ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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1—GENERAL AND PHYSICAL CHEMISTRY

A Study of the surface of carbon brush by means of electron diffraction. N. Kameyama and Y. Kin. *J. Soc. Chem. Ind. Japan*, 42, 597—601 (1939).—The fresh surface of brush which was never used as contact surface of a commutator, being slightly polished by hand, with the emery paper No. 0 gives the normal pattern of graphite. In the surface of brush that was used in the commutator of a motor, the crystals of graphite are reduced in size, and have a preferred orientation with (001) plane parallel to the surface of brush. A number of specimens were prepd. by a testing app. consisting of revolving copper rings and fixed brush holders, on which carbon brushes were installed and, in contact with the revolving rings, the electric current was made to pass under various conditions. In examg. the specimens which were prepd. under the brush press. 1∼2 kg/cm^2, and with direct current density, 8A/cm^2 at the brush surface, the following results were obtained. There was not found any distinct indication of preferred orientation in the specimens in which no current was allowed to pass during the revolution. The orientation of the graphite crystals therefore, appears to be due to the electric current that flows through the ring and brush. The direction of the current seems to influence in some degree the intensity of the orientation; it was shown that the graphite crystals give rise to a little stronger orientation in the case of the direction of current from ring to brush, than in the case of the reverse. The diffraction pattern showed that crystal particles of Cu_2O sometimes adhered on the surface of the brush. Authors.

Dipole moment of cedrene. S. Kambara. *J. Soc. Chem. Ind. Japan*, 42, 630—632 (1939).—A proper solvent is required for studying the dielectric properties of vulcanised rubber. The solvent for this purpose should be non-polar liquid having a sufficient solvent power to dissolve not only soft rubber but also ebonite; moreover, it is desirable that the soln. of vulcanised rubbers can be considered as a molecular soln. or at least approximately as such. Sesquiterpene is known as a powerful solvent for vulcanised rubber and ebonite, but its dielectric properties have not yet been detd. The author prepd. a pure cedrene from ceder oil, and detd. its dielectric const., refractive index and density, and calcd. its dipole moment. The purified cedrene gives the following data:

B.P. 760mm (corr.) 262°C.	n_α^{15}	1.5042	d_{15}^{15}	0.944^{5},
Analysis. calcd. for $(C_5H_8)_3$	H%	11.85	C%	88.15
found		11.97		88.04
		11.92		88.09

The dielectric const. was measured by the zero beat method, using 500 kilocycle dinatron oscillator as reported in the previous paper (*J. Soc. Chem. Ind. Japan*, 38, 506 (1935)). The dipole moment, 0.38×10^{-18} e. s. u. was obtained as a value detd. for cedrence. It may be said that cedrene having such a small dipole moment is very suitable for a solvent of vulcanised rubber. Author.

A study of dyestuff by the method of X-ray diffraction. II. H. Kawamori. *Sci Repts. Kyoto Higher Tech. School,* **1**, 73—78 (1938).— Hydrazobenzene ($C_{12}H_{12}N_2$) was recrystalized, and single crystals of a tolerable size and a fine powder were obtained. With these crystals, the crystal form was detd. by the method of X-ray diffraction. At first, the Laue pattern of four-fold symmetry was seen by means of X-ray diffraction with the single crystal; and it was found that the crystal form of ($C_{12}H_{12}N_2$) is cubic or tetragonal. Then, by the powder method it was found to be tetragonal having the axial ratio of 0.754; and the following quadratic expression was obtained for this crystal: $\frac{4\sin^2\theta}{\lambda^2}=0.00548\,(h^2+k^2)+0.00965\,l^2$. From the value 1.178 of the net density of hydrazobenzene, the unit cell having the volume of 1860 Å.U.^{3} was found to contain 7 groups of ($C_{12}H_{12}N_2$). Author.

On the dry cells. III. Measurement of the solubilities of $ZnCl_2 \cdot 2NH_3$ in the electrolytes of various concentrations. G. Fuseya, Y. Saitô and K. Simazaki. *Bull. Toyoda Research. Imp. Invention Soc. Japan,* **6**, 67—71 (1939).—In connection with the measurement of the potential of Zn electrode in the electrolyte satd. with $ZnCl_2 \cdot 2NH_3$ as reported in Part II, the solubilities of this complex compound in the electrolytes of various concns., and the densities and the pH values of the satd. solns. were measured at 25°C. Both $ZnCl_2$ and NH_4Cl used were of extra pure quality. But, due to hydrolysis, $ZnCl_2$ had the composition of the atomic ratio of 1 Zn : 1.9185 Cl instead of 1 : 2. Therefore in making the soln. of 50 g (or 0.3668 *M*) of $ZnCl_2$ in 1000 g of water, such an amt. of the salt was taken as to make 0.3668 *M* with respect to Zn-component. Practically it contained 0.3668 g atom or 23.986 g Zn and 0.3668 × 1.9185 g atom or 24.956 g Cl. $ZnCl_2 \cdot 2NH_3$ was prepd. by the method given by R. Friess (*J. Am. Chem. Soc.,* **52**, 3083 (1930)). For the detn. of the solubilities, the solns. were analysed with respect to Zn, Cl, and NH_3, before and after the satn. with the complex compd., and mean values of the molal increases of the three components were taken as the solubilities. The pH values were measured with Dubosq colorimeter, using γ-dinitrophenol as indicator. Authors.

Rotatory dispersion of sugars in liquid ammonia and in water. H. Shiba and S. Tanabe. *Bull. Chem. Soc. Japan,* **13**, 3—10 (1938).—The authors detd. the rotatory dispersions of d-glucose, d-fructose, d-galactose, saccharose, lactose and maltose dissolved in liquid ammonia and water for spectra of various wave lengths. To the result obtained, as a whole, is applicable Drude's dispersion formula $[\alpha]=k_0/(\lambda^2-\lambda_0^2)$, and the linear relation holds between $1/[\alpha]$ and λ^2. Fructose in liquid ammonia showed small rotations with pos. and neg. sign according to the value of λ, i. e. an abnormality of the ketose dissolved in liquid ammonia.

J. C. L.

On the statistical mechanical treatment of the absolute rate of chemical reaction. J. Horiuti. *Bull. Chem. Soc. Japan,* **13**, 210—216 (1938).—The author discussed the statistical method for treatment of the absolute reaction rate with a group of atoms having the following properties: (1) displacements of atoms take place adiabatically with regard to the electronic configuration; (2) classical mechanics holds for the motion of centres of gravity of atoms; (3) the group has more or less chance of interchanging energy with its surroundings at a definite temp. by interaction with radiation or with other material system; (4) the group can exist stably in the initial and the final states, which are distinctly different from each other in special relation to the configuration of atoms. He considered the probability of the final system to be produced from the initial system, and also discussed the flow of gas and the encounter of 2 atoms, comparing these with the reaction velocity, by the theory of the transition state.

J. C. L.

The surface-tension-measurements of 100 % phosphoric acid and its structure. T. Taketa. *J. Chem. Soc. Japan*, **60**, 885—894 (1939).—First of all, the specific gravities of 86 %, 90%, and 100 % phosphoric solns. were measured for the purpose of studying the nature and structure of 100 % phosphoric acid. An improvement of surface-tension-measurement by the max.-bubble-press.-method enabled the writer to measure successfully the soln. of very high surface-tension value, and thereby to obtain fruitful results for the above-mentioned three phosphoric acid solns. Through this measurement of surface-tension value the polymerization degree of phosphoric acid solns. were calcd. and thereby the parachor was obtained. Ramann-spectrum of 100% phosphoric acid was photographed. From the exptl. values thus obtained the structure of 100% phosphoric acid was deduced in accordance with Shibata's theory of 100% inorganic acids. Author.

A new simple theory of valency. II. Valence bonds in carbon compounds. R. Tsuchida and M. Kobayashi. *J. Chem. Soc. Japan*, **60**, 583—594 (1939).—A detailed explanation of the article published in this Journal, **13**, 61—73 (1939). Authors.

On the sodium line reversal method of determining the temperature in a gasoline engine. U. Yoshida. *Rept. Aero. Research. Inst. Tokyo Imp. Univ.*, **14**, 195—209 (1939).—The sodium line reversal method of detg. the temp. of a flame was applied to the engine flame. A special cylinder, with two quartz windows, that would cause a beam of light from the source to pass through the combustion chamber was constructed. Upon adding a small quantity of sodium ethylate to the fuel, the temp. of the engine was compared with the apparent temp. of the light source. The D line intensity of the flame was measured by a photoelectric cell. Comparison of this intensity with its flame temp. showed that there is thermal equil. between the sodium vapour and the engine, flame. The temp. measured by this method is the correct temp. of the flame. The spectrum in the visible region of the engine flame consisted of CH bands and the continuous bands. The spectra obtained at various crank angle showed that as the crank angle proceeds, the CH and CC bands become fainter and that the temp. in the cylinder is not uniform. The max. temp. at various air fuel ratios was measured with the engine running at 800 r.p.m. Although the correct air fuel ratio in the fuel under test was 13.8, the temp. was always max. at 11.5 and nearly agrees with the calcd.

Author.

On the change of thermal conductivity of bismuth single crystal due to magnetic field. T. Hirone and S. Matsuda. *Bull. Inst. Phys. Research*, **18**, 711—720 (1939).—The change of thermal conductivity of bismuth single crystals due to magnetic field, which is anomalously large as compared with other metals, is explained on the basis of the electronic structure of bismuth presented by Jones. In single crystals of bismuth the effective mass of electron near the Fermi surface is so small that thermal current carried by such electron changes largely by the influence of magnetic field. The theory indicates that the relative change of thermal conductivity $\Delta\kappa/\kappa$ is proportional to the square of magnetic field H : $\Delta\kappa/\kappa=CH^2$. The proportional const. C is calcd. in the following three cases: (1) The thermal current is perpendicular, while the magnetic field is parallel, to the principal axis of the crystal. (2) The thermal current, the magnetic field and the principal axis of the crystal are perpendicular to each other. (3) The thermal current is parallel to the principal axis of the crystal, and the magnetic field is perpendicular to the thermal current. The result of the present calcn. agrees satisfactorily with the exptl. data.

Authors.

On the thermal expansion of simple liquids. A. Harasima. *Proc. Phys.-Math. Soc. Japan*, **III, 21**, 398—402 (1939).—By using the model proposed by the author in explaining the phenomenon of fusion (*ibid.*,

III, **21**, 156 (1939), the coeff. of thermal expansion of simple liquids is obtained. The author has obtained the theoretical formula $\beta Tm=0.115$, where β is the coeff. of cubical expansion and Tm is the melting temp. The observed values of β Tm for many simple liquids are of the order of the theoretical values. Author.

On the dissociation constants of selenious acid. H. Hagisawa. *Bull. Inst. Phys. Chem. Research*, **18**, 648—656 (1939).—The *p*H values of selenious acid of various concns. were measured at 25°C by means of a glass electrode.

Concentration (Mol/L)	0.511 5	0.189 6	0.097 4	0.054 3
*p*H	1.385	1.612	1.813	1.979
Concentration (Mol/L)	0.021 7	0.020 9		0.010 9
*p*H	2.253	2.248		2.452
Concentration (Mol/L)	0.009 55	0.000 919		0.000 526
*p*H	2.487	3.188		3.355

From these results the first dissocn. const. K_1 was computed as 0.0022 and 0.0025 according to two methods of calcn. The 0.01 and 0.03 molar solns. of selenious acid were titrated with sodium hydroxide soln. at 25°C, and the *p*H value at each stage of titration was measured by a glass electrode. From these *p*H values K_1 was obtained as 0.00235 and 0.00239, and the second dissocn. const. K_2 as 4.7×10^{-9} and 4.9×10^{-9}. Thus the value of K_1 is only a little smaller than that of E. Blanc and of Britton and Robinson, but the value of K_2 is about half that of Willcox and Prideaux and of Britton and Robinson. Author.

The effect of high tension electrical discharge on the catalytic reaction. (IV～V). I. Seto and M. Ozaki. *J. Soc. Chem. Ind. Japan*, **42**; 271—274 (1939).—The effect of high tension elect. discharge on the catalytic reduction of menthone to menthol and that of thymol to menthol were studied. In each case, the material was dissolved in paraffin oil, and mixed with a nickel catalyst; hydrogen gas was passed through the reacting liquid and a high elect. tension was applied on the reaction vessel. The yield of menthol from menthone and that from thymol were 79% and 66—68%, resp. The results of these expts., together with that of the 2nd report (*ibid.*, **40**, 189～191B), proved that the application of elect. discharge could give a favourable effect on the promotion of the reaction velocity even in the case where the material having a weak insulating power was treated and that with the employment of a nickel catalyst, the catalytic reduction of organic compds. could be realized generally in the liquid phase under ordinary press. as a consequence of enormous increase in the speed of the reaction brought about by the action of elect. discharge. Authors.

Note on the Bose-Einstein condensation. T. Nagamiya. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 475—485 (1939).—In an assembly of non-interacting particles which obeys the Bose-Einstein statistics it is known theoretically that a certain phenomenon called the Bose-Einstein degeneracy or condensation occurs at low temps. or at high densities and this phenomenon is not observed in an ordinary perfect gas. In this paper a discussion is given of the occurrence of such a degeneracy in a general Bose-Einstein assembly of particles having the energy states ε_0, ε_1, ε_2,....... Such a discussion is not without interest, for we may expect in a highly condensed state such as liquid helium that each particle is moving in a Hartree mean field of molecular forces. The condensation is first discussed by taking the temp. as const. and changing the total number of particles and it is shown that at a certain critical number N_c all states except ε_0 are are filled up and a further increase of the total number causes to increase only the number of particles of the ground state. The condition of the sharp occurrence of the condensation is given by $N_c(\varepsilon_1-\varepsilon_0)\gg kT$. The discussion for const. total number and varying temp. follows easily. Formulas for the energy, the specific heat, the free energy and the press. are obtained. It is remarked that by choosing a suitable distribution function for ε_0, ε_1, ε_2,...... the characteristic variation of the specific heat of liquid helium can be explained.

Author.

Exchange reaction between ammonia and hydrogen in the presence of platinum catalyst. I. M. Mitani. *Bull. Inst. Phys. Chem. Research*, **18**, 879—883 (1939).—It was theoretically predicted that the platinum catalyst causes an exchange reaction between hydrogen gas and liquid ammonia and that the rate of the reaction decreases when the liquid ammonia in contact with the catalyst evaporates up. To confirm the prediction the reaction between heavy hydrogen gas and ammonia in the presence of platinum black at −20°, 0°, 20°, and 50°C was followed by the decrease of the deuterium content of the gas. The exchange reaction was confirmed but the neg. temp. coeff. of the exchange rate due to the evaporating up of the liquid ammonia, which might possibly be the case at higher temps. was not observed. The latter aspect was attributed to the adhesion of the liquid ammonia on the complicated surface of the platinum black by capillary condensation.

Author.

Catalytic hydro-polymerisation of acetylene. I-II. T. Amemiya. *J. Soc. Chem. Ind. Japan.* **42**, 692—698 (1939).—**I.** Using the Fe-Ni catalyst proposed by F. Fischer and coworkers (*Brenn-Chem.*, **10**, 279 (1929); 14, 165. (1933)), the author detd. by the flow method the reaction temp. and found that flow rate of reaction was suitable for hydro-polymerisation of acetylene to produce liquid hydrocarbons from a gas mixt. of $C_2H_2 : H_2 = 1 : 4$, and studied the proper condition of prepg. the Fe-Ni-Kieselguhr catalyst. **II.** The catalytic activities of the Fe-Ni-Kieselguhr catalysts prepd. by the method as described in Part I varied with their compns., when they were used as catalysts in the hydropolymerisation of acetylene. Pure Fe has almost no ability for promoting hydro-polymerisation of acetylene, although a slight amt. of Ni (even 2.5 %) added to Fe remarkably raises the activity. The more the Ni content, the larger are the concn. of reaction gas, the percentage of reacted acetylene, the consumption of hydrogen and the yield of ethane, tending to increase very quickly until the Ni content amts. to ca. 10% (only in the case of ethane yield, ca. 20%) and thereafter gradually up to pure Ni. The yields of ethylene and liquid products find their optimum points at 5% of Ni. From these tendencies, it is observed that the accelerating ability of the catalysts for hydro-polymerisation of acetylene decreases abruptly, when the content of Ni has surpassed ca. 15%, and those for hydrogenation only are distinctly enhanced. The compn. range (Ni 0∼ca. 15%), in which the catalytic activities of Fe-Ni-Kieselguhr for hydro-polymerisation of acetylene are very large, corresponds with the α-phase of Fe-Ni binary alloys, which is a solid soln. of α-Fe, and has a crystal structure of bodycentered cubic lattice, so it may be qualitatively concluded that the bodycentered cubic lattice of Fe-Ni catalysts are favourable for hydro-polymerisation of acetylene.

Author.

The effects of foreign metallic ions in electrolyte upon the inner structure of electrolytic metals. H. Hirata, H. Koto and M. Hara. *Nippon Kinzoku Gakkai-Si*, **3**, 460—469 (1939).—To make clear the effects of a small quantity of various foreign metallic ions in electrolyte upon the inner structure of electrolytic metals, the crystalline configurations and crystal structures of a few specimens of the electrolytic depositions were investigated with X-rays, As the consequence of this investigation, some metallic ions as Fe^{++} and Mn^{++} ions in stannous solns. were obsd. not to be deposited on the cathode together with Sn^{++} ions. But, this was not always the case with the other foreign metallic ions, i.e., it became clear, on the one hand, that Cu^{++} ions in a stannic soln. and Ni^{++} ions in a silver soln. come to appear in the colloidal state outside of microcrystals of pure white tin and pure silver resp.; while on the other hand, Zn^{++} ions in a cubric sol., were confirmed to form the crystals of alloy belonging to Zn-Cu system, by the procedure of electrolysis.

Furthermore, the presence of the foreign metallic ions was found not only to vary the direction of the max. growth of the electrolytic depositions, but to affect some geometrical properties as twinning relation of them. Especially, it must be noticed that even the direction of the common axis of micro-crystals in electrolytic specimens of white tin having a fibrous nature, was obsd. usually to convert from the direction normal to (101) face to that of (100) face in the presence of Fe^{++} ions.

Author.

Dissociation constant of acetic acid. S. Kaneko. *Bull. electrotech. Lab.* **3**, 783—784 (1939).—The following formula of dissocn. const. K' of weak electrolytes is derived from the theory of non-electrolytes in the previous report

$$\log K' = \log K + 1013 \frac{\sqrt{Ci}}{1+0.327a\sqrt{Ci}} + BCu$$

where K is the thermodynamic dissocn. const., Ci the concn. of ions, a the diameter of an ion, the Cu the concn. of undissociated acid, B the empirical const.

Author.

Study on the formation and its mechanism of sodium oxalate and carbonate by the pyrolysis of sodium formate. S. Takagi. *J. Chem. Soc. Japan*, **60**, 805—825 (1939).—In the pyrolysis of pure sodium formate, under the homogeneous fused state below 300°C. sodium carbonate only produces with the velocity of second order and above 400°C. oxalate simultaneously with the velocity $d(x+y)/dt=(k_1+k_2)(a-x-y)^2$, where x, y, k_1 and k_2 represent mols of formate changed to carbonate, to oxalate, velocity const. related to carbonate and to oxalate resp. The ratio k_1/k_2 is const. at the temp., and temp. coeff. of k_1 is smaller than that of k_2. In the complete heterogeneous system above 360°C. the velocities change both as the S-type curve with inflection point expressed by $dx/dt=kt^2$ at the concave part and by $dx/dt=k(t_\infty-t)^2$ at the convex, and when formate contains a little sodium oxalate initially then oxalate formation is promoted. And therefore this reaction transferring to solid phase from fused is also found to be autocatalytic like a reaction "solid→solid". This induction period is shortened by rapid heating up to a required temp. From these facts the autocatalysis is also considered to be governed by the number of reaction nuclei with active center produced in only the initial period of pyrolysis but not in later heating. The addition of alkali hydroxide gives rise to the formation of oxalate even from the melting point and especially gives enormous yield (over 90%) under rapid heating. This effect is understood by a theory of catalysis in which formate exists in an unstable form $\mathrm{NaO{-}\overset{\vee}{C}{-}OH}$ in fused state and forms an intermediate compound with NaOH.

Author.

2–ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

Production of X-rays by high speed argon ions. M. Tanaka and I. Nonaka —*Proc. Phys.-Math. Soc. Japan*, **III**, **20**, 33-51 (1938).—Argon ions of energies up to 450 k.e.v. were obtained by the method of multiple linear accelerator of Sloan-Lawrence, and X-rays produced when each one of the elements—Li, Be, C, Mg, Al, Si, Ni, Cu, Zn, Mo, Pd, Ag, Cd, Sn, Pt, Au and Pb—was bombarded by these ions were investigated by the Geiger counter. From the measurements of the absorption of the X-rays by thin starch films, these radiations were detd. to be the characteristic K in the cases of Mg, Al and Si, the characteristic L in the cases of Mo, Pd, Ag, Cd and Sn ; and the characteristic M in the cases of Pt, Au and Pb. The relative number of photone of these characteristic radiations when thick targets were bombarded by ions of 440 k.e.v. were obtained. According to the result, the intensities of the characteristic L radiations were far stronger than those of K or M and this is contrary to the cases of proton or α-particle, but agrees with the case of mercury ion. The intensity of each characteristic radiation was found to increase very rapidly with the energy of the ions, and also to be proportional to $W^{3\cdot7}$ in the case of Ag L radiation, where W is the energy of ions. Authors.

The gamma-rays of ^{13}N. Y. Watase and J. Itoh. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 389—394 (1939).—With the use of a magnetic spectrometer the spectrum of secondary electorns emitted from carbon and lead plates by gamma-rays of ^{13}N was investigated. The existence of the gamma-ray 285 +10 kev in energy is confirmed. In connection with analysis of the beta-ray spectrum, some discussions are given. Authors.

On the disintegration of ^{24}Na. S. Kikuchi, Y. Watase, J. Itoh, E. Takeda and S. Yamaguchi. *Proc.-Math. Soc. Japan*, **III**, **21**, 381—389 (1939).—With the use of a magnetic spectrometer the spectrum of secondary electrons by gamma-rays as well as the spectrum of disintegration beta-rays of ^{24}Na was investigated. The upper limit of the beta-ray spectrum was found to be 1.37+0.03 mev. The Fermi plots of the spectrum can be represented by straight lines having breaks at 1.15 and 0.6 mev, while the K-U plots lie on a straight line in the low energy region and deviate from it in high energy side of the spectrum. The gamma-rays of 2.97±0.05 and 1.55±0.05 mev in quantum energy are clearly resolved. The existence of 0.8 mev gamma-rays and those of still lower energies are suggested. Authors.

Zeeman effect in sun-spots. T. Tanaka and Y. Takagi. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 421—431 (1939).—About a remarkably large sun-spot of Nov., 1938, the effective magnetic field was calcd. by means of the theoretical Zeeman patterns. A spectrograph giving a dispersion of about 0.4 Å/mm was used. For every spectral line there seems to exist an effective magnetic field, whose range of magnitude is not very wide. The effective magnetic field for each of the components forming a multiplet coincides with each other. The dependence, for each element, of the effective field on the intensity of a spectral line is small. The effective magnetic fields of different elements are quite different from one another and seem to be capable of being arranged with some regularity in the order of their atomic numbers. On the other hand, an explanation can be given for the existence of the effective magnetic field, the layers of different elements being considered. Authors.

Energy-levels of neon. G. Araki and Y. Yamamoto. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 461—475 (1939).—The general expression of energy-levels of an excited rare-gas atom is derived by using Breit's Hamiltonian. The interactions between all electrons in the atom are taken into account. The derived expression agrees qualitatively with Laporte's formula. The numerical values of intervals between levels are computed for the configurations $1s^2\ 2s^2\ 2p^5\ 3s$, $1s^2\ 2s^2\ 2p^5\ 4s$, and $1s^2\ 2s^2\ 2p^5\ 8s$ of the neon. The self-consistent field radial functions computed by Brown are used for 1s, 2s and 2p. Those of 3s, 4s, and 8s are calcd. from Brown's core-functions by the numerical integrations. The agreement between the calcd. and observed values are satisfactory. Authors.

On the eimission spectrum of the fluoride of tin (SnF). T. Yuasa. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 497—507 (1939).—Stannic fluoride, SnF_4, was vaporised into a Geissler tube and heated at about 700°C, the press. being kept at about 2～3 cmHg. When, under these conditions, the Geissler tube was excited, a system of bands degraded to the red was found in the visible region (λ 4599.11Å—6301.02 Å) which is considered as that of the SnF. As the result of the vibrational analysis of these bands, it was found that the molecular consts. ω_e and $x_e \omega_e$ are about 580cm^{-1} and 2cm^{-1} for the lower level, and 418cm^{-1} and 1cm^{-1} for the upper level resp. The lower level is a doublet, whose separation is about 2318cm^{-1}. The molecular consts. and the doublet separation of this lower level are well in accordance with the results obtained by F.A. Jenkins and G. D. Rochester (*Phys. Rev.* **52**. 1135 (1937)), in the absorption spectrum of the SnF. Their values of x_e and $x_e \omega_e$ for the ground level of the molecule SnF are 582.9 cm^{-1} and 2.69 cm^{-1} resp. and the doublet separation is 2317.3 cm^{-1}. Therefore our lower level may be considered as the ground level of the fluoride of tin, SnF. The high and low frequency components in this system have almost the same intensity and the same distribution of the intensities. Author.

On the inversion of alkali doublets.

G. Araki. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 508—516 (1939).—The inversion of doublets of neutral alkali atoms is explained by the fact that the screening const. due to the spin-orbit interaction between the valence electron and the atomic core is greater than the atomic number. The general formula of alkali doublets is derived, taking into account the electromagnetic interactions between all atomic electrons. The numerical caln. is carried out $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4f\ {}_3F_{2\frac{1}{2},\ 2\frac{1}{2}}$ of Cu. The calcd. interval of the doublet is -4.0 cm^{-1}, which agrees with the observed value 3.6^{-1}. Author.

On the artificial neutron source. I.

I. Nonaka. *Mazda Kenkyu Jiho*, **14**, 129—137 (1939).—A D+D neutron source was built in which heavy hydrogen ions were produced by a low voltage arc of capillary type and were accelerated up to 200 k.e.v. The discharge tube was made of three terex glass tubes, each of which was 15 cm in outer diameter and 30 cm in length, and the accelerating electrodes were made of iron cylinders of 7.5 cm in diameter. At a best condition the max. ion current obtained through a canal of 1.5 mm in diameter and 1 cm in length was 1000 μa and about the half of it could be focused on the target. Following the results of Döpel, several metal targets which contained no heavy hydrogen, for example Pd, Zr or Pb, were bombarded by heavy hydrogen ions for a long time and the neutron yield due to the contaminated heavy hydrogen was measured as a function of the degree of the bombardment. After about 10000 μa · min. bombardments a slight increase in yield was observed in each case, but no more increase could be observed to about 40000 μa · min. and this satd. value was only about one-tenth of that of D_2O ice target cooled by liquid air. This is contrary to the results of Döpel. In the case of D_2O ice target the neutron yield decreased extremly with the time of bombardment when the ion current was greater than about 100 μa. At 190 k.e.v. and 50μa ion current the neutron yield was detd. to be equivalent to 1000 mc Rn+Be, and at continuous bombardment for long time the max. obtainable yield was about 200 mc Rn+Be equivalent. Author.

Note on the absorption of slow mesotrons in matter.

H. Yukawa and T. Okayama. *Sci. Pap. Inst. Phys. Chem. Research*, **36**, 385—389 (1939).—According to the present theory, a mesotron passing through matter loses its energy mainly by ionizing atoms, until it disappears either by changing spontaneously into an electron and a neutrino or by being absorbed by a nucleus. In this paper, it is shown that most of high energy mesotrons are absorbed by nuclei in the dense medium such as water or lead after having been stopped completely, whereas they disintegrate spontaneously in air while they are in motion. Authors.

Determination of the energy of

photo-neutrons liberated from deuteron by radium C Gamma-rays. K. Kimura. *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A**, 22, 237—248 (1939).—The author studied in detail the photo-neutrons liberated from deuterium and beryllium by Ra C γ-rays, and especially for deuterium, detd. the thickness of paraffin wax which was necessary to slow it down to the energy of the resonance absorption of iodine. From this it was ascertained that 2.198 mev. γ-rays really act in the disintegration of deuterium, and the initial energy of liberated neutrons was estimated to be between 0.001 and 0.0076 mev., and hence the binding energy of deuteron was 2.189+0.007 mev. which gave the mass of neutron 1.00895. The relative atomic cross-section for photo-disintegration of deuterium against beryllium was $\sigma D : \sigma Be = 1 : 13$. Author.

Cyclic equations for O_{III} and electron temperature of gaseous nebulae. S. Miyamoto. *Mem. Coll. Sci. Kyoto Imp. Univ.*, A, 22, 249—257 (1939).—The nebulium emission in gaseous nebulae are due to the impact excitation by free electron. The mech. is treated quantitatively. Cyclic eqs. are formulated for O_{III}. The soln. of eqs. gives the population in each quant. level as a function of electron density and temp. Consequently, intensities of nebulium emissions are expressed as a function of the same arguments, of which the intensity ratio of nebular to auroral emission is given numerically. For planetary nebulae, this ratio depends only upon the election temp. and it is evaluated from observation. Electron temp. of the observed nebulae is found to fall in the range 10,000°—25,000°. Author.

Studies on luminescent materials. III. The effects of temperature on the intensity of fluorescence of zinc sulphide crystalphosphors. Y. Uehara; *J. Chem. Soc. Japn*, 60, 900—901 (1939).—The intensity of fluorescence of zinc sulphide crystalphosphors always falls rapidly above the temp. of about 300 K. For this behavior the author gives a theoretical interpretation, based on the quant. mech. theory of solid state, and shows that temp. dependence of the intensity of zinc sulphide phosphors can be given by the following theoretical eq.; $\eta = \frac{1}{1 + A/B\, e^{-W_1/kT}} + \frac{}{\varphi(T)/B\, e^{-W_2/kT}} \doteqdot \frac{1}{1 + 10^5 e^{-W_1/kT}}$ where η is the quant. yield of the fluorescence and W_1 is the activation energy for the transition of electron from the equil. states to excited state to the conduction band. The theoretical results coincide fairly well with the measurements. Author.

Studies on luminescent materials. IV. On the molecular vibrational structure of fluorescence spectra of zinc sulphide crystalphosphors. Y. Uehara. *J. Chem. Soc. Japan*, **60**, 1293—1301 (1939).—In the present paper, the author could show that fluorescence bands of pure zinc sulphide phosphors already found by himself may be correlated with the electronic transitions $^1P^0 \rightarrow {}^1S_0 = 4680$ A° $^3P_2{}^0 \rightarrow {}^1S_0 = 4840$ A° $^3P_1{}^0 \rightarrow {}^1S_0 = 5040$A° $^3P_0{}^0 \rightarrow {}^1S_0 = 5455$A° of Zn atom in the activation centre. Thus he proved that the resonance radiation in the activation centre, in the broad sense, is responsible for the fluorescence of pure zinc sulphide phosphors. By this mechan. of fluorescence, he gave a theoretical eq. for the temp. dependence of the photoconductivity of the zinc sulphide phosphors and the results obtained coincided well with the expts. of Lenz. Further he observed the molecular vibrational structure of the fluorescence bands of zinc sulphide phosphors and gave a theoretical interpretation for the results obtained. As the results he showed that the resonance radiation centre is responsible for the fluorescence of zinc sulphide crystalphosphors. Author.

Band-spectra in sun-spots. T. Tanaka, S. Nagasawa and K. Saito. *Proc. Phys. Math. Soc. Japan*, III, 21, 431—455 (1939).—About a remarkably large sun-spot appeared in Nov., 1938, the molecular spectra were investigated. A spectrograph having a dispersion of about 0.4 Å/mm was used. For the intense spectral lines of the bands of some molecules with known rotational structures, the identification was carefully made with the lines of the sun-spots, the discrepancy of the conditions being taken into consideration. It can be seen from the results that the existence of MgH, TiO and CaH is evident, while no evidence of the existence of BO, AlH, and AlO has been obtained, the coincidences in the latter cases being with the ranges of chance-coincidences. The existence of red CN bands is also doubtful. Authors.

The effect of electric fields on the viscosity of liquids. O. Kimura. *Bull. Chem. Soc. Japan*, **14**, 243—249 (1939).—The viscosities of solns. or lauric, myristic, plamitic, and stearic acids in C_6H_6, and of cetyl alcohol in C_6H_6 and C_6H_{12} were measured under the influence of electric fields, up to 1000 volts with electrodes 0.02 cm. apart. The viscosities incerease with the field strength, the concn. of the soln. and the length of the hydrocarbon chain. With stearic acid the effect ceases at a certain voltage, almost independent of the concn., and cetyl alcohol shows a discontinuous increase. The effect of the electric field is attributed to the orientation of the dipolar molecules of solute, and abnormalities are ascribed to association. A form of Ostwald viscosimeter with a capillary of rectangular cross section is described. Author.

Liberation of fast neutrons in the nuclear explosion of uranium irradiated by thermal nentrons. T. Hagiwara. *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A**, **23**, 19—32 (1940).—Fission neutrons liberated from uranium induced by neutron irradiation were studied concerning the *separated* effect due to thermal neutrons alone. Uranium oxide was either screened from primary thermal neutrons or exposed to them by use of a cadmium sheet shield interposed between the neutron source and uranium oxide. The comparison between the photographically recorded counts of neutrons per definite time interval measured with and without the cadmium shield allowed us to detect and measure the net gain in the number of the fast neutron release from uranium. By a number of sets of such alternating measurements it was possible to ascertain the remarkable *net increase* of the secondary fast neutrons caused by absorbing the thermal neutrons alone. In this way, the average number of the fast neutrons liberated per fission of uranium induced by thermal neutron was found to be *2.6*. From the considerations of the order of the amt. of energy—about 10 Mev.—involved in the fission neutrons, it is probable that the neutron release takes place *immediately* after the main division of the compound nucleus instead of simultaneously with the explosion. Author.

Radioactive arsenic isotopes. R. Sagane, S. Kojima, G. Miyamoto and M. Ikawa. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 660—671 (1939).—Six radioactive decay periods of arsenic have been investigated by bombarding bromine, selenium, arsenic and germanium with fast and slow neutrons and deutrons. General results obtained are summarised in the following table.

Bombardments	Decay Periods					
Br+FN	65m±3		26h±1			
Br+SN	65m		26h	16d±1		
Se+FN	65m		26h			
As+FN			26h	16d		
As+SN			26h			
Ge+D		90d±10		16d	88m±5	50h±5
Chemistry	As	As	As	As		
Assignment	As^{78}	As^{77}	As^{76}	As^{74}	As^{73} ?	As^{71} ?
Sign	e^-	e^-	e^-	$e^\pm$	e^+	e^+
K.-U. Upper Limit (MeV)	1.4	0.12	2.75 1.31	0.9(e^+) 1.3(e^-)		
γ ray (MeV)	0.27	yes	1.5	yes	yes	yes

Authors.

On the resonance capture of slow neutrons and emission of gamma-rays. I. Nonaka. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 594—608 (1939).—Intensity of gamma-rays emitted from Fe, Cd, Hg and Bi by slow neutron capture was measured as a function of the thickness of paraffin layer interposed between a D+D neutron source and a detector. From analysis of the gamma-ray intensity curves and measurements of energy by the boron absorption method it is shown that Hg has a clear resonance group of about 10 e.V. in energy, Cd has several groups of energies from several tens to a few e.V. and the mean energy of these groups plus the residual part of the first group (Er 0.17 e.V.) not absorbed by a Cd filter of 0.43 g/cm^2 thickness is about 2 e.V., Bi has resonance groups giving a max. of gamma-ray intensity at about 57 cm thickness, and Fe has no distinct resonance groups. Author.

β-Rays from radioactive isotopes, Ni^{63}, Zn^{63}, Nn^{65}, Zn^{69}, Zn^{69*}, Ga^{68}, Ga^{70}, Ga^{72}, Ge^{71}, Ge^{75} and Ge^{77}. R. Sagane, S. Kojima and G. Miyamoto. *Proc. Phys.-Math. Soc. Japan*, **III, 21,** 728—742 (1939).—The β-ray spectra of Ni^{63}, Zn^{63}, Zn^{65}, Zn^{69} (57 m), Zn^{69*} (13.8 h), Ga^{68}, Ga^{70}, Ga^{72}, Ge^{71}, Ge^{75} and Ge^{77} have been investigated by measuring the curvature of the tracks in a cloud chamber situated in a known magnetic field. The upper limit derived from K.-U. plots are summarised as follows:

Ni^{63}	2.5h	e^-	1.65×10^6 eV	0.67×10^6 eV
Zn^{63}	35m	e^+	1.92×10^6 eV	
Zn^{65}	210d	e^+	0.37×10^6 eV	0.19×10^6 eV
Zn^{69}	57m	e^-	0.99×10^6 eV	
Zn^{69*}	13.8h	e^-	0.99×10^6 eV	
Ga^{68}	66m	e^+	1.37×10^6 eV	
Ga^{70}	20m	e^-	1.68×10^6 eV	
Ga^{72}	14h	e^-	1.71×10^6 eV	
Ge^{71}	26h	e^+	1.15×10^6 eV	
Ge^{75}	81m	e^-	1.10×10^6 eV	
Ge^{77}	8h	e^-	1.92×10^6 eV	

From the consideration of energy balance, the min. neutron energies to produce neutron loss processes for Cu^{62}, Zn^{63} and Ga^{68} are estimated roughly to be 12.7, 9.8 and 9.0 MeV resp., which are in good agreement with the values reported by one of the authors except the last case. A suggestion is also given that the 13.8 h period is most likely to be an isomer of Zn^{69} (57 m) of the first kind mentioned by Bethe. Authors.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

The mechanism of the hydrogen electrode process. I. The catalytic Mechanism. J. Horiuti and G. Okamoto. *Bull. Chem. Soc. Japan*, **13**, 216—227 (1938).—Using various kinds of electrolytic solns. on the surface of Ni, the exchange reaction of heavy hydrogen was measured. From the result obtained it is concluded that the rate detg. reaction of the mechanism of $H_2 \rightleftarrows 2H^\cdot$ on the surface of Ni is the combination reaction of the hydrogen atoms. J. C. L.

The mechanism of the hydrogen electrode process. II. The electrochemical mechanism. The existence of hydrogen molecule ions on the surface of the electrode. K. Hirota and J. Hriuti. *Bull. Chem. Soc. Japzn*, **13**, 228—233 (1938).—The authors tried to verify the existence of hydrogen molecule ions at the electrode-soln. interface, using such an electrode as calomel electrode | 0.1 *N* KCl | 0.1 *N* HCl | Hg, and inferred from the oscillograph records taken that the change of the hydrogen molecule ions adsorbed on the Hg surface: $[(H_2^\cdot)_{ads}] \rightarrow (H_2)_{ads} \rightarrow (H_2^\cdot)_{ads} + H^\cdot + \ominus$, is the rate detg. reaction in the H_2 electrode in which Hg is used. J. C. L.

The thermodynamic properties of non-aqueous solutions. S. Kaneko. *Bull. Electrotech. Lab.*, **3**, 486—488 (1939).—The osmotic and activity coeffs. of the aqu. solns. of glycerin, cane sugar and urea are calcd. by assuming the applicability of Hippel's equ. of state of gases to the soln. From thermodynamic reasoning the following relation is obtained between osmotic coeff. g and activity coeff. γ

$$\ln \gamma = g \frac{\bar{v}_1}{M_1} \frac{c}{m} - 1 + \int_0^c \frac{g-1}{c} dc + \ln \frac{c}{m\delta}$$

where $\bar{v}_1$ is partial molal volume of the solvent, M_1 the molecular weight of the solvent, C concn., m molarity, δ density of the solvent.
Author.

On the thermodynamical properties of the dilute solution of non-electlytes. S. Kaneko. *J. Chem. Soc. Japan*, **60**, 763—768 (1939). The relations between the concns. and the osmotic coeffs., activity coeffs., heats of dilution, relative heat contents, partial molal heat capacities, partial molal volumes of non-electrolytes in the dilute soln. are derived by assuming that Hippel's equ. of state of gases holds in the dilute soln.
Author.

Apparent molal volume of strong electrolytes. S. Kaneko. *Bull. Electrotech. Lab.*, **3**, 719—722 (1939).—There are the following relation between the apparent molal volume of strong electrolytes φ and the decrease of the free energy of the soln. by dilution W

$$\varphi=\bar{V}_2{}^0+\frac{\partial W}{\partial P}$$

$$W=-\int_{r_1'}^{r_1}(\bar{F}_1-F_1)\cdot dr_1$$

where P is the press., $\bar{V}^\circ_2$ the partial molal volume of the solute at infinite dilution, F_1 the partial molal free energy of the solvent, F_1 the molal free energy of the pure solvent, r, the molar ratio between the solvent and the solute, r_1' the molar ratio in the extremely dilute soln. Introducing the value of W deduced in the previous report the formula of φ is obtained.
Author.

Determination of the vapour pressures of solid salts. III. Vapour pressures of $TlCl$, $TlBr$, TlI, $PbCl_2$, $PbBr_2$, PbI_2, $ZnCl_2$, $ZnBr_2$, ZnI_2, $CdCl_2$, $CdBr_2$ and CdI_2, and their thermodynamic calculations. K. Niwa, M. Sato and M. Yoshiyama. *J. Chem. Soc. Japan*, **60**, 918—928 (1939).—In the previous work of this series, some improvement of the app. was carried out for the purpose of detg. the vapour press. of solid salts at higher temps. and by using it the vapour press. of solid alkali halides were detd. and a crystallo-chem. regularity was found to exist between the thermodynamic values obtained from the above results. The present paper is concerned with a detn. of the vapour press. of solid halides of non-rare-gas type ions. In this work the vapour press. of $TlCl$, $TlBr$, TlI, $PbCl_2$, $PbBr_2$, PbI_2 $ZnCl_2$, $ZnBr_2$, ZnI_2, $CdCl_2$, $CdBr_2$ and CdI_2 were detd., and using these results, thermodynamic calcns. were carried out, and then a crystallo-chem. regularity which was found to exist between the values obtained above was compared with the results on halides of rare-gas type ions obtained in the previous paper.
Authors.

Determination of the vapour pressures of solutions. II. Vapour pressure of deuterium oxide solution of potassium chloride and the thermodynamic calculations. K. Niwa and E. Shimazaki. *J. Chem. Soc. Japan*, **60**, 985—994 (1939).—In the previous work of this series, the vapour press. of aq. soln. of potassium chloride was detd. by the method devised by Z. Shibata and K. Niwa, and it was found that the thermodynamical values calcd. from the above results were sufficiently concordant with the calorimetric data which detd. by E. Lange. This paper is concerned with a detn. of the vapour press. of deuterium oxide soln. of potassium chloride using a similar app. somewhat improved for the present purpose. In the first place, the vapour press. of deuterium oxide soln. of potassium chloride was detd. between 4° and 13°C, then, from those results, thermodynamic values, such as total heat of soln. ("Ganze Lösungswärme") of satd. soln., differential heat of dilution, differential heat of soln. of satd. soln. ("Letzte Lösungswärme"), and activity coeff. were calcd. The values thus obtained are compared with the results on aq. soln. of potassium chloride obtained in the previous paper.
Authors.

Libration of neutrons in the nuclear explosion of uranium irradiated by thermal neutron. T. Hagiwara. This Journal, **13,** 145—150 (1939).

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Extended co-ordination theory of valency. IV. Configuration of compounds of transition elements. R. Tsuchida, M. Kobayashi, and H. Kuroya. This Journal, 13, 151—165 (1939).

On the capacity of a lead storage cell. M. Kubokawa. This Journal, 14, 11—24 (1940).

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

On the nature of foam. IV. Phase inversion and foaming of emulsion consisting of acetic acid, ethyl ether and water. T. Sasaki. *Bull. Chem. Soc. Japan*, 14, 63—72 (1939).—It was discovered that a certain heterogenous system consisting of acetic acid, ethyl ether and water, sometimes becomes foamy and sometimes not according to the difference in the modes of shaking. This is due to the difference in the types of the emulsions produced. The heterogeneous system is divided into three parts, according to the types of the emulsions produced by shaking, namely, oil-in-water region, water-in-oil region and phase inversion zone. In the phase inversion zone, both types of emulsions are possible to be produced by different modes of shaking. Observation and discussions are made upon these emulsions.

Author.

On the nature of foam. VI. Emulsion and formation of ternary system, ethyl alcohol-ethyl ether-water. T. Sasaki. *Bull. Chem. Soc. Japan*, 14, 250—258 (1939).—The mutual solubility curve, tie-lines and the foam stability of the homogeneous and heterogeneous systems of ethyl alcohol-ethyl ether-water (EEW) were measured. The diagram was established to show the relation between the foam stability and the compn. it shows two max. of foam stability, one of which is situated along the mutual solubility curve, and the other on the line of ethyl alcohol-water. The former is more remarkable in its magnitude than the latter as in the system of acetic ethyl ether-water (AEW). The diagram shows the third max. of foam stability, but it is uncertain. The heterogeneous system of EEW is divided into three portions referring to the types of emulsions produced by shaking, namely, W-in-O region, O-in-W region and phase inversion zone. In W-in-O or O-in-W region, a system simply produces W-in-O or O-in-W emulsion resp., whatever the modes of shaking; while in the phase inversion zone, the system occasionally produces both types of emulsions according to the different modes of shaking. In the phase inversion zone, the tendency to produce W-in-O emulsion gradually decreases and the tendency to produce O-in-W emulsion increases as the system changes in compn. from those near W-in-O region to those near O-in-W region. Foam-non-foam system can also be observed in this system as in AEW or acetic acid-benzene-water system. The region of its existence was detd.

Author.

Studies on the oiliness of liquids. VII. Measurements of the static friction coefficients of esters, ketones and glycerine. T. Isemura. *Bull. Chem. Soc. Japan*, 14, 270—273 (1939).—The static friction coeffs. were measured when esters, ketones and glycerine were placed on the glass surface as lubricants. The friction coeffs. of these liquids are very high. Some considerations are made on the high friction coeffs. of these liquids. The friction coeffs. of water and methyl alcohol are revised.

Author.