observations of changes in crystalline state by electron irradiation and subsequent annealing are interpreted in terms of the change in molecular orientation in a lamella, the decrease of interlamellar distance and the introduction of various defects in crystalline core which are caused by *interlamellar* and *intralamellar* cross-linking.

Deformation Mechanism of Polyethylene Spherulites. K. Shimamura, S. Murakami, M. Tsuji, and K. Katayama. *J. Soc. Rheology, Japan*, **7**, 42 (1979), in Japanese.—Internal structure exposed by fracturing necking part of drawn polyethylene has been examined by a scanning electron microscope and the deformation mechanism of spherulites has been clarified. Drawing of unoriented specimens at 100°C gave a structure composed of macrofibrils whose diameters were strongly dependent on the period of lamellar twisting in the original spherulites. On the other hand, in the specimens drawn at 0°C, many slender regions of complex structure existed among macrofibrils; the structure, about 1~2 μm diameter, stems from the lamellae perpendicular to the draw direction.

Characterization of Graft Copolymers. Y. Ikada. *Advances in Polymer Science*, **29**, 48 (1978).—The product of graft copolymerizations and grafting reactions is mostly a mixture of A homopolymer, B homopolymer and A-B graft copolymer. The efficient methods for separating the graft copolymer from products and determining its purity are described. In addition, the chemical structure of separated graft copolymers, *i.e.*, the number of branches, the length of branch and backbone polymers is discussed.

Intramolecular Crosslinking in Gelation. H. Iwata and Y. Ikada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 184 (1979).—Acetalization of poly(vinyl alcohol) (PVA) carrying mostly two terminal aldehyde groups was studied in aqueous acidic solution at different PVA concentrations. The transition from sol to gel or *vice versa* took place at the temperature, where an equilibrium was reached between acetalization and deacetalization. Using known rate constants for intra- and intermolecular acetalization as well as that for deacetalization, we could evaluate the extent of reaction at the sol-gel transition temperature, *i.e.*, at the gel point. Comparison of the observed with the theoretical extent of reaction at the gel point revealed that contribution of intramolecular acetalization to the overall reaction was too large to be neglected. It was concluded that two types of intramolecular crosslinkings, both ineffective for gelation, were operative, the one producing a small ring and the other a large ring.

Structure and Properties of Lightly Crosslinked Polyvinylidene Fluoride Crystallized from the Deformed Molten State. S.-H. Hyon and R. Kitamaru. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 193 (1979).—Effects of the deformation upon the supermolecular structure and thermal properties of lightly crosslinked polyvinylidene fluoride are investigated by X-ray diffraction and calorimetric technique. It is confirmed that the molecular chain conformation in drawn samples depends markedly on the draw temperature and draw ratio, and that the long period revealed by low angular X-ray scattering and the scattering intensity increase with increasing draw ratio, when uniaxially stretched in the molten state. On the contrary, when samples are uniaxially stretched at a high temperature below the melting point, the long period and scattering intensity decrease with increasing draw ratio. Furthermore, when compressed uniaxially in the molten state, a special planar orientation of the crystal planes of the orthorhombic form of this polymer appears, while no appreciable amount of the β -form appears. The (200) crystal plane is preferentially oriented parallel to the film surface for samples made in such a mode, but when compressed or biaxially

stretched in the partially crystallized state, other planar orientations such as (010) and (110) are produced without the (200) orientation.

Small-Angle Scattering of Microparacrystallites (mPC's). R. Hosemann, J. Loboda-Čačković, and K. Kaji. *J. Appl. Cryst.* **11**, 540 (1978).—Two-dimensional small-angle X-ray scattering (SAXS) analysis combined with wide-angle X-ray scattering (WAXS) from highly oriented polymers proves that the polymers consist of mosaic blocks with paracrystalline distortions—the so-called microparacrystallites (mPC's), which are the bricks of a paracrystalline superlattice—the so-called macroparacrystal (MPC). The concept of meso-phases fails, because the MPC's show simultaneously both nematic and smectic properties. All this new information cannot be obtained with slit-smearing cameras and unoriented samples.

Kinetic Study on the Inter- and Intramolecular Acetalization Reactions of Polymeric Reactants. H. Iwata and Y. Ikada. *Macromolecules*, **12**, 287 (1979).—Inter- and intramolecular acetalizations of poly(vinyl alcohol) (PVA) carrying one or two terminal aldehyde groups were carried out in aqueous solutions as well as in dimethyl sulfoxide (Me_2SO) solutions over a wide range of the polymer concentration. The observed rate constant for intermolecular acetalization was in both the solutions independent of the polymer concentration and not significantly different from that for the acetalization of a conventional PVA with aldol, a homologous low molecular weight aldehyde. The results strongly suggest that the polymer coils interpenetrate rather freely with each other in concentrated solutions even of Me_2SO which is a good solvent of PVA (water is almost a θ solvent of PVA). This finding is in agreement with the theory predicting that the excluded volume effect may not be large enough to be detectable under the experimental conditions of this study. In addition, the observed OH concentration effective for the intramolecular acetalization was compatible with that predicted by the statistics of polymer chains.

Radiation Processing in the Biomedical Materials. Y. Ikada and I. Kaetsu. *Genshiryoku Kogyo (Atomic Energy Industry)*, **25**, 73 (1979), in Japanese.—Review.

Biomedical Application of Polymers. Y. Ikada. *Kagaku (Chemistry)*, **33**, 850 (1978), in Japanese.—This article covers the biomedical applications of polymers which have been established mostly in our laboratory.

Water Fogging and Repellency. Y. Ikada. *Kobunshi (High Polymer)*, **28**, 258 (1979), in Japanese.—Review.

Neurosurgery and Polymers. Y. Ikada and H. Iwata. *Kobunshi Kako (Polymer Processing)*, **27**, 467 (1978), in Japanese.—Examples are described on polymer applications to neurosurgery which have been developed in our laboratories. They include balloon catheters to be used for embolization, a small-diameter artificial blood vessel and a soluble splint for anastomosis.

High Resolution NMR for the solid and complex states of substances. R. Kitamaru and F. Horii. *Kobunshi Kako (Polymer Processing)*, **28**, 277 (1979), in

Japanese.—Recent development of high resolution nmr technique applicable to the solid state of substances is briefly reviewed. It is suggested by introducing some recently published papers that new techniques such as proton-enhanced ^{13}C nmr and magic angle sample-spinning method must be very powerful to study the solid state or complex state of substances.

Swelling of Heat-Treated Polyelectrolyte Complexes Prepared from Carboxymethylated and Amino-acetalized Derivatives of Poly(vinyl alcohol). S. Sugii, M. Hosono, and R. Kitamaru. *Kobunshi Ronbunshu (The Society of Polymer Science, Japan)*, **35**, 441 (1978), in Japanese.—The effects of a heat-treatment on swelling properties for an ionic complex made from carboxymethylated and aminoacetalized derivatives of poly(vinyl alcohol) are investigated in terms of its molecular structure, *i.e.*, ionic bonds, and the formation of amide and hydrogen bonds. Much lower degree of swelling in water was found for a heat-treated product of the ionic complex of equivalent composition polyelectrolytes than the value calculated with an assumption that the ionic and amide bonds comprised intermolecular crosslinkages using the Flory's equation developed for the swelling of polymer networks. It is concluded from studies of the swelling behavior of the heat-treated product in aqueous solution with various values of pH that this low degree of swelling has been brought about by hydrogen bonds due to amino groups produced simultaneously with amide bonds through the annealing. The complex films annealed under slack state exhibited excellent mechanical properties in water. An X-ray analysis has revealed that the complex is amorphous regardless of the heat-treatment.

Surface Grafting onto PVA Films. Y. Ikada, H. Iwata, T. Mita, and S. Nagaoka. *Nippon Kagaku Sen-i Kenkyusho Koenshu (Annual Report of the Research Institute for Chemical Fibers, Japan)*, **35**, 1 (1978), in Japanese.—Grafting of dialdehyde starch and proteins has been carried out on PVA as well as ethylene-vinyl alcohol (EVA) films in aqueous media. Acetalization and Schiff-base formation are used for this grafting. It is shown that surface grafting takes place when EVA is used as the substrate.

NMR Studies of the Phase Structure of Fibers—Effects of Annealing on the Phase Structure and Dyeability.—R. Kitamaru, K. Konishi, F. Horii, S.-H. Hyon, T. Yasuda, and T. Okuno. *Nippon Kagakusen-i Kenkyusho Koenshu (Annual Report of the Research Institute for Chemical Fibers, Japan)*, **35**, 51 (1978).—The phase structure of nylon 6 and polyethylene terephthalate fibers is studied with broad-line ^1H nmr spectrum analysis. The spectra for the fibers annealed or dyed to different degrees were decomposed into three components; broad, medium and narrow, and the effects of annealing and dyeing on each component were examined. It is found by the nmr analysis that the molecular mobility of the amorphous material is heightened by annealing in compliance with the increase of dyeability.

Surface Energy of Polymers. Y. Ikada and T. Matsunaga. *Nippon Setchaku Kyokai Shi (Journal of the Adhesion Society of Japan)*, **14**, 427 (1978), in Japanese.—Review.

Surface Energy of Polymers (2). Y. Ikada and T. Matsunaga. *Nippon Setchaku Kyokai Shi (Journal of the Adhesion Society of Japan)*, **15**, 18 (1979), in Japanese.—Review.

Surface Energy of Polymers (3). Y. Ikada and T. Matsunaga. *Nippon Setchaku Kyokai Shi (Journal of the Adhesion Society of Japan)*, **15**, 91 (1979), in Japanese.—Review.

Application of the Balloon Catheters to Embolization and Superselective Angiography of the Intracranial Arteries. W. Taki, H. Handa, S. Yamagata, I. Matsuda, Y. Yonekawa, Y. Ikada, and H. Iwata. *Noshinkei Geka (Neurosurgery)*, **7**, 431 (1979), in Japanese.—This report describes that embolization and superselective of the intracranial arteries have been successfully performed with the use of unreleasable balloon catheters.

Biochemistry

Continuous ATP Regeneration Utilizing Glycolysis and Kinase Systems of Yeast. M. Asada, K. Nakanishi, R. Matsuno, Y. Kariya, A. Kimura, and T. Kamikubo. *Agric. Biol. Chem.*, **42**, 1533 (1978).—During the course of phosphorylation of adenosine and AMP by Acetone dried cells of yeast, enzymes in related to glycolysis and adenosine kinase as well as adenylate kinase were found to be released into the supernatant of the reaction mixture. The supernatant effectively phosphorylated adenosine and AMP at high phosphate concentrations utilizing glucose as an energy source, and the ATP accumulated was maintained at a high level still after 24 hr of incubation. A continuous reaction apparatus for regeneration of ATP equipped with a semi-permeable membrane was designed and constructed taking into account the specific characteristic of the present enzyme reaction systems. The released enzymes were applied to the apparatus equipped with semi-permeable membranes, and continuous phosphorylation of adenosine to ATP was examined under different operational conditions. When the residence time was 18 hr, 80% of the initial adenosine was continuously phosphorylated to ATP by this apparatus, in which the collodion membrane was used as a semi-permeable membrane.

Leucine Dehydrogenase of *Bacillus sphaericus*: Sulfhydryl Groups and Catalytic Sites. T. Ohshima, T. Yamamoto, H. Misono, and K. Soda. *Agric. Biol. Chem.*, **42**, 1739 (1978).—Leucine dehydrogenase was inhibited by *p*-chloromercuribenzoate and HgCl_2 , but not by 5,5'-dithiobis(2-nitrobenzoic acid), 4,4'-dithiopyridine and N-ethylmaleimide. Modification of sulfhydryl groups of the enzyme with *p*-chloromercuribenzoate and HgCl_2 was accompanied with a loss of the enzyme activity. The 6 reactive sulfhydryl groups per enzyme molecule play an essential role for catalysis. Approximately 12 sulfhydryl groups were titrated per molecule in the presence of 8 M urea: the enzyme contains 2 sulfhydryl groups per subunit, and one of them participates in the catalytic action. Fluorometric and gel filtration studies on binding of NADH to the enzyme revealed that the enzyme contains 6 coenzyme binding sites per molecule.

These results are compatible with the hexameric structure of leucine dehydrogenase composed of identical subunits, showing that each subunit has one catalytic site and one indispensable sulfhydryl group.

Determination of Branched-chain L-Amino Acids and Their Keto Analogs with Leucine Dehydrogenase. T. Ohshima, H. Misono, and K. Soda. *Agric. Biol. Chem.*, **42**, 1919 (1978).—The simple and sensitive spectrophotometric method for determination of branched-chain L-amino acids and their keto analogs with leucine dehydrogenase (EC 1.4.1.9) is described. Branched-chain L-amino acids were determined with the enzyme by measuring the formation of NADH spectrophotometrically. A linear relationship was established between the absorbance at 340 nm and the concentration of the amino acid (0.02~0.20 μ mol). The determination of branched-chain keto acids (0.01~0.12 μ mol) is based on the measurement of NADH disappeared. This method can be used to assay D-amino acid aminotransferase (EC 2.6.1.21), and is applicable to the assay of other enzymes catalyzing the formation or decomposition of branched-chain L-amino acids and their keto analogs as well.

Occurrence of a Novel Enzyme, L-Lysine Oxidase with Antitumor Activity in Culture Extract of *Trichoderma viride*. H. Kusakabe, K. Kodama, H. Machida, Y. Midorikawa, A. Kuninaka, H. Misono, and K. Soda. *Agric. Biol. Chem.*, **43**, 337 (1979).—An aqueous extract of culture of *Trichoderma viride* Y244-2 on wheat bran showed antitumor activity against L5178Y mouse leukemic cells *in vitro* and L1210 mouse leukemia *in vivo*. The principle of the antitumor activity was proved to be an L-lysine-oxidizing enzyme. Oxygen consumption was accompanied by the formation of α -keto acid, ammonia and hydrogen peroxide in the enzyme reaction with L-lysine. The ratio of amount of oxygen consumed to those of α -keto acid and ammonia formed in the presence of catalase was approximately 1:2:2. This enzyme is an L-amino acid oxidase which is highly specific for L-lysine. Thus, we designated it as L-lysine oxidase. Identity of the antitumor substance with the enzyme was confirmed by DEAE-cellulose column chromatography: the elution pattern of growth-inhibitory activity against L5178Y cells coincided with that of L-lysine oxidase activity.

Lysine Production by S-(β -Aminoethyl)-L-cysteine Resistant Mutants of *Candida pelliculosa*. E. Takenouchi, T. Yamamoto, Donka K. Nikolova, H. Tanaka, and K. Soda. *Agric. Biol. Chem.*, **43**, 727 (1979).—S-(β -Aminoethyl)-L-cysteine (SAEC), a sulfur analog of L-lysine, significantly inhibited the growth of wild-type strains of *Candida* species. The growth inhibition of *C. pelliculosa* depended on SAEC concentrations, but L-lysine and L- α -aminoadipate restored growth effectively. SAEC-resistant mutants were induced from the wild-type strain of *C. pelliculosa* by ultraviolet irradiation and N-methyl-N'-nitro-N-nitrosoguanidine treatment. Almost all resistant mutants excreted some L-lysine into the medium. Lysine excretion increased after repeated mutations. The mutant strain SR-V-1263 extracellularly produced about 2 mg/ml of L-lysine after shaking culture for 96 hr. The effect of various factors on lysine accumulation was investigated with strain SR-V-1263. The concentration of extracellular lysine reached a maximum (3.2 mg/ml) in medium containing 2% polypeptone under the experimental conditions.

Antibacterial Activity of L-Lysine α -Oxidase against *rec*⁺ and *rec*⁻ Strains of *Bacillus subtilis*. H. Kusakabe, M. Sugi, K. Kodama, A. Kuninaka, H. Misono, and K. Soda. *Agric. Biol. Chem.*, **43**, 1371 (1979).—The recombinationless mutant strain

of *Bacillus subtilis* is more sensitive to the cell-killing action of L-lysine α -oxidase, which is a novel fungal enzyme discovered by us, than the wild strain is when examined by the method of Kada *et al.* (*Mutat. Res.*, **16**, 165 (1972)) (*rec* assay). The *rec*⁻ mutant is more sensitive to O₂⁻ and OH[•] than the wild strain.

Coenzyme B₁₂-Dependent Diol Dehydrase: Purification, Subunit Heterogeneity, and Reversible Association. A. A. Poznanskaja, K. Tanizawa, K. Soda, T. Toraya, and S. Fukui. *Arch. Biochem. Biophys.*, **194**, 379 (1979).—A purification procedure for diol dehydrase (DL-1,2-propanediol hydro-lyase, EC 4.2.1.28) of *Klebsiella pneumoniae* (*Aerobacter aerogenes*) ATCC 8724 has been developed which gives the highest specific activity for this enzyme obtained so far. The purified enzyme is homogeneous by the criteria of ultracentrifugation ($S_{20,w}=8.9\ S$) and disc gel electrophoresis in the presence of substrate. The molecular weight of approximately 230,000 was obtained by gel filtration and ultracentrifugal sedimentation equilibrium. The enzyme is composed of components *F* and *S* whose molecular weights were determined to be approximately 26,000 and 200,000, respectively, by gel filtration. The incubation of both components *F* and *S* with the substrate leads to complete reassociation of the components. Disc gel electrophoresis in the presence of sodium dodecyl sulfate and terminal amino acid analyses indicate that component *S* consists of at least four nonidentical subunits. The reversible association and heterogeneity of the subunits were also demonstrated with the crude enzyme by immunoelectrophoresis.

Catalytic Action of L-Methionine γ -Lyase on Selenomethionine and Selenols. N. Esaki, H. Tanaka, S. Uemura, T. Suzuki, and K. Soda. *Biochemistry*, **18**, 407 (1979).—We examined the catalytic action of L-methionine γ -lyase (EC 4.4.1.11) on selenomethionine (2-amino-4-(methylseleno)butyric acid), methaneselenol, 1-hexaneselenol, and benzeneselenol. The enzyme catalyzes α,γ -elimination of selenomethionine to yield α -ketobutyrate, ammonia, and methaneselenol, and also its γ -replacement reaction with various thiols to produce S-substituted homocysteines. Selenomethionine is an even better substrate than methionine in α,γ -elimination but is less effective in γ -replacement. In addition, L-methionine γ -lyase catalyzes γ -replacement reaction of methionine and its derivatives with selenols to form the corresponding Se-substituted selenohomocysteines, although selenols are less efficient substituent donors than thiols. This is the first proven mechanism for the incorporation of selenium atom into amino acids.

Fermentative Phosphorylation of Glucosamine by Yeast. Y. Kariya, T. Yamamoto, Y. Sameshima, T. Yoshida, A. Kimura, and T. Tochikura. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 245 (1979).—Phosphorylation of glucosamine was investigated under the conditions of yeast fermentation (dissolution of glucose). Air-dried cell preparation of baker's yeast was used as enzyme source of fermentation and phosphorylation of glucosamine. By use of the energy derived from glucose dissolution, 20 mM of Gm 6-P were formed during 8 hr of incubation.

FBP, an intermediate of glycolysis, was found to be a suitable energy source than glucose in both efficiency of energy transference to glucosamine and rate of Gm 6-P formation.

A higher concentration of phosphate ion was required in the reaction mixture which contains glucose than that required in the reaction mixture containing FBP. Initiation of glucosamine phosphorylation in the reaction mixture containing glucose was closely related to the amount of glucose added. Gm 6-P formation was initiated immediately before the maximum accumulation of FBP and proceeded simultaneously with the degradation of accumulated FBP. Formation of Gm 6-P continued until FBP was consumed.

The remarkable catalytic action of an added ATP was observed in both glucose and FBP systems.

Crystallization and Properties of Aspartate Aminotransferase from *Escherichia coli* B. T. Yagi, H. Kagamiyama, K. Motosugi, M. Nozaki, and K. Soda. *FEBS Letters*, **100**, 81 (1979).—Aspartate aminotransferase (EC 2.6.1.1.) has been extensively studied as a representative of the pyridoxal 5'-phosphate (pyridoxal-P)-dependent enzymes. The enzyme catalyzes the reversible transfer of the amino group between L-aspartic acid and α -ketoglutaric acid, and plays an important role in nitrogen metabolism. Animal and plant tissues contain both mitochondrial and cytosolic isoenzymes [1]. The primary structures of both isoenzymes from pig heart muscle have been elucidated [2, 3]. Preliminary crystallographic data have been reported for the large and single crystals of cytosolic [4, 5] and mitochondrial isoenzymes [6]. Mammalian aspartate aminotransferases are immunochemically distinct from the bacterial enzymes [7]. Structural studies of the bacterial enzymes have not been done. The enzyme has been purified to homogeneity from *Pseudomonas striata* and crystallized [8]. However, its low content in cells and low yield in purification prompted a search for other bacterial sources to produce it more abundantly. The aspartate aminotransferases have been highly purified from *Escherichia coli* K-12 [9], its mutant [10] and Crooks strain [11], but none of them have been obtained in a crystalline form.

We describe here high yield purification, crystallization and some properties of aspartate aminotransferase from *Escherichia coli* B as a first approach to the comparative studies on the enzyme.

meso- α,ϵ -Diaminopimelate D-Dehydrogenase: Distribution and the Reaction Product. H. Misono, H. Togawa, T. Yamamoto, and K. Soda. *J. Bacteriol.*, **137**, 22 (1979).—A high activity of meso- α,ϵ -diaminopimelate dehydrogenase was found in extracts of *Bacillus sphaericus*, *Brevibacterium sp.*, *Corynebacterium glutamicum*, and *Proteus vulgaris* among bacteria tested. *B. sphaericus* IFO 3525, in which the enzyme is most abundant, was chosen to study the enzyme reaction. The enzyme was not induced by the addition of meso- α,ϵ -diaminopimelate to the growth medium. The reaction product was isolated and identified as α -amino- ϵ -ketopimelate by a comparison of the properties of its 2,4-dinitrophenylhydrazone with those of an authentic sample in silica gel thin-layer chromatography, absorption, infrared and proton nuclear magnetic resonance spectrometry, and elemental analyses. The α -amino- ϵ -ketopimelate formed enzymatically was decarboxylated by H_2O_2 to yield L- α -amino adipate. This suggests that the amino group with D-configuration in the substrate is oxidatively deaminated: the enzyme is a D-amino acid dehydrogenase. L- α -Amino- ϵ -ketopi-

melate undergoes spontaneous dehydration to the cyclic Δ^1 -piperidine-2,6-dicarboxylate. The enzyme reaction is reversible, and *meso*- α,ϵ -diaminopimelate was formed in the reductive amination of L- α -amino- ϵ -ketopimelate.

Purification and Properties of Pig Liver Kynureninase. K. Tanizawa and K. Soda. *J. Biochem.*, **85**, 901 (1979).—Kynureninase [L-kynurenine hydrolase, EC 3.7.1.3] was purified from pig liver by a procedure including DEAE-cellulose chromatography, hydroxyapatite chromatography, ammonium sulfate fractionation, DEAE-Bio Gel chromatography, Sephacryl S-200 gel filtration, Kynurenine-Sepharose affinity chromatography, and Sephadex G-200 gel filtration. The enzyme was found to be homogeneous by the criterion of disc-gel electrophoresis. The enzyme has a molecular weight of about 100,000 and exhibits absorption maxima at 280 and 420 nm. The optimum pH and the isoelectric point of the enzyme are 8.5 and 5.0, respectively. The Michaelis constants were determined to be as follows: L-kynurenine, 7.7×10^{-4} M; L-3-hydroxykynurenine, 1.3×10^{-5} M; and pyridoxal 5'-phosphate, 1.8×10^{-6} M. L-3-Hydroxykynurenine is hydrolyzed more rapidly than L-kynurenine; the liver enzyme can be regarded as a 3-hydroxykynureninase.

Comparison of Inducible and Constitutive Kynureninases of *Neurospora crassa*. K. Tanizawa and K. Soda. *J. Biochem.*, **85**, 1367 (1979).—Two types of kynureninase were isolated from *Neurospora crassa* IFO 6068. The formation of one of them, which was separated from the inducible kynureninase by DEAE-cellulose chromatography, was independent of the presence of tryptophan in the growth medium. Ouchterlony double-diffusion analysis and immunochemical titration indicated that the constitutive-type enzyme is immunologically different from the inducible enzyme. We confirmed by a selective assay method with antiserum that the addition of tryptophan to the medium does not affect the formation of one of the enzymes (constitutive-type). The constitutive kynureninase was purified approximately 650-fold and was free of the inducible enzyme as judged by analytical gel electrophoresis. The molecular weight and optimum pH values of both enzymes are very similar. However, the constitutive enzyme shows much higher activity and affinity for L-3-hydroxykynurenine than for L-kynurenine, suggesting that the enzyme functions biosynthetically as a 3-hydroxykynureninase.

Constitutive kynureninase activities were widely found in all the fungi tested, whereas the inducible enzyme activity was not present in *Mucor* or *Rhizopus* species. The inducible enzymes of all the *Neurospora* strains examined were shown to be immunologically identical.

Properties of Crystalline Leucine Dehydrogenase from *Bacillus sphaericus*. T. Ohshima, H. Misono, and K. Soda. *J. Biol. Chem.*, **253**, 5719 (1978).—The distribution of bacterial leucine dehydrogenase (L-leucine:NAD⁺ oxidoreductase, deaminating, EC 1.4.1.9) was investigated, and *Bacillus sphaericus* (IFO 3525) was found to have the highest activity of the enzyme. Leucine dehydrogenase, which was purified to homogeneity and crystallized from *B. sphaericus*, has a molecular weight of about 245,000 and consists of six identical subunits ($M_r=41,000$). The enzyme catalyzes the oxidative deamination of L-leucine, L-valine, L-isoleucine, L-norvaline,

L- α -aminobutyrate, and L-norleucine, and the reductive amination of their keto analogues. The enzyme requires NAD⁺ as a cofactor, which cannot be replaced by NADP⁺. D-Enantiomers of the substrate amino acids inhibit competitively the oxidation of L-leucine. The enzyme activity is significantly reduced by both sulfhydryl reagents and pyridoxal 5'-phosphate. Purine and pyrimidine bases, nucleosides and nucleotides have no effect on the enzyme activity. Initial velocity and product inhibition studies show that the reductive amination proceeds through a sequential ordered ternary-binary mechanism. NADH binds first to the enzyme followed by α -ketoisocaproate and ammonia, and the products are released in the order of L-leucine and NAD⁺. The Michaelis constants are as follows: L-leucine (1 mM), NAD⁺ (0.39 mM), NADH (35 μ M), α -ketoisocaproate (0.31 mM), and ammonia (0.2 M). The *pro*-S hydrogen at C-4 of the dihydronicotinamide ring of NADH is exclusively transferred to the substrate; the enzyme is B-stereospecific.

Kynureninases: Enzymological Properties and Regulation Mechanism.

K. Soda and K. Tanizawa. *Advances in Enzymology and Related Areas of Molecular Biology*, **49**, 1 (1979).—This review summarizes the current knowledge of microbial and mammalian kynureninase, with emphasis on the regulatory mechanism. Two distinct types of kynureninases occur in nature; inducible kynureninase and constitutive kynureninase. They differ from each other most strikingly in the reactivity of their two preferred substrates, kynurenine and 3-hydroxykynurenine, and the ability to catalyze transamination of the bound coenzyme (pyridoxal 5'-phosphate) to control the rate of kynurenine hydrolysis. The constitutive enzyme (3-hydroxykynureninase) is found in organisms such as fungi, yeast, and mammals having the tryptophan-NAD biosynthetic pathway, and it functions anabolically. The inducible kynureninase ("kynureninase" in a narrow sense) is involved in the catabolism of tryptophan and occurs in the organisms in which tryptophan is metabolized through the aromatic pathway.

The constitutive enzyme is inhibited by 3-hydroxyanthranilate, a product from the best substrate, but the inducible enzyme is not. The constitutive enzyme is little influenced by alanine and ornithine, but the inducible enzyme is under the control of the amino acids and pyruvate. Alanine serves as a negative effector and pyruvate serves as a positive effector.

Aminotransferases Participating in Metabolism of Taurine and Hypotaurine in Microorganisms.

K. Soda, H. Tanaka, S. Toyama, and K. Yonaha. *Ganryu Aminosan (Sulfur-containing Amino Acids)*, **1**, 199 (1978), in Japanese.—The high activity of taurine- α -ketoglutarate aminotransferase and taurine-pyruvate aminotransferase (ω -amino acid aminotransferase) was found in *Achromobacter superficialis* and *Ach. polymorph*, and in strains of *Pseudomonas*, respectively. Both aminotransferases were produced inducibly by the addition of β -alanine to the growth medium. The deamination product from taurine in both enzymatic reactions was identified as sulfoacetaldehyde. Both enzymatic transaminations were found to proceed stoichiometrically and reversibly. Taurine- α -ketoglutarate aminotransferase (M.W., 156,000) and ω -amino acid-pyruvate aminotransferase (M. W., 172,000) were purified to homogeneity and crystallized from the cell free extract of *Ach. superficialis* and *Pseudomonas sp.*

F-126, respectively. The absorption spectrum of the former enzyme was closely similar to that of the latter. The same absorption maxima were observed at 280 and 345 nm. In addition the former exhibits a shoulder at 400–430 nm and the latter at 390–400 nm. Both enzymes catalyze transamination of hypotaurine, a best amino donor, β -alanine and various ω -amino acids in addition to taurine, though the amino acceptor specificity is very low. Hypotaurine is transaminated with α -ketoglutarate irreversibly by taurine- α -ketoglutarate aminotransferase to yield L-glutamate, acetaldehyde and sulfite. The activity of taurine- α -ketoglutarate aminotransferase is significantly diminished by treatment of the enzyme with $(\text{NH}_4)_2\text{SO}_4$ in the course of purification, and recovered with pyridoxal phosphate at high temperatures such as 60°C.

Nucleotide Sequence of Bacteriophage fd DNA. E. Beck, R. Sommer, E. A. Auerswald, C. Kurz, B. Zink, G. Osterburg, H. Schaller, K. Sugimoto, H. Sugisaki, T. Okamoto, and M. Takanami. *Nucleic Acids Res.*, 5, 4495 (1978).—The sequence of the 6408 nucleotides of bacteriophage fd DNA has been determined. This allows to deduce the exact organization of the filamentous phage genome and provides easy access to DNA segments of known structure and function.

Nucleotides Sequence at the Insertion Sites of a Kanamycin Transposon. A. Oka, N. Nomura, K. Sugimoto, H. Sugisaki, and M. Takanami. *Nature (London)*, 276, 845 (1978).—The transposon Tn903 carrying a gene for kanamycin resistance is 3,100 base pairs in size and contains an inverted repeat of 1,050 base pairs at both ends. We transposed this transposon to three different sites on small colicin E1 plasmid derivatives of about 1,600 base pairs, and the nucleotide sequences in these target sites and of the corresponding junctions between Tn903 and the small ColEI were determined. As a result, we found that a nine-base-pair repeated sequence was generated at the insertion sites. However, comparison of the three target sites indicated that neither the duplicated regions nor their vicinity contained a unique sequence common to three insertions. This suggests that no recognition of a specific sequence is involved for Tn903 translocation, and that Tn903 can be transposed to any site on DNA.

Structural and Functional Properties of the *Escherichia coli* Origin of DNA Replication. Y. Hirota, S. Yasuda, M. Yamada, A. Nishimura, K. Sugimoto, H. Sugisaki, A. Oka, and M. Takanami. *Cold Spring Harbor Symp. Quant. Biol.*, 43, 129 (1979).—The replication origin of *Escherichia coli* has been cloned on a nonreplicating DNA fragment coding for ampicillin resistance. This recombinant replicates depending on the presence of the replication origin and can be recovered as a closed circular plasmid. Since this plasmid was integrated into the chromosome due to nucleotide sequence homology in recA^+ cells, the integration site was mapped to be at about 83 min on the genetic map of *E. coli*. The nucleotide sequence in the region carrying the replication origin was also determined. The origin region was particularly rich in various repeat sequences having the same or opposite direction, suggesting that this region provides numerous interaction sites for proteins.

Nucleotide Sequence of *Escherichia coli* K-12 Replication Origin. K. Sugimoto, A. Oka, H. Sugisaki, M. Takanami, A. Nishimura, S. Yasuda, and Y. Hirota.

Proc. Natl. Acad. Sci., U.S.A., **76**, 575 (1979).—From subfragments of an *Eco*RI fragment (9 kilobase pairs) that contained the replication origin of the *Escherichia coli* chromosome and had been cloned as a recombinant with a nonreplicating DNA fragment coding for ampicillin resistance, small derivative plasmids were constructed. The smallest of these, pTSO151, contained a segment of 463 base pairs as the chromosomal component. Another plasmid, pSY314, constructed from *Bam*HI digests of the *Eco*RI fragment and mini-F(pMF21), contained a region of 422 base pairs identical with a corresponding region in pTSO151. We concluded that the replication origin of *E. coli* chromosome is located within this 422 base-pair segment. The nucleotide sequence of this segment has been determined.

Nucleotide Sequence of Small ColEI Derivatives: Structure of the Regions Essential for Autonomous Replication and Colicin EI Immunity. A. Oka, N. Nomura, M. Morita, H. Sugisaki, K. Sugimoto, and M. Takanami. *Molec. Gen. Genet.*, **172**, 151 (1979).—A small ColEI derivative, pA02, which replicates like the original ColEI and confers immunity to colicin EI on its host cell has been constructed from a quarter region of ColEI. The entire nucleotide sequence of this plasmid was determined based on its fine cleavage map. DNA regions indispensable for autonomous replication were examined by constructing plasmids from various restriction fragments of pA02 DNA. As a result, a region of 436 base pairs was found to contain sufficient information to permit replication. The occurrence of initiation and termination codons and of the ribosome-binding sequence on pA02 DNA suggested that a polypeptide chain consisting of 113 amino acid residues can be coded by the region in which the colicin EI immunity gene has been mapped.

The Structure of a Transcriptional Unit on Colicin EI Plasmid. M. Morita and A. Oka. *Eur. J. Biochem.*, **97**, 435 (1979).—In an RNA synthesizing system *in vitro*, a low-molecular weight RNA consisting of about 110 residues was efficiently synthesized on DNA of colicin EI plasmid and its deletion derivatives. The DNA region directing this RNA was sequenced and the RNA sequence was assigned on the DNA sequence based on the nearest-neighbor data of RNA. The sequences of its promoter and terminator region were also deduced. Although the function of this small RNA species is unknown, a unique secondary structure could be constructed from its sequence and sensitivity to RNase.

Subunits of RNA Polymerase in Function and Structure. 7. Structure of Premature Core Enzyme. A. Ishihama, H. Aiba, T. Saitoh, and S. Takahashi. *Biochemistry*, **18**, 972 (1979).—The structure of premature core enzyme, an obligatory intermediate in both *in vivo* and *in vitro* assembly of *Escherichia coli* DNA-dependent RNA polymerase, was compared with that of native core enzyme. Though this assembled but inactive form of core enzyme harbors the gross conformation similar to that of native enzyme, minor and presumably local differences exist, which were identified by near-ultraviolet circular dichroism spectra, tritium-hydrogen exchange rate, protease sensitivity, intersubunit cross-linking rate by bifunctional reagents, sedimentation behavior, and elution profile from phosphocellulose. Taken together these results indicate that the core enzyme subunits are loosely associated in the premature

core. The temperature-dependent maturation is required for the core subunits to be tightly associated, leading to the formation of structurally stable and functionally active RNA polymerase.

Flexibility of Bovine Pancreatic Trypsin Inhibitor. T. Ooi, K. Nishikawa, M. Oobatake, and H. A. Scheraga. *Biochim. Biophys. Acta*, **536**, 390 (1978).—The native conformation of a protein may be expressed in terms of the dihedral angles, ϕ 's and ψ 's for the backbone, and χ 's for the side chains, for a given geometry (bond lengths and bond angles). We have developed a method to obtain the dihedral angles for a low-energy structure of a protein, starting with the X-ray structure; it is applied here to examine the degree of flexibility of bovine pancreatic trypsin inhibitor. Minimization of the total energy of the inhibitor (including nonbonded, electrostatic, torsional, hydrogen bonding, and disulfide loop energies) yields a conformation having a total energy of -221 kcal/mol and a root mean square deviation between all atoms of the computed and experimental structures of 0.63 Å. The optimal conformation is not unique, however, there being at least two other conformations of low-energy (-222 and -220 kcal/mol), which resemble the experimental one (root mean square deviations of 0.66 and 0.64 Å, respectively). These three conformations are located in different position in ϕ, ψ space, i.e., with a total deviation of 81° , 100° and 55° from each other (with a root mean square deviation of several degrees per dihedral angle from each other). The nonbonded energies of the backbones, calculated along lines in ϕ, ψ space connecting these three conformations, are all negative, without any intervening energy barriers (on an energy contour map in the ϕ, ψ plane). Side chains were attached at several representative positions in this plane, and the total energy was minimized by varying the χ 's. The energies were of approximately the same magnitude as the previous ones, indicating that the conformation of low energy is flexible to some extent in a restricted region of ϕ, ψ space. Interestingly, the difference $\Delta\phi_{i+1}$ in ϕ_{i+1} for the $(i+1)^{\text{th}}$ residue from one conformation to another is approximately the same as $-\Delta\psi_i$ for the i^{th} residue; i.e., the plane of the peptide group between the i^{th} and $(i+1)^{\text{th}}$ residues re-orient without significant changes in the positions of the other atoms. The flexibility of the orientations of the planes of the peptide groups is probably coupled in a cooperative manner to the flexibility of the positions of the backbone and side-chain atoms.

An Integral Method to Analyze Sedimentation Equilibrium. Y. Kubota, S. Takahashi, and T. Ooi. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 220 (1979).—Experimental data of the sedimentation equilibrium on ideal or non-ideal associating systems are analyzed successfully by an integral method, which gives optimum values of parameters at the minimum of standard deviation. According to this procedure, the concentration at meniscus, c_a , the weight average molecular weight, M_w , and the second virial coefficient, B , can be obtained simultaneously, without calculating the derivatives of the standard deviation. This procedure was applied to the sedimentation equilibrium data on tropomyosin, one of muscle proteins, in 1 M NaCl, and on maleylated tropomyosin in the absence of salts. The analyses based on monomer-dimer equilibrium for tropomyosin, and on subunit-monomer equilibrium for maleylated

tropomyosin, gave the good fit for the data. The applicability of the integral method is discussed in relation to the usual gradient method.

Subunit-Monomer Equilibrium of Maleylated Tropomyosin. Y. Kubota, S. Takahashi, and T. Ooi. *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 254 (1979).—Tropomyosin, one of the muscle proteins, is a typical fibrous molecule constituted of two subunits, which has almost 100% of α -helix, forming a coiled-coil molecule. The molecule dissociates into subunits with a conformational change from α -helix to random coil when the lysine residues are maleylated. The modified molecule recovers its α -helical conformation with the increase in a salt concentration owing to the shielding effect of small ions added around negative charges. In order to clarify the problem whether or not any subunit of α -helical conformation can exist in solution, the circular dichroic spectra to estimate the α -helical content, and the sedimentation equilibrium to determine an apparent molecular weight of the protein were measured as a function of salt concentration. The results show that there is no single subunit molecule which has the α -helical conformation, and a conformational change from random coil to α -helix induces association of subunits.

Conformational Stability of Ribonuclease T₁. I. Thermal Denaturation and Effects of Salts. M. Oobatake, S. Takahashi, and T. Ooi. *J. Biochem.*, **86**, 55 (1979).—The thermal transition of RNase T₁ was studied by two different methods; tryptophan residue fluorescence and circular dichroism. The fluorescence measurements provide information about the environment of the indole group and CD measurements on the gross conformation of the polypeptide chain. Both measurements at pH 5 gave the same transition temperature of 56°C and the same thermodynamic quantities, ΔH_{tr} (=120 kcal/mol) and ΔS_{tr} (=360 eu/mol), for the transition from native state to the thermally denatured state, indicating simultaneous melting of the whole molecule including the hydrophobic region where the tryptophan residue is buried. Stabilization by salts was observed in the pH range from 2 to 10, since the presence of 0.5 M NaCl caused an increase of about 5°C to 10°C in the transition temperature, depending on the pH. The fluorescence measurements on the RNase T₁ complexed with 2'-GMP showed a transition with ΔH_{tr} =167 kcal/mol and ΔS_{tr} =497 eu/mol at a transition temperature, about 6°C higher than that for the free enzyme. The large value of ΔH_{tr} for RNase T₁ indicates the highly cooperative nature of the thermal transition; this value is much higher than those of other globular proteins. Analysis of the CD spectrum of thermally denatured RNase T₁ suggests that the denatured state is not completely random but retains some ordered structures.

Conformational Stability of Ribonuclease T₁. II. Salt-Induced Renaturation. M. Oobatake, S. Takahashi, and T. Ooi. *J. Biochem.*, **86**, 65 (1979).—In the presence of high concentrations of the monovalent salts, sodium chloride and potassium fluoride, disulfide-reduced RNase T₁ having four cysteinyl residues intact regenerates the spectral properties characteristic of native RNase T₁, i.e., the fluorescence spectrum of the aromatic side chains and the ultraviolet circular dichroism spectrum. The folding of the polypeptide chain proceeded without formation of disulfide bonds to yield an enzymatically active species having an activity toward RNA equivalent to

25% of that of the native enzyme at the salt concentration of 2 M. Unfolding of RNase T₁ by a denaturant, urea, was suppressed in the presence of salts, and the salt-induced chain folding was observed spectroscopically even in 6.9 M urea solution. The salts also induced the chain folding of disulfide-reduced and modified (carboxymethylated or carboxamidomethylated) RNase T₁ into the native conformation, as indicated by its spectroscopic properties, but did not restore the enzymatic activity.

Chain Dimension and Effective Potential Energy of Globular Proteins.

K. Nishikawa and T. Ooi. *Macromolecules*, **11**, 644 (1978).—In this study, a statistical analysis on chain dimensions of irregular parts in native proteins, three-dimensional structures of which are known, has revealed that short segments (up to $n=8$) of the irregular backbone conformations in a protein can be treated, in the sense of a statistical ensemble, as the “unperturbed” (devoid of explicit long-range interactions) polypeptide chain. The single-residue energy primarily responsible for this unperturbed chain dimension is, however, the Pohl’s empirical potential energy rather than the atom pair potential energy usually employed. The distinct quantitative difference between the Pohl’s energy map and the atom pair energy map is clearly shown in the difference of the characteristic ratios calculated from both energy maps. These evidences indicate that the potential energy for a single residue within a globular protein is modified due to long-range interresidue interactions. Theoretical calculations were carried out on the unperturbed polypeptide chain to obtain the mean squares of end-to-end distances by the method of Flory and distributions of end-to-end distances by the Monte-Carlo technique and served for comparison with the corresponding observed data taken from 19 globular proteins.

C-Terminal Side of α -Helix is More Stable Than N-Terminal Side.

S. Takahashi, S. Ihara, and T. Ooi. *Nature*, **276**, 735 (1978).—Stability of α -helical conformations of (L-Glu)₂₀-(L-Ala)₂₀Phe (I) and (L-Ala)₂₀-(L-Glu)₂₀Phe (II) were compared from their CD spectra at various solution conditions. At the pH near five both of the CD spectra for (I) and (II) showed a pattern typical to α -helix. When the pH of the solution was increased, α -helices of (I) and (II) were gradually decreased and reached a plateau at pH higher than 6.5. Such residual amounts of helices were considered due to polyalanyl blocks and the amount was higher for (I) than for (II), showing that the stability of the α -helix of the polyalanyl block must be affected differently by the conformation of the polyglutamyl block and depended on which side the block was connected, the polyalanyl helix more unstable when the randomly coiled block was attached to the C-terminus of the helix.