

ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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1—GENERAL AND PHYSICAL CHEMISTRY

Polymorphy. K. Fuchino. *Kagaku-Hyoron*, 3, 41-52 (1937). The relation between allotropies of H, N, O, C, and S, and their crystal and atomic structures, the polymorphy of the org. and the inorg. compd. and their structures in transition are generally discussed.

J. C. L.

Effect of supersonic wave on KI and H_2O_2 . S. Kusano. *Tohoku J. Exp. Med.*, 30, 175-180 (1936).—Supersonic wave separates I from KI. Dilute H_2O_2 is slightly increased in concn. owing to the oxidation of water by the action of supersonic wave.

J. C. L.

Graphical solution of a differential equation of diffusion and chemical reaction. J. Kunz and H. F. Johnstone. *Sci. Repts. Tohoku Imp. Univ., Honda Anniv.* Vol., 418-429 (1936).—When two gases were diffused in a liquid phase to react on each other and left the reaction range, their concn. at certain point were increased by the diffusion and decreased by the reaction. The increase and decrease are graphically calcd.

J. C. L.

Concentration of heavy hydrogen in a carbohydrate. T. Morita and T. Titani. *Bull. Chem. Soc. Japan*, 11, 695-698 (1936).—Water formed by burning a carbohydrate in the air is 5-8 γ heavier than ordinary water. In the case of cane sugar, cotton and cedar, the said excessive density is attributed to the condensation of heavy hydrogen; the increase with heavy hydrogen is less than 1 γ . The concn. of heavy hydro-

gen in water formed by burning cane sugar with the oxygen 1.6 γ less than in ordinary water is the same as that in ordinary water, so that oxygen in cane sugar is some γ heavier. By examn. of the liquid formed by means of dry distillation of cane sugar, it was found that the oxygen was $4 \pm 1 \gamma$ heavier. This value is accounted for by the assumption that oxygen carbonic acid gas in the atm. is $10 \pm 1 \gamma$ heavier.

J. C. L.

The magnetic properties of elements. A survey. S. Edmund. *Sci. Repts. Tohoku, Imp. Univ., Honda Anniv.* Vol., 283-305 (1936).—A survey is made of the magnetic properties of the elements. And it is pointed out that the elements in the solid state are not generally magnetically simple, and that their exptl. result is hard to be explained. The theory of magnetic susceptibility is outlined under six heads,—atomic, molecular and crystalline diamagnetism, atomic and molecular paramagnetism, and collective electrons, both free and bound, and the temp. variation, are considered in some detail as being of primary importance in connection with the susceptibility of metals, comprising the great majority of the elements. A table gram is given showing the room temp., atomic susceptibility, the variation with temp., and the change at melting point for all elements for which reasonably reliable results are available. The elements are then discussed in turn in appropriate groups corresponding either to the columns of the periodic table or for the transition elements, the rows.

J. C. L.

The rotatory dispersion of several derivatives from alkyl tartrate. Y. Tuzuki. *Bull. Chem. Soc. Japan*, **11**, 586-592 (1936). The rotatory dispersion of the liquids was measured over the wave lengths between $6,708\text{\AA}$ and $4,358\text{\AA}$ with respect to the derivatives of alkyl tartrates. It was found that it could be expressed with Drude's expression of 1st term. The absorption band of condensation compd. from keton lies in the neighbourhood of $1750\text{\AA}$; and that from aldehyde in the neighbourhood of $2,100\text{\AA}$. The relation between these values and chemical structures is discussed. Judging from the dispersion ratio ($a_{4,358}/a_{5,461}$) and the value of the wave-length of the bands, it is concluded that the rotatory dispersion is very simple.

J. C. L.

The exchange reaction between chloroform and heavy water. J. Horiuchi and Y. Sakamoto. *Bull. Chem. Soc. Japan*, **11**, 627-628 (1936).—A KOH soln. neutral water, H_2SO_4 , each contg. heavy water, and mixed with CHCl_3 , were heated in boiling water. From the estimation of the amt. of heavy hydrogen which exchanged into CHCl_3 and that of Cl' from the decompn. of CHCl_3 it was found that the exchange is much faster than the decompn. in KOH soln.

J. C. L.

The exchange reaction between chloroform and heavy water. Y. Sakamoto. *J. Chem. Soc. Japan*, **57**, 1169-1174 (1936).—When chloroform was put in contact with neutral heavy or acid heavy water (0.01N H_2SO_4) at 100°C , no exchange reaction occurs between them, while with alkaline heavy water (0.1N KOH) at the same temp., it is found that an exchange reaction proceeds slowly. A small quantity of alkaline chloroform is decomposed, but its rate of decompn. is only a few percents of the rate of the exchange reaction. Further, general consideration of the influences of acid and base on the exchange reaction was made, and it was concluded that (I) when oxygen in carbonyl radical and Brönsted acid have made hydro-

gen bond, the H_2 united with carbon is transmitted to the Brönsted base, and the final step is the process of H_2 united with carbon being transmitted to the base. (II) The final step of the exchange reaction of chloroform is the process of its ionisation.

J. C. L.

Studies on the dielectric constants of gases and vapours. VI. M. Kubo. *Sci. Papers Inst. Phys. Chem. Research*, **30**, 169-179 (1936).—The dielectric consts. of the vapours of methylene glycol diethyl ether, ethylidene diethyl ether and diethyl carbonate, the molecules of which contain two active axes of free rotation, were measured and used to calc. the dipole moments at various temps. The moment of methylene glycol diethyl ether increases with rising temp. from 1.22 D at 55.5°C to 1.26 D at 202.5°C . The results were treated theoretically in the same way as in a foregoing paper (*ibid.* **26**, 179 (1936).) with the following conclusions. Intramolecular rotations are hindered: the molecule executes rotatory oscillations about the position of min. potential energy, in which two ethyl groups are not located on the plain contg. the central carbon atom and the two oxygen atoms. The same is true for ethylidene diethyl ether (from 1.07 D at 55.3°C to 1.21 D at 203.1°C). The moment of methylene glycol diethyl ether is higher than that of methylene glycol dimethyl ether, and thylidene diethyl ether has lower moment than the former. This is explained in terms of intramolecular forces. The moment of diethyl carbonate (1.06 D) is, on the contrary, independent of temp. The suggestion is made that this is due to quantum resonance.

Author

Studies on the dielectric constants of gases and vapours. VII. M. Kubo. *Sci. Papers Inst. Phys. Chem. Research*, **30**, 238-243 (1936).—The dielectric consts. of the vapour of 1,4-dioxane were measured and used to calc. the dipole moments at various temps. (from 55.6°C to 205.8°C). The moment found (0.43-0.49 D) can be

accounted for by the presence of polar form (cis-form) in molar percentage less than 5%. This is not in contradiction to the results of the electron diffraction investigation as well as of the Raman effect obtained by other investigators. Author.

Measurement of air content in water. F. Numachi. *Sci. Repts. Tohoku Imp. Univ. Honda Anniv. Vol.*, 501-509 (1936).—In the course of a study on the occurrence of incipient cavitation in water, the writer was compelled to determine the air content in water when it is either unsatd. or supersatd. As far as the writer is aware, however, no reliable method for this purpose has as yet been investigated, although the amt. of air to be absorbed to form a satd. soln. in water is well-known and is of practical use in phys. chem. The chem. method, such as that of Winkler, is well known to be very complicated and subject to much error in measurement, especially when the water contains nitrites, iron salts or dissolved org. matter; and Van Slyke's method is also not a simple one especially in preparing and preserving the air-free reagents. The method here devised, the writer thinks, is free from these difficulties and complications, and is made effective by the following precautions:—(i) Boiling the water at room temp. to expel the air, by which the error arising from the process of condensing the water, by the usual boiling method, can be avoided. (ii) Making an asymptotic decrement of the partial pressure of air in such a way that not the slightest remaining quantity of air may fail to be expelled, (iii) Allowing not the slightest adherence of air on the inside wall of the app. on taking out the sample and to let the expelled air not be absorbed back in the water during the process, (iv) Being able to determine the constituents of the air initially dissolved in the water. Author.

Raman spectrum of deuterio-methanol. S. Mizushima, Y. Morino and G. Okamoto. *Bull. Chem. Soc. Japan*, 11, 698-699 (1936).—Raman spectra of methanol and

deuterio-methanol were investigated with the following results— CH_3OH : 1033 (6), 1107 (2), 1165 (1), 1464 (5b), 2835 (10), 2911 (1), 2940 (9), 2993 (3), 3270~3480. CH_3OD : 1029 (5), 955 (1), 1163 (1), 1463 (5b), 2834 (10), 2905 (1), 2943 (9), 2992 (3), 2420~2560. In conformity with the observation of Redlich and Pordes (Wiener Berichte 145, 67 (1936), the authors found a large isotopic shift for the band 3270~3480, which is assigned to the OH valency vibration. Another large effect, which was found for the first time, was observed for the line 1107 of CH_3OH (955 of CH_3OD). It is very probable that this line corresponds to the deformation vibration of the hydroxyl hydrogen. Authors.

Specific volumes of heavy water and its ice at the freezing point and etc. T. Takeuchi and T. Inai. *Jap. J. Physics*, 11, 67-68 (1936).—As far as we know, there is yet no report of measurement of volume change of heavy water and its ice at the freezing point. So we decided to measure it, by using an app. made of hard glass which was shaped like a Bunsen ice-calorimeter and put in a Dewar vessel, having an exposed horizontal capillary 20 cm long and 1 mm diameter, and following the principle of that kind of calorimeter. The sample used was 1 g of 99.2% concn. The temps. were read with a Beckmann thermometer. The max. density of water was found to occur at 11.4°C. The cooling- and the heating-curves were taken near the freezing point, from which we got the difference of specific volumes of heavy water and its ice as function of temp. The results are expressed by following formula empirically, $\frac{v_l - v_s}{m} = 8.35 + 0.285t \times 10^{-6} \text{ cm}^3/\text{g}$ for $-5^\circ\text{C} > t > +3.8^\circ\text{C}$. We also measured the velocities of super-sonic wave of frequency 5×10^6 per sec. in this heavy water at temps. 13° and 20°C, which were found to be 1370 and 1381 m/sec. The method was based on the well known Brillouin formula. The light used was green light of mercury and the second diffraction patterns were taken on an orthochromatic plate, the duration of ex-

posure being 3 sec. The sample used was 2 g. only.

Authors.

Rhythmic precipitates. VII. On the rhythmic precipitates of lead iodide in silicic acid gel. T. Isomura, *J. Chem. Soc. Japan*, 58, 58-62 (1937).—When the potassium iodide soln. is forced to diffuse in the silicic acid gel contg. lead acetate, fern-like fronds grow down in the gel, mixed with hexagonal plates. It has been believed that lead iodide does not form the rhythmic ppts. in the silicic acid gel. But it was found in rare cases that this rhythmic ppt. occurred accidentally. The author studied the condition under which the rhythmic ppts. are formed, and found that when the crystals become relatively small, the rhythmic ppts. are generally formed. To make the crystals small, the increase of the concn. of inner and outer electrolytes is favourable. In order to make sure the formation of rhythmic bands, the third substance which makes the crystals of lead iodide very small, must be added. Citrates and tartrates are fit to this purpose. A 1.06 water glass—*N* acetic acid contg. 0.9cc. of *N* lead acetate and 0.55cc. of 3% potassium citrate to every 10cc. was poured into a test-tube. After the silicic acid gel had set firmly, it was covered with 2*N* potassium iodide. By this procedure, good rhythmic bands from fine crystals are always formed. Similarly, a 1.06 water glass—*N* acetic acid contg. 1.2cc. of *N* lead acetate and 0.8cc. of 3% tartaric acid to every 10cc. was poured on it. Beautiful well-defined rhythmic ppts. from relatively large crystals were produced. These results show the bands as the true Liesegang's phenomenon. But the crystallisation of lead iodide is much influenced by temp. and light. In day time the crystallisation is more active than at night. On the other side, lead iodide is decomposed by bright light, especially in the presence of citrate, and the crystals blacken. For these reasons, two other periodic ppts. are produced as the reflex of outer periodicities. Frequently, these three periodicities appear at the same time in one test-tube, and

the complicated bands are obtained.

Author.

Emission spectrum of the oxygen-hydrogen flame and its reaction mechanism. (1) Formation of the activated water molecules in high vibrational states. T. Kitagawa, *Proc. Imp. Acad. Tôkyô*, 12, 281-284 (1936). Also see this Journal, 10, 317-332 (1936).—The emission spectrum of the flame of oxygen burning in the hydrogen atm. was photographed for the purpose of the elucidation of its reaction mechanism. A very complex band system was found and about twenty emission bands were measured in the region between $227000-5500\text{\AA}$. The band system was interpreted as the rotation-vibration band of the water molecule, because the wave length of some emission bands of the flame coincided well with that of the absorption bands of water vapour, which were photographed through the absorption tube 8 meters long heated electrically up to 144°C , at that temp. the vapour pressure of water in the tube being 4 atms. The length of the layer of the water vapour, therefore, corresponded to about 32 meters at the pressure of 1 atm. It becomes clear that a large number of the activated water molecules (H_2O^*) in the high vibrational states (max. vibrational energy of about 50 kcal.) are formed in the reaction between hydrogen and oxygen. The mechanism of the formation of the activated water molecule was explained as follows: (1) $2\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}^* + \text{H}_2\text{O}^*$, (2) $\text{H} + \text{O}_2 + \text{H}_2 = \text{H}_2\text{O}^* + \text{H}_2\text{O}$, (3) $\text{H} + \text{O}_2 + \text{H}_2 = \text{H}_2\text{O}^* + \text{H}_2\text{O}$, (4) $\text{O} + \text{H}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}^* + \text{H}_2\text{O}$. The activated water molecule with large vibrational energy will take part as an important intermediate product in the mechanism of the oxygen-hydrogen combustion.

Author.

Studies on the Raman effect of organic substances. VII. Raman effect of furane derivatives. K. Han, *Bull. Chem. Soc. Japan*, 11, 701-711 (1936).—The Raman spectra of the following substances

have been measured: α -furfuryl methyl ether, α -furfuryl ethyl ether, α -furfuryl-acetone, α -furyl ethylene, α -furyl cyanide, 2, 5-dimethyl-furan, 2-methyl-furyl cyanide-(5) and ethyl 2-methyl-furoate-(3). The characteristic frequencies of the α -furfuryl-radical are confirmed. The constitutive influences exerted on the Raman frequencies in the region between $\Delta\nu$ 1400 and 1600 cm^{-1} are observed. The Raman lines at $\Delta\nu$ 1642 and 1292 cm^{-1} in α -furyl-ethylene are associated with the structure of $\text{R}-\text{CH}:\text{CH}_2$, and those at 183, 570, and 2233 cm^{-1} in α -furyl cyanide with the structure of $\text{R}-\text{C}\equiv\text{N}$, when R is taken as furyl radical.

Author.

Additive properties and the method of least squares. Supplement. S. Kaneko. *J. Chem. Soc. Japan*, 58, 192 (1937). Supplement to the former report (*ibid.*, 57, 665 (1936)).

Author.

The unit cell and the space group of acetylsalicylic acid. I. Nitta and T. Watanabe. *Sci. Papers Inst. Phys. Chem. Research*, 37, 125-128 (1937). Oscillation and Weissenberg photographs give acetylsalicylic acid, $\text{C}_6\text{H}_4(\text{OCOCH}_3)\text{COOH}$, a monoclinic unit cell of the dimensions $a=11.37\text{\AA}$, $b=6.54\text{\AA}$, $c=13.37\text{\AA}$, $B=95.7^\circ$. This unit contains four molecules and possesses the symmetry of space group $\text{C}_{2h}-\text{P}_2/\text{a}$. The density of the crystal is calcd. from these X-ray data to be 1.41. All the atoms are in general positions. A chain-like structure is suggested. The above result is completely different from that reported by Kôzu and Takanô.

J. C. L.

Ionospheric measurements during the total solar eclipse of June 19, 1936. K. Maeda and Y. Isagawa. *J. Inst. Elec. Eng. Japan*, 57, 83-93 (1937).—This report gives the results of ionospheric measurements obtained at Asahigawa, Hokkaido, over a period of several days centering on the total solar eclipse of June 19, 1936. The critical penetration frequencies of various regions were measured by employing waves ranging from

3.2 to 18.6 megacycles. The results obtained for the E and F_1 regions were practically the same as those secured during other eclipses. The effect of the eclipse on the F_2 region was not as clear as in the case of the E and F_1 regions. There were also the additional effect of a severe magnetic storm on the day of the eclipse, and throughout the daytime the F_2 region appeared to be under the influence of some disturbances. Although no pos. evidence of the influence of neutral particles was obtained from the exptl. results, several factors are pointed out which seem to indicate that the results were in some way related to the particles.

Authors.

Note on Dirac's generalized wave equations. S. Sakata and H. Yukawa. *Proc. Phys.-Math. Soc. Japan*, 19, 91-95 (1937).—A few elementary results of Dirac's relativistic theory of the particle with the spin larger than $\frac{1}{2}$ are deduced. Namely, the expressions for the velocity, the current density, the spin angular momentum and the electric and magnetic moments, which had not been given explicitly in Dirac's paper, are obtained. It is noticeable that the spin and the magnetic moment are not proportional to each other in general. The invariance of the wave equations under reflection (Spiegelung) is also discussed.

Authors.

On the diamagnetic susceptibility of heavy water. T. Takéuchi, T. Sugita and T. Inai. *Bull. Tokyo Univ. Eng.*, 6, 116-117 (1937).—Theoretical calculations of the diamagnetic susceptibility of heavy water molecule and its variation with temperature based on Thomas-Fermi atom model are shown. The arrangement for determining the susceptibility of small quantity of heavy water is also described.

Authors.

On the reducing action of amalgams. V. The mechanism of the interface reaction. I. K. Masuda. *J. Chem. Soc. Japan*, 58, 162-172 (1937).—The author has been studying amalgams for

several years, with a view to explaining the mechanism the reducing action. The reducing power of liquid zinc amalgam upon the soln. of ferric sulphate contg. sulphuric acid rises as the zinc content diminishes; and the logarithm of the former is a linear function of that of the latter. This relation holds good within the limits of the zinc content 2.00~0.010%. But at 0.010~0.005%, the reducing power increases five or eightfold, and the amalgam moves spontaneously with the soln. that is, the interface trembles violently, just as, the sea surface is rippling. We have given provisionally the same "rippling" to this marvellous phenomenon, considered its reason, and observed facts connected with this. The phenomenon has given us the key to solve the mechanism. Author.

Chemical investigations of the ancient metallic implements in orient. IX. On the ancient Chinese copper implement. V. On the ancient Chinese bronze implement. VII. Especially, on the transitional period between the copper and bronze ages in ancient China. (Supplementary). T. Dôno. *J. Chem. Soc. Japan*, 58, 187-191 (1937).—The author made chem. and metallographical researches of six halberds equipped with socket unearthed in the Yin site in Honan. These halberds with socket are known to be among the oldest and the most primitive of the existing relics of the metallic implements of ancient China. Four of these six halberds are found to be copper implements rather than bronze ones, owing to their contg. insignificant or no amount of tin. The remaining two are found to be bronze contg. tin to some extent. Thus, these investigations confirm the author's opinion that, in ancient China, before and after the time when these metallic implements were manufactured, there was the transition from the Copper to the Bronze Ages. Author.

The viscosity of mixed salt solutions. T. Ishikawa. *Bull. Chem. Soc. Japan*, 12, 16-24 (1937).—An application of the

author's viscosity formula for ideal or phys. mixs. is given to the viscosity of mixed salt solns. His formula runs:

$$\eta = \frac{\eta_1}{1 + K \frac{z_m}{1 - z_m}} + \frac{\eta_2}{1 + \frac{1}{K} \frac{1 - z_m}{z_m}}, \text{ where } \eta_1,$$

η_2 , and η are the viscosities of component 1, 2, and the mix.; z_m a formal molar fraction of component 2 in the mix.; K the characteristic const. for the mix. The author's precognition that the formula may hold for the viscosity of non-reacting salt solns. having a common solvent and a const. total concns. during admixture is satisfactorily realized by using the data for urethane—urea and ZnSO_4 — K_2SO_4 (observed by Banchetti) and for HCl — KCl , KCl — NaCl , and HCl — NaCl (observed by Ruby and Kawai). He also gives severe tests for $\text{C}_2\text{H}_5\text{OH}$ — $\text{i-C}_4\text{H}_9\text{OH}$ (observed by Parks and Kelley) and for $\text{C}_2\text{H}_4\text{Br}_2$ — $\text{C}_2\text{H}_4\text{Cl}_2$ (observed by MacFarlane and Wright), and obtains better agreement than with fourteen other formulae. Author.

On the additivity of diamagnetic susceptibility of organic compounds. K. Kido. *Sci. Repts. Tohoku Imp. Univ. Honda Anniv. Vol.*, 329-346 (1936).—By using the values of the magnetic susceptibility of the ions obtained in the previous investigation, the molecular susceptibilities of org. compds, 177 in number, were calcd. by the modified additive law and compared with the observed values. It was found that the additive law holds good for org. compds. as well as for inorg. compds. In the case of the compd. with double and triple bonds, a little effect caused by these combinations was observed on the molecular susceptibility. J. C. L.

Paramagnetic susceptibility of colloidal powder of platinum. N. Takatori. *Sci. Repts. Tohoku Imp. Univ. I*, 25, 489-503 (1936).—In the present investigation, the paramagnetic susceptibility of small particles of platinum was measured in connection with the particle size. The result showed that the paramagnetic susceptibility of platinum de-

creases from 1.01×10^{-6} to 0.78×10^{-6} during the change of particle size from 15×10^{-4} to 0.20×10^{-4} mm.

J. C. I.

Magneto-optical rotation and natural dispersion of heavy water. A. Okazaki. *Proc. Phys.-Math. Soc. Japan*, III., 19, 286-294 (1937).—By the use of Slack's data for Verdet's const. of H_2O , D_2O and a mix. of H_2O and D_2O for $\lambda 5893\text{\AA}$ and $\lambda 5461\text{\AA}$, the corrected molecular rotations $M[D]$ of H_2O , HDO , and D_2O were calcd. for these wave-lengths. The formulae for the dispersion of molecular refraction of H_2O , HDO , and D_2O were derived from Luten's data for the refractive indices of H_2O , D_2O , and their mix. in the region from $\lambda 6563\text{\AA}$ to $\lambda 4358\text{\AA}$. With these $M[D]$ -values and dispersion formulae, the magneto-optical anomaly of H_2O , HDO , and D_2O was evaluated by application of Becquerel's formula for magneto-optical rotation.

Author.

Studies on the oiliness of liquids. I. J. Sameshima, M. Kidokoro and H. Akamatu. *Bull. Chem. Soc. Japan*, 11, 656-657 (1936).—An app. has been devised for the measurement of the static friction coeff. of liquid. It is simply composed of a prescription balance and sliding surfaces. The slider is made of a watch glass connected with the pointer of the balance by a wire. The friction coeff. is computed from the wt. on the balance-pan which is just sufficient to start the moving of the slider. The measurements have been done using the glass surfaces on the following liquids, the results being given in tables and figures. Methyl alcohol, ethyl alcohol, propyl alcohol, n-butyl alcohol, n-amyl alcohol, secondary amyl alcohol, tertiary amyl alcohol, n-hexyl alcohol, n-heptyl alcohol, n-octyl alcohol, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, heptylic acid, caprylic acid, nonylic acid, n-hexane, n-octane, n-nonane, benzene, toluene, liquid paraffine, glycol, ethyl acetate, oleic acid, and a lubricant oil.

Authors.

The production and absorption of cosmic ray secondary particles in lead. J. Itoh. *Proc. Phys.-Math. Soc. Japan*, 19, 271-285 (1937).—According to the view of Geiger and Fünfer (*Z. Physik*, 93, 541 (1935)), cosmic ray showers are produced in many successive processes from their parent radiations and some parts of them are composed of electrons and positrons having a range of few cm in lead. It is the scope of this work to obtain the absorption curve of the secondary particles of cosmic ray. Four counters were placed vertically in line in such a way that, the top one being larger than the lower three, the system was able to select only the secondary particles which were produced from non-ionizing primary radiation in lead plate of 1.5 cm thickness placed between the top and the second counter. The absorption curve was obtained by inserting lead plate of various thickness between the third and the lowest counter. From the result of the absorption measurement, it is concluded that the secondary particles are composed of two components; one being soft one of about 0.5 cm in range, and the other being very hard one having its half value thickness of ca. 15 cm in lead. By putting the third counter out of line, also the same result was obtained. These facts indicate that there is no evidence for the existence of C-radiation (electrons having their range of a few cm in lead) suggested by Geiger and Fünfer. The hard component would have relation to the second max. of Rossi-curve. The production of secondary particles from lead plate of various thickness in vertical direction was also measured and it was concluded that those were more predominant in the soft component than the shower particles observed in the triangle arrangement of counters.

Author.

On equations for Dirac's electron in general relativity. H. Yamamoto. *Jap. J. Physics*, XI, 2, 35-65 (1937).—A covariant formulation of a system of equations of the first order is obtained by the method of usual tensor analysis of four dimensional

manifold, without making use of any auxiliary spaces and quantities. It is shown that this system of equations can naturally be regarded as a possible generalisation of Dirac's wave equation for an electron. A scheme of a world geometry is developed, which is intended to be descriptive of the phys. world consisting of space, time and electron.

Author.

The H-theorem in quantum mechanics. T. Sakai. *Proc. Phys.-Math. Soc. Japan*, III, 19, 172-189 (1937).—There are Pauli's theory and Neumann's theory on the H-theorem in quantum mechanics, but the author, selecting a special system of axis in Hilbert space, obtained the more general H-theorem from the standpoint of Gibbs' statistical mechanics. The theory obtained is discussed, comparing with the results from the above two theories. J. C. L.

Refracting coefficient of solutions. F. Kojima. *Kyoto Furitu Ika Daigaku Zasshi*, 16, 182-198 (1936).—By using a refractometer, $[n]^{20-65^\circ}$ was measured with respect to pure water and solns. different in concn., of KCl, NaCl, LiCl, grape sugar, starch and ovalbumin. Each index of refraction decreased as temp. rose, and its temp. curve ran always parallel with that of the pure water.

J. C. L.

The concentration of heavy water in the atmospheric moisture. K. Okabe and T. Titani. *Bull. Chem. Soc. Japan*, 12, 11-15 (1937).—Under different conditions of atmospheric humidity vapour in the air was extracted and purified fully. The specific gravities of the samples thus obtained were 0.8~6.8 γ , all smaller than those of standard water, and, though they were different according to samples, their av. was 3.7 γ . This value approximates to that, 3 γ , calcd. when vapour and water at ordinary temp. were considered to be in equil. with respect to the concn. of heavy water. J. C. L.

The exchange reactions between heavy water and amino acids and car-

bohydrates. E. Ogawa. *Bull. Chem. Soc. Japan*, 11, 367-374 (1936).—In the measurement of the av. equil. const. Km glutamic acid and aspartic acid were used as amino acids, and glycerine, glucose, fructose, galactose, maltose, lactose, starch and inulin as carbohydrates. The equil. of the exchange reaction between these samples and heavy water was examd. at 50°C and 100°C. With this result the structure of the above org. compds. is discussed. J. C. L.

On the reversibility of quantum electrodynamics. S. Watanabe. *Sci. Papers Inst. Phys. Chem. Research*, 31, 109-129 (1937).—Quantum electrodynamics allows the existence of solns. ψ_1 and ψ_2 , such that if ψ_1 at the initial instant represents the reversed state of ψ_2 at the initial instant, then ψ_1 at the final instant will represent the reversed state of ψ_2 at the initial instant. Thus, the irreversibility of any kind is excluded from the microscopic law governing the causal development of the state in quantum theory. The only place, where to find the source of the thermodynamical irreversibility, must therefore be the statistical treatment of the result of the observation. J. C. L.

Abnormality in diffusion. M. Taniguchi. *Gakujitu Kyoho*, 12, 52-56 (1937).—By preparing a soln. of acetyl glucose in benzene (or toluene, methyl formate or pyridine) the diffusion velocity of the soln. was measured, and it was observed that the diffusion const. was always held, independent of the concn. Considering this result, it was found that the abnormality of diffusion of the high molecular weight solute, generally accepted hitherto, was due to the convection or other chem. disturbances in the course of the exp. J. C. L.

Chemical investigations of the ancient metallic implements in Orient. VIII. On the ancient Chinese copper implements. IV. Especially, on the existence of the copper age in Ancient China. (Supplementary). T. Dôno. *J. Chem*

Soc. Japan, 58, 182-186 (1937).—The author performed some chem. and metallographical investigations of five spear-heads of the so-called Yin site type unearthed from the Yin site in Honan, generally regarded as the oldest and the most primitive of the relics of metallic weapons of ancient China. These were found to be copper implements rather than bronze ones, owing to their compositions almost devoid of tin. Thus, the author finished his investigations of nine metallic spear-heads in toto, five this time, in add. to the four already referred to in the first and the fourth papers. The conclusion is drawn that all these spear-heads are copper implements cong. insignificant or no amt. of tin,—more and more confirming him in his proposed opinion that there truly existed the Copper Age in Ancient China. Author.

On the variation with temperatures of the electrical conductivity of a thin film of NaCl and rock salt crystal. H. Saegusa and T. Matsumoto. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 805-816 (1937).—The electrical conductivity of a thin film of NaCl about 10 cm in thickness was measured for various temps. and it was found that the variation of the electrical conductivity with the temp. of a fresh film nearly satisfied the formula $\log \sigma = B + \frac{A}{T}$, and that after heating the film up to 160°C, its electrical conductivity satisfied extremely well the above expression, and further we found that its magnitude decreased to about one-tenth of that of the fresh film. To explain this fact the X-ray pattern by the Deby-Scherrer method and the reflection pattern by the electron beam were taken, and then confirmed that the thin film made by the evaporation of a NaCl crystal showed a fibrous structure and that it became sharp as the film was heated. We also investigated the variation of the electrical conductivity with the temp. of a natural rock salt crystal and an artificial NaCl crystal which was made in our laboratory, and found that the latter satisfied closely the above equation. Authors.

Magneto-optical rotation and natural dispersion in gases. A. Okazaki. *Mem. Ryugun College Eng.*, 10, 19-25 (1937).—Natural dispersion formulac of Ketteler-Helmholz type, with a single ultra-violet absorption term, together with Becquerel's formula for magneto-optical dispersion are found to fit the exptl. data in the case of the gases, hydrogen, carbon monoxide, hydrogen sulphide, cyanogen, sulphur dioxide, methyl chloride and gaseous chloroform. The computed wave-lengths of absorption bands lie within the experimentally detd. bands for these gases, except for cyanogen and chloroform for which the observations have not been extended to the extreme ultra-violet region. Consts. of the two dispersion formulac and the calcd. values of e/m for the dispersion electrons are given. Author.

Studies on the promoting action of a catalyst promoter and carrier. II. Activity of a catalyst prepared by the roasting method. S. Tsutsumi. *J. Chem. Soc. Japan*, 58, 63-70 (1937).—According to the present author, the promoting action of a catalyst promoter and carrier is mainly due to their preventing action of the sintering of the reduced nickel and cobalt at a higher hydrogen reduction temp., and the optimum hydrogen reduction temp. of a catalyst may be raised by an increase of the added amt. of promoter and carrier for nickel and cobalt with bad heat conductance. A catalyst prepd. by the roasting method is, as compared with that prepd. by the pptn. method, compact, and its contact surface is smaller so that its activity depression by the elevation of hydrogen reduction temp. seems to be fairly large. Cobalt-thoria, cobalt-urania, cobalt-mangan and cobalt-copper-urania catalysts were prepd. by the roasting method, and their catalytic activity for the gas mixt. of 1CO and 2H₂ at 190°-210°C was measured in varying hydrogen reduction temps. as well as an added amt. of kieselguhr for cobalt metal, and the results are summarised as follows:—(1) The optimum hydrogen reduction temp. of a catalyst prepd. by the roasting method is lower than that

prepd. by the pptn. method, and its activity depression by the elevation of hydrogen reduction temp. is larger, so that it is necessary to add a larger amount of kieselguhr for cobalt metal to obtain the same active catalyst as one prepd. by the pptn. method. The optimum added amt. of kieselguhr for cobalt metal was found to be 2:1-3:1 as compared with 1:1 and 4:3 in the case of the pptd. (2) The activity difference between catalysts prepd. by the pptn. and roasting methods was larger in the case of a cobalt-mangan catalyst, followed by cobalt-thoria and cobalt-urania catalysts, or decreased with the increasing atomic wt. of the promoter itself.

Author.

On the change of magnetic susceptibility in metals during melting and allotropic transformation. Y. Shimizu. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 921-938 (1937).—An accurate measurement of the abrupt change of magnetic susceptibility in metals during melting and allotropic transformation was made. An attempt is also made to explain quantitatively these abrupt change of susceptibility by applying the theory, which was proposed in the explanation of the change of susceptibility in metals caused by cold working. As is well known, tin changes the sign of its magnetic susceptibility twice as the temp. rises, that is, at the transformation point and also at the melting point. These interesting phenomena have been satisfactorily explained by the above theory. A good agreement has also been found between the observed change of susceptibility during melting and its theoretical value in the case of copper, silver, gold, aluminium, mercury, sodium, potassium, rubidium and caesium.

Author.

Determination of the number of interchangeable hydrogen atoms in complex salts. J. Horiuti and G. Okamoto. *Sci. Papers Phys. Chem. Research*, 31, 205-210 (1937).—It is remarked that the current method in finding the number of interchangeable atoms by means of dilute heavy

water is associated with difficulty. A method is proposed to eliminate this difficulty by means of 100% deuterium oxide, and it is applied to complex salts. All hydrogen atoms in complex salt have been found to be interchangeable.

Authors.

On the instability and breaking up of a ring of liquid into small drops. S. Oka. *Proc. Phys.-Math. Soc. Japan*, 18, 524-534 (1936).—It is a well-known observed fact that if a small drop of ink be brought on the still surface of water and be left to itself, it begins to sink and the form is gradually flattened and ultimately changes from the original spherical shape to a small horizontal circular ring. As this ring falls down through water, its radius becomes larger and larger until the ring becomes unstable and varicose, showing the tendency to the production of bead-like swellings and contractions along the circumference of the ring. A series of drops of a uniform size will then be formed, under favourable circumstances, at nearly equal distances along the circumference. In connection with these interesting hydrodynamical phenomena, the instability of a circular ring of liquid under the action of surface tension is discussed by the method of small oscillations, supposing that the motion of the liquid is proportional to $e^{m\phi}$ as well as to $e^{i\omega t}$ where the azimuth ϕ is taken along the circumference of the ring. The expressions for determining q as a function of m is obtained and it is found that the system is stable or unstable according as the wave-length of the varicosity is less or greater than the circumference of the cross-section of the ring, in agreement with Lord Rayleigh's results in the case of a cylindrical column of liquid. Max. instability occurs in every case at a certain definite value of the wave-length of the varicosity, indicating that drops of definite size would be formed, and this wave-length varies with the ratio of the radius of the ring to that of the cross-section.

Author.

Kerr-constants of gases in relation to density. S. Oka. *Proc. Phys.-Math. Soc.*

Japan, III, 19, 156-160 (1937).—As an addn. to Kubo's theory of the molecular polarisation of gases a formula has been derived for the Kerr-cont. of gases at high pressures, by inserting a correction in the dipole term to account for the interaction of the dipoles. This term is zero for non-polar gases, for which the formula of Langevin and Born is always valid, confirmation being afforded by measurements on CO_2 , CH_4 , C_2H_4 and C_2H_6 . For polar gases, however, no measurements are yet available for testing the above theory.

Author.

Studies on the oiliness of liquids.

III. Measurements of the kinetic friction coefficients. J. Sameshima and M. Miyake. *Bull. Chem. Soc. Japan, 12, 96-103 (1937).*—The kinetic friction coeff. of alcohols, hydrocarbons, acids and the mixtures of water and ethyl alcohol have been measured. The app. used was composed of a rotating cylinder and a prescription balance, sometimes a damper being attached. The friction coeff. of liquids between steel surfaces were measured. The method of cleaning of the surfaces were described.

Authors.

Studies on the oiliness of liquids.

IV. Measurements of the static friction coefficients by the method of inclination. J. Sameshima and Y. Tsubuku. *Bull. Chem. Soc. Japan, 12, 127-132 (1937).*—The static friction coeffs. of liquids have been computed by the measurements of the min. angle of inclination at which the slider begins to move. The friction coeffs. of alcohols and acids between the glass surfaces were detd. The decrease of the friction coeffs. by the increase of molecular wt. is conspicuous in the alcohols, but not in the acids. This fact may be explained by the assumption that the carboxyl group in the acid molecule has greater affinity with glass than the hydroxyl group in the alcohol molecule.

Authors.

Exchange of hydrogen between pyrrol and water. M. Koizumi and T. Titani. *Bull. Chem. Soc. Japan, 12, 107-108*

(1937).—Pyrrol was shaken with heavy water at 50°C for 40~50 hours, but only one of the five H atoms in the molecules gave rise to the exchange of deuterium. When HCl solns. of 0.1N acidity was used, instead of heavy water, all the hydrogen atoms could be easily exchanged by shaking within an hour at 30°C . The partition coeff. between pyrrol and water in the secondary exchange was as follows: $k(\text{CH pyrrol}/\text{H}_2\text{O}) = 0.70$. When the acidity of heavy water was below 0.01N and when it was alkaline with KOH, such a secondary exchange as the above could not be seen though the heavy water was shaken for 40~50 hours at concn. of 1N. But, when the acidity was made 0.01N~0.1N, the secondary exchange reaction took place slowly. These results seem to have some close relation with the tautomerism of pyrrol.

J. C. L.

Partition of deuterium between methyl alcohol and water.

G. Okamoto. *Sci. Papers Inst. Phys. Chem. Research, 31, 211-216 (1937).*—In order to investigate the partition of deuterium between methyl alcohol and water, the following indirect procedure was taken. First, methyl alcohol was shaken for a few hours in the presence of deuterium and platinum black, and it was assured that H in OH radical alone of methyl alcohol took part in the exchange reaction. After such treatment the hydrogen left was burned and the deuterium in the water produced was measured. From these results was obtained the partition coeff. between deuterium and OH of methyl alcohol. And similarly the partition coeff. of deuterium between water and hydrogen was precisely obtained. Combining the results obtained from the above two procedures, the partition coeff. between methyl alcohol and water could be obtained. Thus, it was elucidated that the partition coeff. takes no preference within $\pm 1\%$.

J. C. L.

Isotopic exchange reaction between water and oxygen. T. Morita and T. Titani. *Bull. Chem. Soc. Japan, 12, 104-106*

(1937).—When liquid water was put in contact with gaseous oxygen at the presence of platinum black, there was found no exchange reaction between them. When the mix. of vapour and gaseous oxygen were introduced to the surface of copper oxide heated to 290°C, or of silver oxide or of iron oxide heated to 400°C, no exchange reaction occurred. But, when the mix. was put in contact with highly heated platinum wire, the exchange reaction took place. And by using platinum sponge, the contact was carried out at const. velocity at various temps. and in measurement of the quantity of exchange caused by the contact, it was found to be very little below 400°C, but it increased rapidly at 400~500°C. Over 500°C the exchange took place almost perfectly.

J. C. L.

Cell-dimensions and space-group of acetylsalicylic acid. T. Koza and K. Takane. *Proc. Imp. Acad.*, 11, 381-382(1935).—The cell-dimensions detd. by a photograph taken by a Röntgen goniometer, after being

obtained from three different photographs taken by the rotation of three different crystal-rods parallel to $[100]$, $[010]$ and $[001]$, are $a_0=11.36\text{\AA}$, $b_0=13.22\text{\AA}$, $c_0=22.30\text{\AA}$ and $\beta=94^\circ$. The number of molecules in $C_9H_8O_4$ is 15 in a unit cell. And in the reflections of X-ray, there was found no special relation in these indices, except $K=\text{even}$ in (OKO) . The space group which satisfies the condition stated above must be C_{2h}^{11} or C_2^2 . J. C. L.

Chemical separation of nitrogen isotopes. E. Ogawa. *Tech. Repts. Kyushu Imp. Univ.*, 11, 77-78 (1936).—By adding excess of Br_2 to NH_4Cl (720g) and dropping $NaOH$ into it with stirring, N_2 was produced in fine bubbles. The concn. of NH_4Cl was made 1/3.54 or 1/12.26, and $NaOH$ was added to produce NH_3 , NH_3 being absorbed by HCl , NH_4Cl was obtained. From the detn. of Cl , it is stated that the law, "The element in more pos. state is richer in heavier isotope" is general. Valence electrons of atoms in molecules or outer electrons are also considered. J. C. L.

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

Studies on luminous flame. I. Absorption spectra of soot layers. II. Absorption spectra of luminous flames. S. Yagi. *J. Soc. Chem. Ind. Japan*, 40, 90-93; 93-98 (1936).—As a fundamental study of luminous flames the author measured the absorption spectra of soot layer on mica plates at visible and infrared regions, and then the absorption spectra of luminous flames at infrared region, using a specially designed stable luminous flame burner. On the other hand G. Mie's theory (*Ann. Physik*, 25, 377, (1908)) applicable to colloidal solns, is extended to soot-particles. From the expil. results and the derived theory, the following conclusions are obtained: (1) Absorption spectra of soot plate or luminous soot are

expressed as $kl=39.5p^3Nl(1-15[pn]^2)$, where k is the absorption coeff. of soot in cm^{-1} , l , the thickness of soot layer (or thickness of luminous layer) in cm, p , the radius of a soot particle in μ , N , the number of particles in cm^3 , and ν , the wave number $\text{cm}^{-1} \times 10^4$. (2) From the max. absorption at $\nu=0.6\sim 0.5 \times 10^4 \text{ cm}^{-1}$, p is calcd. to be about 0.1μ , and obtained $kl=0.395 Nl(1-0.15\nu^2) \times 10^{-9}$. (3) By adding benzene or acetylene to the fuel gas, it is ascertained that N is proportional to the carbon atoms in the fuel gas. The absorption strength is generally expressed as $kl=C\omega Lv(1-0.15\nu^2) \times 10^4$, where ω is the grams of carbon contained in cm^3 of fuel gas C , a const. depending upon the characteristics of burner or method of burning. Author.

Studies on luminous flame. III. Properties of luminous flames and Kirchhoff's law. S. Yagi and S. Kawai. *J. Soc. Chem. Ind. Japan*, 40, 144-149 (1937).—The authors measured the absorption spectra of the luminous flame adding primary air in various proportions to the fuel gas by the method already reported (*ibid.* 1937, 40, 508). From the results they calcd. (Radiation quantity of the flame)/(Absorption of the flame) = F^ν at each wave length. F^ν is supposedly the black body radiation of the flame, if the temp. of the flame is uniform and the Kirchhoff's law can be applied to the flame. The applicability of Kirchhoff's law, the effective flame temp. for radiation calcn. and the properties and structure of the luminous flames are considered. As to the properties of the luminous flame the following conclusions are obtained: (1) Kirchhoff's law is applicable to the luminous flames at shorter wave lengths (no conspicuous absorption band of CO_2 and H_2O). Therefore, the mean temp. of the flame can be calcd. from the emission and absorption spectra of this region. (2) At longer wave lengths this law is difficult to apply, as the mean temp. of gas and soot do not coincide, which makes F^ν curve uneven. (3) By adding primary air to the fuel gas, the temp. of soot particles increases and the number of soot particles in the flame diminishes corresponding to the quantity of the added primary air. (4) The temp. of the flame becomes lower by adding the hydrocarbon to the fuel gas. This is due to the increase of emissivity of flame, or the increased heat loss to the surroundings. (5) The radiation of the luminous flame is not always the sum of those of soot and gas. The total radiation of luminous flame may become less than that of soot only. (6) The true temp. measured with optical pyrometer does not generally coincide with the effective temp. calcd. above. The former is considered to show that of burning soot of very high temp., which is not the major part of soot radiation in luminous flames. Authors.

On the energy states of valency electrons in some metals. I. 3. The stationary states of valency electrons in Zn-crystal. M. Sato. *Sci. Rep's. Tohoku Imp. Univ.*, 1, 25, 771-779 (1936).—The photo-electric threshold, photo-electric selective emissions and selective absorptions of light of Zn, are explained in the terms of the energy levels of the valency electrons that were determined in the papers already published, and the nature of the so-called potential energy barrier in the surface layer of solid-Zn is thus clarified. Based on the results above obtained and referring to photoconductive effect, it is concluded that the levels E_3 and E_4 are the conduction levels of the valency electrons and that, in the bulk mass of solid-Zn, the levels, E_1 , E_2 , E_3 and E_4 , at least, are stationary ones. A discussion regarding the origin of the catalytic action in the surface layer of solid-Zn is also made. Author.

On the energy states of valency electrons in some metals. I. 4. The nature of electrode potentials of Zn and H_2 and the mechanism of catalytic action of metal surface. M. Sato. *Kinzoku no Kenkyu*, 13, 486-514 (1936).—The exptl. results of the electrode potential of single Zn-crystal, which was done by M. Straumanis were analysed and the potential values of the surfaces (0001), $\{10\bar{1}0\}$, $\{10\bar{1}0\}$, $\{10\bar{1}1\}$ and $\{11\bar{2}1\}$, for the solns. of H_2SO_4 and of ZnSO_4 were detd. The regularity existing among these values and the relation between these and atom spectrum of zinc, were sought and it was found that these values may be arranged in energy distances between some two energy levels, each belonging to one of the level groups, whose structures have some close relations with those of $(4s, 4p)^3P$; $(4s, 5p)^3P$ and $(4s, 4d)^3D$, of ZnI. Based on the concept that the difference between the potential barriers existing on each electrode of a cell is the origin of the difference of the electrode potential, and assuming that one of the photoelectric potential barriers, due to Dillon, is identical with one of the barriers in the present case, the absolute

values of the potential barriers on the surfaces of Zn single crystal were computed. Combining these values with the electrode potentials above detd., the absolute value of the potential barrier, existing on hydrogen electrode was computed. Comparing this with the molecular level values of H_2 , detd. through its band spectrum, it was found that barrier is the level interval between $H_2(B, 1s\sigma, 2p\sigma^1\Sigma u, v=0)$ and II_2^+ . Further the exptl. results of the photo-electric behaviors of Mg with adsorbed film of H_2 , due to R. J. Cashman and W. S. Huxford, were studied and it was confirmed that hydrogen is adsorbed on metal surface, in the state B, under the condition which is satisfied by hydrogen electrode. Furthermore, reviewing the adsorption heats of hydrogen on tungsten, which were measured by J. K. Roberts, the mechanism of adsorption and absorption of H_2 by metal surface, i.e., the mechanism of the catalytic action of a metal surface, was clarified. Author.

The third absorption bands of coordination compounds. I. $[Co(NH_3)_4ClNO_2]Cl$ and $[Co(NO_2)_6]Na_3$. R. Tsuchida and S. Kashimoto. *Bull. Chem. Soc. Japan*, 11, 785-790 (1936).—Y. Shibata has shown that a number of nitro-ammine cobaltic compounds have three absorption bands and concluded that the third band is due to the pair of nitro-radicals co-ordinated in trans-position to each other. One of the present authors has recently found that trans-dichloro-tetrammine cobaltic salt has also a third absorption band, and has thus been led to the conclusion that Shibata's theory might possibly be extended to the effect that the third band is due to the pair of negative radicals co-ordinated in trans-position to each other. In order to verify the postulate, extinction-coeffs. of sodium hexanitro-cobaltate and chloro-nitro-tetrammine cobaltic chloride were measured. Aqueous solns. of both salts were proved to have the third bands such as had been predicted from the postulate. The absorption data of all the cobaltic complex salts of three band series hitherto found were

summarized and regularities among the frequencies of the first, the second, and the third band were pointed out; viz., for the cobaltic complex salts, which show the third band, $\nu_3-\nu_2$ and $\nu_2-\nu_1$ are about $33 \times 10^{13} \text{ sec}^{-1}$ and $18 \times 10^{13} \text{ sec}^{-1}$, whereas for the pentammine and the tetrammine cobaltic salts, $\nu_2-\nu_1$ is about $27 \sim 24 \times 10^{13} \text{ sec}^{-1}$.

Authors.

The quantum theory of the electrical conductivity of alloys in the superlattice state. I & II. T. Muto. *Sci. Papers Inst. Phys. Chem. Research*, 30, 99-120 (1936), 31, 153-160 (1937).—The quantum theory of alloy-conductivity (Nordheim) was extended to the case of superlattice alloy, using Bragg-Williams' statistical theory of superlattice-formation. The computation was carried out for the case of the typical superlattice-alloy, Cu_3Au , but the method of treatment developed there was easily generalized to include the other types of superlattice alloys. The electrical conductivity of the alloy mentioned was shown to become a function of temp., atomic concn. and long distance order, which fact led to the very rapid change of resistance in the order-disorder transition of the superlattice alloy. The theoretical results were found to be in fair agreements with the expts. of S. Kurnakow and N. W. Ageew, and H. J. Seemann. In Part II of the paper, the X-ray structure factor of the superlattice alloy was worked out theoretically, using v. Laue's method of computation. It is pointed out that the correct value of S can be accurately detd. with the aid of the measurements of the relative intensities of X-rays reflected by the alloy. Author.

Studies on the high pressure mercury lamps. 2. T. Harada and T. Azuma. *Mazda Kenkyu Jiho*, 12, 20-22 (1937).—1. Spectrum of mercury at high vapor pressure. Spectrum of mercury at high vapor pressure up to 100 atm. is studied on the exptl. quartz capillary lamps and on the practical type 1 k.w. water cooled lamp. An example of the spectrogram in the visible

part taken with the grating spectrograph is given. We see in the figure that the sharp series lines 4047, 4078, 4358 and 5461 Å broaden very much and asymmetrically to the long wave length side, whereas the lines 5770 ($2^1P_1-3^1D_2$) 5791 ($2^1P_1-3^1D_3$) broaden almost symmetrically. The latter decreases in intensity relative to the former at high vapor pressure. In the red part of the spectrum all the lines disappear in the continuous spectrum which becomes very strong at high vapor pressure. 2. The efficiency of the high pressure mercury lamp. Relative values of candles and efficiency is studied on the exptl. quartz capillary mercury lamp with use of photocell and amplifier. The arc current is varied from 60 to 200 mA. and the mercury vapor pressure from 2 to 100 atm. It is shown that to obtain the high efficiency in the high pressure mercury lamp we must increase both the arc current and the arc drop, i.e. the mercury vapor pressure.

Authors.

Absorption spectrum of nitrocellulose. K. Masaki. *Bull. Chem. Soc. Japan*, 12, 1-3 (1937).—The author studied the ultraviolet absorption spectra of nitrocellulose in the film state instead of the ordinary solns. which appeared to be extremely difficult to raise to a considerable concn. owing to its slight solubility. Spectra were obtained with a number of films of about 1/100 m.m. thickness. The spectrum showing two absorptions (3300-2500 Å and below 2500 Å) is compared with those of a number of nitro-esters and nitro-compounds reported in the authors' previous paper. It is deduced that the two diffuse bands are due to the nitro-groups.

Author.

Molecular spectrum of MgD. Y. Fujita and Y. Tanaka. *Sci. Papers Inst. Phys. Chem. Research*, 30, 121-137 (1936).—The secondary molecular spectrum in the green range of MgD was photographed by means of a concave grating 6m. and seven kinds of $^2\Pi-^2\Sigma$ bond spectrum, $0\rightarrow0$, $0\rightarrow1$, $1\rightarrow1$, $1\rightarrow0$, $1\rightarrow2$, $2\rightarrow2$ and $2\rightarrow1$ were analysed,

From the analysis the consts. in $^2\Sigma$ and $^2\Pi$ were calcd. and compared with those of MgH.

J. C. I.

Absorption band of vapour covering Lyman line 1251 Å. T. Wakejima. *Proc. Phys.-Math. Soc. Japan*, 10, 341-343 (1936).—Making use of the fact that a strong prediss. spectrum 1224 Å, one of the OH band spectra, covers the Lyman line 1215 Å of hydrogen, the author exposed water vapour to hydrogen light under strong radiation, and studied the decompn. of the water vapour molecule by the absorption of the line. To one end of a discharge tube 0.8 cm in diameter and 60 cm in length, was attached an absorption tube with quartz window. The pressure in it was 0.3~0.5 mm. From the results, it seems that the dissoen. spectrum is not caused by the Strahlunglose Übergang to the decompn.: $H_2O\rightarrow H+OH^*(\Sigma^*)$.

J. C. I.

A note on the osmotic coefficient and the activity coefficient at the surface. K. Ariyama. *Bull. Chem. Soc. Japan*, 12, 44-51 (1937).—The osmotic pressures and the activity coeffs. for strong electrolyte soln. and for solns. of mix. of electrolyte and non-electrolyte at the surface are calcd. on the basis of Debye-Hückel theory. Some relations between the activity coeffs. for two cases are given. Author.

The fine structure of X-ray K-absorption of Ni. I. Hayashi. *Sci. Repts. Tohoku Imp. Univ.*, 1, 25, 1-10 (1936).—K-absorption edge of the X ray of Ni was investigated by means of Johansson's spectro-scope, and it was found that it had two levels. The intensity of the absorption at longer wave length was about half for that of the shorter. A part of weak absorption was noticed at shorter wave length side of the level at shorter wave length. K-absorptions of Ni and Cu have the similar fine structure.

J. C. I.

Spectro-photometrical measurement of temperature of positive column. T.

Hamada. *J. Inst. Elec. Eng. Japan*, 57, 72-77 (1936).—The pos. column¹ present in a narrow part of the tube enclosing nitrogen was observed from the direction of the axis, and the rotation band spectra $3.998\text{\AA}$ and $3.914\text{\AA}$ were photographed by means of diffraction grating. The distribution of intensity in the band was measured with a microphotometer, and the temp. and the band energy were calcd. graphically. Their distribution on the diameter of the narrow tube was measured, and their changes owing to pressure and discharging current were observed. The av. thermal conductivity of gas was calcd. to be about 10^{-4} joule/cm²/sec.

J. C. L.

On the electric explosion spectrum of metals. T. Futagami. *Sci. Papers Inst. Phys. Chem. Research*, 31, 1-29 (1937).—(1) With a view to investigate the behaviour of the spectrum of the rapidly changing light source, a new spectrograph with a rotating photographic film was constructed. (2) Electric explosion spectra of Cu, Ag, Mg, Ca, Zn, Cd, Hg, Al, Ti, Sn, Pb and Bi emitted at the beginning of the discharges were photographed. The spectra consisted of arc and spark lines, the former being generally reversed, but the latter not. The spectrograms and the corresponding microphotometer curves are given. (3) The characteristic features of the spectra emitted at the first phase of the oscillations broadening, bending, weakening etc. An indication of a complex structure was noticed on a few lines. (4) The phys. nature of the emitting vapour was considered and the effective temp., the effective pressure and the effective strength of the electric field developed in the vapour at the first state of discharge were estimated.

Author.

A study on the emission of positrons. K. Shinohara. *Sci. Papers Inst. Phys. Chem. Research*, 31, 174-186 (1937).—The intense emissions of natural positrons from Ra C and Th (B+C) were confirmed by using the trochoidal focussing method. Expressing as the ratio with the number of

electrons emitted, the values obtained were 4.7×10^{-1} and 4.2×10^{-1} resp. The number of positrons emitted from a thick piece of lead by pair production by γ rays were also estimated. These were 1.0 and 2.2 times of those of positrons from the source of Ra C and Th (B+C) resp.

J. C. L.

Fine structure of the Laue X-ray pattern obtained by the method of convergent X-rays. T. Fujiwara. *J. Sci. Hiroshima Univ.*, A, 7, 179-182 (1937).—The fine structure of the Laue X-ray pattern obtained with fine single crystal wire by using the method of convergent X-rays is examd. minutely in the present expt.

Author.

An investigation on the interaction of neutron with deuteron. S. Kikuchi, H. Aoki and E. Takeda. *Sci. Papers Inst. Phys. Chem. Research*, 31, 195-204 (1937).—The γ -rays existed in D_2O bombarded with fast as well as slow neutrons were searched for. No pos. effects could be observed. It is concluded that the upper limit of the cross section for emitting γ -rays under the action of fast neutrons (2.4 m.e.v) is 0.037 times that for Cu; i.e. about 1×10^{-28} cm², and that the cross section for combining slow neutrons with 3H to form 4H must be smaller than 0.2×10^{-28} cm². The ability of D_2O to slow down neutrons was also investigated. Under our exptl. condition, no slow neutrons of C or A group created in D_2O could be confirmed. The efficiency was smaller than 1/27 of that for H_2O . It is shown that the result of Dunning and others concerning this problem should be interpreted in another way.

Authors.

On the scattering of fast electrons by thin metal foils. H. Saegusa and K. Kikuchi. *Sci. Repts. Tohoku Imp. Univ.* I, 25, 817-828 (1937). Using the same Geiger electron counter as that described in our previous paper (1), and apps. improved to some extent, we investigated the total angular distribution of the electrons scattered by some

metallic foils such as Au, Pt, Ag and Ni, impinging fast electrons of such velocities as 10, 20 and 30 kv. Further, we studied the velocity distribution of the electrons scattered by such metals as Au and Al at an angle of 45° . Thus, we confirmed that the exptl. result of the above angular distribution did not coincide with the theoretical result given by considering Coulomb's field. Hence we calcd. the ratio of the number of the scattered electrons to that calcd. from the theory of Rutherford at various angles of scattering, assuming that the above ratio at the angle of 45° is equal to 1, and found that the ratios increased linearly with the angle of scattering from 45° to 80° and then, except in some cases, they tended to a stationary value. Thus it seems probable that there exists some scattering due to a non-coulombian field, as in the case of the anomalous scattering of the α -ray.

Authors.

On the non-diagramlines of K-spectra of the elements Ni and Cu. I. Hayashi. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 785-803 (1937).—With focussing spectro-photograph many non-diagramlines of K-spectra of Ni and Cu were taken. The results show that the non-diagramlines have very close connection with the fine structure of K-absorption spectrum. The $\Delta\nu/R$ -value of each non-diagramline, which is calcd. with regard to appropriately chosen diagramline, coincides satisfactorily with the $\Delta\nu/R$ -value, with regard to the absorption max. A₁ or A₂, of absorption max.

J. C. I.

On the continuous absorption spectra of some polyatomic molecules. VI. Y. Fukumoto. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 1162-1169 (1937).—This paper deals with the continuation of our investigations of the continuous absorption spectra of the following polyatomic molecules:—(1) ethylen hydrins; (2) ethylen derivatives; (3) mercaptan derivatives; (4) benzyl derivatives; (5) benzyl derivatives of primary alcohols and other miscellaneous alcohols. The results obtained, together with some of the already

available data, are discussed in the light of certain characteristic common configurations of molecules.

Author.

On the K-absorption spectra of Ni. II. I. Hayashi. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 606-620 (1937).—The absorption of Ni in NiCO_3 , Ni(OH)_2 has only one edge and nearly coincides with the shorter-wavelength-edge K_1 of pure Ni. The absorption of Ni in intermetallic compds., NiAl and NiSn , has also one edge but it coincides with longer-wavelength edge of pure Ni. The absorption of Ni_2O_3 consists of two edges, but this entirely differs from that in pure Ni; the longer-wavelength-edge lies near the longer-wavelength-side of K_2 of pure Ni and the shorter-wavelength-edge coincides with K_2 of pure Ni. The fine structure near the principal edge differs in various kinds of compds. It is concluded, therefore, that the niveau values of outer electron shell differ in various aggregate states. The fine structure in compds. NiCO_3 , Ni(OH)_2 , Ni_2O_3 and NiSn , whose crystal structure have hexagonal symmetry, resembles to a certain extent in somewhat shorter-wave region than the principal edge. The absorption edge K_1 of pure Ni lies near the emission line, $\text{Ni-K}\beta_1$, and this fact shows the existence of quadrupole-selection-rule in absorption process.

J. C. I.

The near ultra-violet ' $\Sigma \rightarrow \Sigma$ ' band system of gold deuteride, and a new analysis of gold hydride spectrum. S. Imanishi. *Sci. Papers Phys. Chem. Research*, 31, 247-264 (1937).—Gold arc in D_2 atm. is photographed with $1.75\text{\AA}$ per mm dispersion. 11 bands of $\text{AuD } \Sigma \rightarrow \Sigma$ system, involving $v' = 0, 1, 2$ and $v'' = 0, 1, 2, 3$ levels are analyzed in the region $\lambda\lambda 3370\text{--}4440$. A new analysis of the corresponding $\text{AuH } \Sigma \rightarrow \Sigma$ system is made with the same accuracy, and molecular consts. of the two emitters are compared. An electronic isotope shift of $21\text{--}6\text{ cm}^{-1}$ is found. From vibrational consts. for normal Σ states, a value of ρ is obtained, which is slightly larger than that required by the simple isotope theory.

Author.

The emission of the electron from the substances traversed by fast neutrons. S. Kikuchi, H. Aoki and K. Husimi. *Proc. Phys.-Math. Soc. Japan*, 18, 727-744 (1936).—It was confirmed that the simultaneous discharges taking place in two thin walled Geiger-Müller counters placed side by side near the target contg. ^2H bombarded with ^2H are not due to stray gamma-rays excited by neutrons in the different parts of the apps. It was also confirmed that the gamma-rays are not emitted in the reaction of ^2H with ^2H . As the result of absorption measurement we are forced to the conclusion that the electrons are emitted from the substances (so far, C, Al, Fe, Ni, Cu, Zn, Ag, Cd, Pt, and Pb, are investigated) traversed by the neutrons. The energy of the electrons is independent of the substances from which they are emitted, being about 1 mv. The cross section of the process seems to increase with the atomic number, being of the order of 10^{-28} cm^2 for Al and 10^{-24} cm^2 for Pb. It is shown that there is no reasonable explanation of the observed effect in terms of nuclear process hitherto known. Some new types of interaction of the neutrons with the atoms are suggested.

Authors.

Researches on the concentration of hydrogen ions contained in the aqueous solutions of complex cobaltamines and their absorption spectra. III. Aqueous solutions containing ethylene diamine. T. Uemura and N. Hirasawa. *Bull. Tokyo Univ. Eng.*, 6, 217-231 (1937).—One of the writers (Uemura) has already discussed with H. Sueda on the spectrochemical effects given by the solns. of various cobaltamines. Now, we similarly intend to take some complex cobaltamines that contain the ethylene diamine (en) molecules in their complex radicals. Out of the eleven samples taken, the absorption curves given by $[\text{Co}(\text{en})_3]\text{Cl}_3$ are little affected by the variation of its hydrogen ion concn. Both configurations, cis- and trans-, of the three complex salts, $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{Cl}_2$, $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ and $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, show similar absorption curves

in their alkaline solutions, i.e. absorption max. at about $370 \text{ m}\mu$ and min. at about $320 \text{ m}\mu$; it is hard to change these salts in their acidic soln, but they easily become changeable in their neutral solns, and are transformed into $[\text{Co}(\text{en})_2\text{OH}(\text{H}_2\text{O})]\text{Cl}_2$ when their solns. are alkaline. The complex salt $[\text{Co}(\text{en})_2\text{NO}_2(\text{H}_2\text{O})](\text{NO}_3)_2$, both in its cis- and trans-forms, loses the selective absorption in the alkaline soln. and probably the cis-type of the salt changes into cis $[\text{Co}(\text{en})_2\text{NO}_2\text{OH}]\text{NO}_3$ when its soln. becomes alkaline.

Authors.

On the Zeeman effect of the cadmium lines $5^3\text{P}_{0,1,2}-6^3\text{S}_1$. S. Sato. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 207-216 (1936).—The observed results of the Zeeman effect of the cadmium line $5^3\text{P}_{0,1,2}-6^3\text{S}_1$ in a magnetic field of varying intensities are reported, and it is proved that these results are in good agreement with those which may be deduced from Goudsmit and Bacher's formula.

Author.

On the energy states of valency electrons in some metals. I, 5. The threshold value of over potential of hydrogen on zinc electrode. M. Sato. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 871-878 (1937).—From the exptl. data obtained by M. Knobel, P. Caplan and M. Eisenman, the threshold value of over potential of hydrogen on zinc electrode was detd. as 0.713 V. By adding the normal electrode potential of Zn, 0.761 V. to this value, we obtain 1.474 V., and this was taken as a threshold potential value of hydrogen on Zn-electrode, which is referred to normal hydrogen electrode. From this and the potential barrier on hydrogen electrode, which was already detd. by the writer, the potential barrier acting in the threshold state was detd. to be 2.68 V. This value was compared with the energy, 2.51 e.v. required for the process $\text{E}_1 \rightarrow \text{E}_2$ (in the surface layer of Zn-electrode) combined with $\text{H}^+ + \text{H} \rightarrow \text{H}_2^+$ (in soln.) and found that they are in agreement within the limits of exptl. errors. Thus, the nature of threshold was clarified.

Author.

On the absorption band spectrum of magnesium at 3000Å. E. Matsuyama. *Sci. Repts. Tohoku Imp. Univ., Honda Anniv. Vol.*, 207-216 (1936).—By using a steel absorption tube filled with helium and neon gases, the author photographed the absorption spectrum of magnesium, and observed regularly arranged heads and partially resolved rotational line structures at about 3000Å, and continuous absorption near the line $1\ ^1S_0-2\ ^1P_1$ (2852Å). Author.

On the Zeeman effect of lead line $6p^2\ ^3P_2-6p.7s\ ^3P_1$ (4058Å). S. Sato. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 686-712 (1936).—The writer reports on the results of the observation of the Zeeman effect of the lead line $6p^2\ ^3P_2-6p.7s\ ^3P_1$, together with the theoretical interpretation of it. J. C. L.

On the magnetic moment of an atom according to Dirac's equation. K. Ueda. *Sci. Repts. Tohoku Imp. Univ., Honda Anniv. Vol.*, 256-258 (1936).—The magnetic moment of the s-electron is calcd. exactly. Author.

Scattering of gamma-rays by spinning electrons. T. Takéuchi. *Bull. Tokyo Univ. Eng.*, 6, 123-125 (1937).—The scattering of gamma-rays by cloud of spinning electrons in a magnetic field is discussed. Author.

Thomas-Fermi's method and Bohr's nuclear model. M. Kobayashi. *Bull. Inst. Phys. Chem. Research*, 16, 219-227 (1937).—Last year, N. Bohr published his views of nuclear structure, pointing out that in nuclear reactions the mode of energy exchange among its constituent particles is essentially different from that in the case of atoms. In this paper it was attempted to illustrate his views somewhat quantitatively, (1) by calcd. the second order correction of the heavy nucleus, and (2) by comparing the probability of the process where the incident neutron or proton is captured by the nucleus leaving one of its constituent particles excited, with that of the

process where two of its constituent particles are excited and the incident particle is captured. Results were as follows: (1) the correction of the nuclear energy calcd. is greater than several MV per particle for Hg ($Z+N\sim 200$), and since this is comparable to or greater than the distance between the neighbouring levels of a particle in the Hartree field of that nucleus, it was concluded that in the heavy nucleus the correlation between its constituent particles plays so important a role that it is almost meaningless, as was expected from Bohr's views, to calc. its energy by the Thomas-Fermi method; and (2) two transition probabilities calcd. are of the same order, therefore one can not apply the method of perturbation to these processes, and with the same reasoning as was used by Heisenberg in his theory of cosmic ray showers, one should expect that when the incident particle encounters the nucleus, they will form together one nucleus, in which the superfluous energy is distributed among a great number of its constituent particles. And this nucleus will be almost stable because of the small probability of emitting its constituent particles, unless the incident particle is of extraordinarily high energy. Author.

The third absorption bands of coordination compounds. III. The configuration of $[\text{Co d}_2\text{NH}_3\text{Cl}]$ R. Tsuchida and M. Kobayashi. *Bull. Chem. Soc. Japan*, 12, 83-85 (1937).—By the method of asymmetric adsorption on quartz powder, the authors have proved that chloro-bisdimethylglyoximo-ammine-cobalt is resolvable into optical antimers. On the other hand, by measuring the extinction coeffs. of the complex compd., it was found that it has the third absorption band at $\nu=121\times 10^{13}\text{ sec}^{-1}$. From these facts and the hypothesis on the third band, the authors have given to the compd. in question a configuration belonging to a new type of optically active complex compds. Authors.

Secondary cosmic ray and its photographic impression. T. Takéuchi, T.

Sugita and T. Inai. *Bull. Tokyo Univ. Eng.*, 6, 250-251 (1937).—A metallic plate such as Mg and Cd, being cleaned, was placed on a photographic plate, which was separated by a thin plate of mica having a window from the metallic plate. It was acted about 20 hours either outside or inside of a

Pb screen, sufficiently deep. The photographic action produced at a distance by the metals was more intense at the outside than at the inside. It must be considered, at least partially, as the action of secondary cosmic ray emitted by the metals. Authors.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

Theory of fine structure of helium. G. Araki. *Proc. Phys.-Math. Soc. Japan*, 19, 128-155 (1937).—The theory of the fine structure of optical terms of helium atom is worked out, using the Breit Hamiltonian method which includes all the spin-orbit and spin-spin interactions. The zeroth order eigenfunctions are constructed taking into account the polarisation effect of the outer electron on the probability distribution of the inner electron. The problem of transformation to the principal axes is solved in the four dimensional eigenspace belonging to the definite magnetic quantum number of the atom. The general expressions representing the levels of triplet and singlet terms are derived. The numerical computations are carried out for the triplet septets of the terms which have been experimentally analysed hitherto: $1s2p^3P$, $1s3p^3P$, $1s3d^3D$ and $1s4d^3D$. The agreement with the expl. values is quite satisfactory.

Author.

On the decomposition voltage of fused magnesium chloride. K. Iwasé and K. Sano. *Kinzoku no Kenkyu*, 13, 478-482 (1936).—The decomposition voltage of fused magnesium chloride has been calcd. from the free energy of formation at 25° which was obtained by detn. of the oxidation equil. of crystalline magnesium chloride.

Authors.

Studies of potassium bisulphate. H. Hagiwara and T. Takai. *Bull. Inst. Phys. Chem. Research*, 16, 29-41 (1937).—The

equil. in the system $\text{KHSO}_4\text{--K}_2\text{S}_2\text{O}_7$ was studied, the compn. of the eutectic mix. being found to be $\text{KHSO}_4\text{:K}_2\text{S}_2\text{O}_7=9\text{:}1$ (mol ratio) and its melting point 203.5°C. The melting points of KHSO_4 and $\text{K}_2\text{S}_2\text{O}_7$ were detd. as 211.7°C and 413.7°C resp. The solubility of KHSO_4 in concd. sulphuric acid was measured at various temps. between 135-200°C from which the transition points between different forms of KHSO_4 were detd. as 154.2°C and 184°C. The rate of disson. of KHSO_4 was studied with a thermobalance. At 300°C the disson. proceeds slowly, at 350°C much quicker and at 400°C a little faster than at 350°C. At intermediate period the velocity may be expressed as $dx/dt=k(x-x)^2$ corresponding to $2\text{KHSO}_4=\text{K}_2\text{S}_2\text{O}_7+\text{H}_2\text{O}$. The disson. pressure was measured by the statical method in a range of temp. between 140-250°C, the result being expressed by the equation $\log p_{\text{atm}} = \frac{-3965.60}{T} + 9.36683$ (140°-210°C, KHSO_4 , $\text{K}_2\text{S}_2\text{O}_7$ both solid). $\frac{1}{2}\text{K}_2\text{S}_2\text{O}_7(s) + \frac{1}{2}\text{H}_2\text{O}(l) = \text{KHSO}_4(s)$, $\Delta F_{298}^\circ = -3620$ cal.

Authors.

The faraday effect of strong electrolytes in aqueous solutions. V. LiCl, NaCl, KCl, LiI, NaI and KI. A. Okazaki. *Mem. Ryofun College Eng.*, 9, 101-118 (1936).—The relation between the magneto-optical rotation and the concn. of the aq. solns. of the chlorides and iodides of lithium, sodium and potassium is studied for D-lines. It is found that the "corrected" molecular rotation $M[D_\lambda]$ of these salts decreases with increasing

concn. On the assumption that these electrolytes in a soln. have only one absorption band in the ultra-violet, the decrease of $M[D_2]$ with increasing concn. is found to be attributed to the existence of undissociated molecules in concd. solns. The value $M[D_2]$ in the completely dissociated state is detd. by graphical extrapolation to infinite dilution. Using this value and the corresponding molecular refractivity R_m , the number of dispersion electrons in the molecules and the values of the absorption bands of these salts in the completely dissociated state are calcd. The values of e/m for the dispersion electrons of these electrolytes, together with those of the corresponding bromides, in the completely dissociated state are evaluated using the magneto-optical rotation for D lines and the ordinary dispersion data. It is also found that the $M[D_2]$ -values of these electrolytes in the completely dissociated state are given by the sum of the rotations due to the two component ions, and that the order of the magnitudes of the ionic rotations in question can be expressed by the following series: $\text{Cl}^- < \text{Br}^- < \text{I}^-$ and $\text{Li}^+ < \text{Na}^+ < \text{K}^+$.

Author.

On the activity coefficient of thallous thiocyanate in some salt solutions. F. Ishikawa and N. Hasegawa. *Bull. Inst. Phys. Chem. Research*, 16, 146-151 (1937).—The solubilities of TlCNS in solns. of strong electrolytes have been measured at 25°C. The electrolytes used were KNO_3 , KCNS , K_2SO_4 , TlNO_3 , Tl_2SO_4 . From the results the activity coeff. in the respective solns. of various ionic strength were detd. using $(1/m \pm)_{\mu=0} = 7.6.0$ which was obtained by assuming that in the range of small ionic strength the activity coeffs. of TlCNS in KNO_3 solns. are equal to those of KNO_3 , the assumption being supported by the constancy of the values of $(1/m \pm)/\gamma$.

Authors.

On the vapour pressures of $\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$ and saturated solutions of Na_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 7\text{D}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$

in heavy water. I. Higuti. *J. Chem. Soc. Japan*, 58, 193-200 (1937).—The vapour pressures of the above entitled systems and those of the corresponding systems with ordinary water have been measured over a range of temp. from 20° to 50° by means of slightly modified Frowein tensimeter. The deuterate and the satd. solns. were prepared in vacuo by distilling a required quantity of heavy water (99.2%) on the anhydrous salt. The results are represented by the following equations:

$$\log P^{\text{sat}} = 10.6489 - 2814.02/T$$

for the dissocn. pres. of $\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$

$$\log P = 10.4310 - 2726.75/T$$

„ of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

$$\log P = 9.2430 - 2381.82/T$$

for the vap. pres. of satd. soln. of Na_2SO_4 in D_2O

$$\log P = 9.0700 - 2311.47/T$$

„ of Na_2SO_4 in H_2O

$$\log P = 8.4547 - 2145.23/T$$

„ of $\text{Na}_2\text{SO}_4 \cdot 7\text{D}_2\text{O}$ in D_2O

$$\log P = 8.3748 - 2112.19/T$$

„ of $\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$ in D_2O

$$\log P = 8.2045 - 2045.47/T$$

„ of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in H_2O

From the above results were obtained the values of 34.6°~34.9° and 26.6°~27.0° for the transition points betw. the anhydrous salt and the decadeuterate or the heptadeuterate. These values are found to be higher by ca. 2.4°, than those of the corresp. ones of the ordinary hydrates.

Author.

Electro-endosmosis through a single capillary. (A) Apparatus. H. Muraoka. *J. Elec. Assoc. Japan*, 5, 64-65 (1937).—An expil. procedure of measuring electro-endosmotic velocity through a single capillary is described. The app. is like that of Briggs and the velocity is read by the movement of a bubble in the wider reading tube. The velocity of the bubbles with the same electro-endosmotic pressure varies with their size. For the correction, from the curve of the velocity of the bubble and its size, the size of the bubble giving the true electro-endosmotic velocity was found. The expt. was carried out with any suitable size of the bubble and

then the velocity obtained was converted into the true velocity to be measured. Author.

On the end-point voltage of the lead-acid storage cell. K. Kinoshita. *Bull. Chem. Soc. Japan*, 12, 25-31 (1937).—The expts. have been undertaken to study the relation between the "end-point voltage" and the discharge hour rate of the lead acid storage cell. The cells under examn. were discharged by the const. current of 1.5, 2.0, 2.5, and 3.0 Amp. taking the end-point voltage at about 1.3 volts. Thus the relation betw. the terminal voltage e of the cell and the values of C in the following equation was examd.; $C = (t_0 - t/t_0) \times 100$, where t_0 denotes the total time of discharge and t the time at which the terminal voltage is e . The values of $t_0 - t$ in the equation will be proportional to the remaining capacity of the cell provided the discharge is undertaken at const. current. Consequently, the value of C indicates the percentage ratio of the remaining capacity to the total capacity of the cell. The curves representing the relation between $\log C$ and $\log e$ were examd., and it was found that the curves are almost linear in the upper part of the figures, while the curves are concave to the C axis at the lower part. We see moreover, that the linear part becomes the more predominant in the case of the higher discharge current, so that in the ranges of linear part of the curves, the relation betw. C and e can be denoted by the equation: $e = KC^n \dots (1)$, where n and K are const. Discussing the progress of chem. reaction at the electrodes of the cell, the conclusion is reached that the ranges, where the equation (1) holds betw. C and e , are the most favourable working condition of the plates. It follows that the values of e , where the equation (1) does no more hold between C and e , is the most reasonable end-point voltage of the cell. Author.

A study of the enzyme action by thermal analysis of reaction velocity. II. The action of inorganic ferment. E. Suito. *Proc. Imp. Acad. Tokyo*, 11, 229-

232 (1936). And also see **Thermal analysis of the catalytic action of colloids. I. Catalytic decomposition of hydrogen peroxide by colloidal platinum.** This Journal, 10, 251-270 (1936). Author.

On the photochemical union of hydrogen and chlorine. M. Tamura. This Journal, 11, 1-15 (1937).

Reduction equilibria of titanium dioxide by hydrogen. N. Nasu. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 510-526 (1936).—The equil. $\text{TiO}_2 - \text{H}_2 - \text{Ti}_2\text{O}_3 - \text{H}_2\text{O}$ has been investigated at various temps. ranging from 749° to 1009°C , by a gas circulation method and by using a quartz spring balance. The gas circulation pump and the method by which the compn. of the mixt. of hydrogen and water vapour can be deid. were both devised by the present writer. The relation between $\log K_p$ and $1/T$ has been found to be $\log K_p = 1.9305 \frac{2754}{T}$.

Author.

Dissociation pressure of vanadium pentoxide. K. Iwase and N. Nasu. *Sci. Repts. Tohoku Imp. Univ.*, Honda Anniv. Vol., 476-479 (1936).—The dissocn. pressure of solid vanadium pentoxide has been measured in the temp. range $220^\circ \sim 325^\circ\text{C}$. The relation betw. $\log P_{\text{O}_2}$ and $1/T$ was found to be $\log P_{\text{O}_2} (\text{atm}) = 6.684 - \frac{6202}{T}$. By means of this result, the following data were calcd., $\text{V}_2\text{O}_5 = \text{V}_2\text{O}_4 + 1/2 \text{O}_2$; $\Delta H = 14540 - 0.75T + 0.00025T^2$. $\Delta F_0 = 14540 + 0.75T \ln T - 0.00025T^2 - 2.05T$. $\text{V}_2\text{O}_5 + \text{H}_2 = \text{V}_2\text{O}_4 + \text{H}_2\text{O}$; $\Delta H = -42885 - 1.69T - 0.0014T^2 + 0.00000074T^3$. $\Delta F^0 = -42885 + 1.69T \ln T + 0.0014T^2 - 0.00000037T^3 - 16.53T$. U_2 (lattice energy of V_2O_5) = 9773 Kcal. Author.

Individual activity coefficient of ions. Supplement. S. Kaneko. *J. Chem. Soc. Japan*, 58, 273-274 (1937).—Supplement to the previous report (*ibid.* 57, 10 (1936)). Author.

Extension of Debye-Hückel's theory of strong electrolytes. S. Kaneko. *Researches Electrotech. Lab.*, 403, 1-15 (1937).—This report is the systematized collection of the author's papers on electrochem. published mainly in *J. Chem. Soc. Japan* and contains the discussion on activity coeff., osmotic coeff., heat of dilution, conductivity and diffusion of strong electrolytes. All of them are extension of Debye-Hückel's theory of strong electrolytes. Author.

Some notes on the calomel electrode. K. Nomura. *J. Biochem. Japan*, 18, 301-309 (1933). (1).—By comparing the potential of four kinds of 3.5 N KCl-calomel electrode, it was found that the potential reached a const. value in 2 days at the latest after a new preparation, if the KCl-soln. for the electrode had been thoroughly satd. with HgCl before its preparation. (2). Single electrode potential of 3.5 N KCl-calomel electrode (π 3.5) at several temps. were investigated and the values expressed by the two following formulae. π 3.5 = $0.28382t - 0.03988$ ($13^\circ \sim 25^\circ$). π 3.5 = $0.30249t - 0.05967$ ($25^\circ \sim 43^\circ$). Author.

Standard membrane potential difference of filter papers immersed in paraffin. T. Matui. *Kyoto Furitu Ika Daigaku Zasshi*, 18, 1358-1360 (1936).—Five kinds of filter paper different in their capacity of filtration were immersed in dissolved paraffin of M.P. $56 \sim 58^\circ$, and their standard film potential differences were measured. The result proved that each of the papers acted as an neg. film and that the greater the denseness of the filter papers, the larger became its potential difference. J. C. L.

Potassium chloride calomel electrode and diffusion of chloride from potassium chloride solution. T. Matunaga and K. Ituji. *Kyoto Furitu Ika Daigaku Zasshi*, 18, 511-516 (1936).—The author examd. the relation between the quantity y of chlorine diffused from satd. potassium chloride soln. to distilled water and a cross section $x(\text{mm}^2)$ of a glass tube, and obtained

the following empirical equation: $y = 0.429x + 0.0087$. J. C. L.

Measurement of P_H of polyatomic electrolyte soln. by glass electrode. T. Takagi. *Kyoto Furitu Ika Daigaku Zasshi*, 15, 401-419 (1935).— P_H of the various kinds of metal solns. and of FeCl_2 - FeCl_3 oxydation-reduction system which could not be measured by hydrogen gas electrode or quinhydrone electrode were measured by glass electrode. The result obtained was approximate to that by collodium membrane dried incompletely. J. C. L.

The influence of organic substances on zinc cell. I The influence of acetic and formic acids. M. Akamatsu. *Bull. Toyoda Res. Imp. Invention Soc. Japan*, 4, 1-32 (1936).—The effect of adding acetic and formic acids on a zinc cell were investigated: the effect of untreated wooden diaphragm which caused the formation of these acids, was examd. The results obtained are as follows: (1) 2.5% of an org. acid mixed had no bad effect: about 0.5% of the acid was favourable to the capacity, voltage, life and others: more than 2.5% of it was unfavourable to the terminal voltage, capacity and life. (2) The gas produced decreased according to the mixing of the organic acids: the decrease was proportional to the mixing. (3) The influence of an untreated wooden diaphragm was similar to that of org. acid: it affected the capacity more favourably than a treated one, but to the life of the cell it was unfavourable. J. C. L.

Making of a cell by application of free energy of formation of NaCl. E. Shibata, T. Takeda, and S. Imai. *J. Chem. Soc. Japan*, 58, 1-3 (1937).—If a cell is designed with the relation of $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) = \text{NaCl}(s)$ and $F^\circ_{298} = -91.762 \text{ cal}$, it gives about 4v. By combination of 0.2% Na-amalgam electrode, 20% salt solns., and choline carbon electrode, a cell which had 3v. and 2-3 Amp. for a continuous current, 4 Amp. for a max. was made, and with it a

light could be obtained. The comparison of the structure with its theoretical value is reported.

J. C. L.

Theory of negative adsorption of Debye-Hückel electrolyte. K. Ariyama. *Bull. Chem. Soc. Japan*, 11, 687-691 (1936).—The theory of neg. adsorption of strong electrolyte in soln. is discussed with simple calcn.

J. C. L.

A theory of surface tension of Debye-Hückel electrolyte. K. Ariyama. *Bull. Chem. Soc. Japan*, 12, 32-37 (1937).—A very comprehensible theory of surface tension of Debye-Hückel electrolyte is proposed. An explicit formula for surface tension is derived and compared with expt. very satisfactorily. A qualitative explanation of Heydweiller effect is given. Interfacial tension is also discussed very briefly.

Author.

Potential difference of completely dry collodium membrane with respect to mixed solutions. H. Takahashi and T. Matui. *Kyoto Furitu Ika Daigaku Zasshi*, 15, 506-512 (1935).—Membrane potential difference of completely dry collodium membrane for $N/800 \sim N/6,400HCl$ was not changed by the addn. of $N/5SrCl_2$. Potential difference of $N/1,000HCl$, when KCl of $N/160 \sim N/640$ was added, did not vary. Yet, when KCl was added to the strength of $N/10 \sim N/640$, it was varied. And when KCl of the strength of $N/10 \sim N/640$ was added to $N/1,000HCl$, P_H was not varied. With $N/20 \sim N/40H_2SO_4$, there were found no effect on $CuSO_4$.

J. C. L.

A study of manganese dioxide prepared for a dry cell. K. Sasaki, T. Kurano and G. Fuseya. *Bull. Toyoda Res. Imp. Invention Soc. Japan*, 4, 33-47 (1936).—The authors proved that, when MnO_2 was put in contact with solns., P_H of the solns. was changed, and that the linear relation held between the P_H and the polar potential of MnO_2 . From this proof, they could further elucidate the reasons for the cases

when the linear relation held, and also when it did not hold.

J. C. L.

A study of the fundamental questions of ion biology. S. Muramoto. *Kyoto Furitu Ika Daigaku Zasshi*, 16, 1271-1320 (1936).—(I). Ionization of hydrochloric acid.—From the electric power of the cell,—hydrogen electrode | hydrochloric acid | silver chloride electrode—, the activities of $N/10 \sim N/500HCl$ at $18^\circ \sim 38^\circ C$ were experimentally calcd. The value calcd. corresponded to those by the activity of hydrochloric acid were so small that it could not be calcd. by means of the method of measuring potential difference. (II) The activity of ion in KCl and $NaCl$ soln.—By using $N/10 \sim N/643KCl$ and $NaCl$, the cell,—amalgam electrode | KCl or $NaCl$ ($10^{-1}N$ $640^{-1}N$) $HgCl$ | Hg —, not contg. the potential difference of diffusion at $18.0^\circ \sim 38^\circ C$, owing to K and Na -amalgam electrode, was constructed. The activities (a) at the concns. were measured, and it was found that (a) did not vary with temp. (III) Amalgam electrode and membrane potential difference.—The effect upon the potential difference of $Na-Hg$ with respect to $NaCl$ solns. by K , Mg , Ca , Ba , Cd , Cu , Sr , H , Br , J , OH , NO_3 and SO_4 contg. in the $NaCl$ solns. and the effect upon the potential difference of $K-Hg$ with respect to KCl solns. by Na contg. in KCl , were examd.

J. C. L.

The individual activity coefficient of ions. M. Utumi. *J. Chem. Soc. Japan*, 58, 297-300 (1937).—An argument is given to refute Kaneko's theory as to indiv. activ. coeff. of ions.

J. C. L.

An apparatus for measuring the dipole moment with alternating current. S. Mizusima. *J. Chem. Soc. Japan*, 201-206 (1937).—A figure of a new app. is given, which is the Earp-Glasstone app. with alternating current, suitable for measuring the dielectric const., to determine the dipole moment of molecules. The result obtained from measuring dielectric const. of isopropylketone and thiophene is reported, and the

errors of measurement are shown to be within 10^{-4} . With respect to the three states of gas, liquid and solid, the value of each term in the formula, $P = P_0 + P_A + P_E$ (P denotes molecule polarization, P_0 orientation polarization, P_A atomic polarization, P_E electron polarization) was detd. J. C. L.

Measurement of the vapour pressure of concentrated aqueous solutions. T. Kume. This Journal, 11, 16-24 (1937).

The electrochemical study on hydrated sodium silicate. E. Shibata, T. Takeda and S. Imai. *J. Sci. Hiroshima Univ.*, A, 7, 183-189 (1937).—By the application of the alkali metal amalgam electrode designed by the authors, a following cell was constructed: Na-amalgam | $\text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$ crystals and satd. soln. HgO | Hg. The temp. of the stable region of various hydrates was detd. The crystals formed in the temp. region were analyzed, and the following results were obtained:

$\text{Na}_2\text{SiO}_3 \cdot 15\text{H}_2\text{O}$	$\text{Na}_2\text{SiO}_3 \cdot 14\text{H}_2\text{O}$	$\text{Na}_2\text{SiO}_3 \cdot 13\text{H}_2\text{O}$
6.8°	12.3°	17.5°
$\text{Na}_2\text{SiO}_3 \cdot 12\text{H}_2\text{O}$	$\text{Na}_2\text{SiO}_3 \cdot 10\text{H}_2\text{O}$	$\text{Na}_2\text{SiO}_3 \cdot 10\text{H}_2\text{O}$
21.6°	28.6°	41.7°
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	$\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$	
50.6°		

J. C. L.

A study of Donnan's membrane potential difference. (Supplement) Y. Imai. *Kyoto Furitu Ika Daigaku Zasshi*, 15, 66-72 (1935).—By putting two kinds of collodium membrane, —one having 4mV potential difference and the other 25mV resp., —between $\text{N}/20 \sim \text{N}/640$ HCl, contg. 1% gelatine and HCl, the membrane potential difference was measured after the osmotic pressure reached equil. And it was found that the membrane potential difference was equal to electric power of a concn. cell of Cl ion constructed with both liquids inner and outer in the equil. state, independent of the standard membrane potential difference, accordingly of its permeability, and that the direction of the potential difference was quite opposite to the electric power. J. C. L.

Cellulose acetate membrane and copper - ferrocyanide - collodium membrane. T. Matunaga. *Kyoto Furitu Ika Daigaku Zasshi*, 17, 450-463 (1936).—By dissolving cellulose acetate in acetone, cellulose acetate membrane was made with the method similar to that of making collodium membrane. Its standard membrane potential difference and its behavior towards KCl, NaCl, HCl and KOH were examd. The result obtained showed that its potential difference reached the equil. in 2 hours in salt solns., but it did so in 30 mnt. in solns. of acid or of alkali. And the equil. of swelling of the membrane was established within 2 hrs. and the standard membrane potential difference had the quality of neg. membrane 12~20mV. The concn. effect of the potential for KCl, NaCl and HCl of the membrane had the linear relation with the concn. logarithm. J. C. L.

A method measuring of the standard membrane potential difference of incompletely dry collodium membrane. T. Matunaga and S. Muramoto. *Kyoto Furitu Ika Daigaku Zasshi*, 16, 1103-1112 (1936).—In order to measure the potential difference E_0 of collodium membrane dried incompletely, it is reasonable to measure the membrane potential difference and to obtain C_1 and C_2 (the concns. of Cl of the inner and the outer liquids) in 30~60 mnt. after the membrane cell was set up. Calcn. was made on the basis of the following equation: $E_0 = E - \log (C_2/C_1)$. J. C. L.

Phase boundary potential. T. Matunaga. *Kyoto Furitu Ika Daigaku Zasshi*, 17, 377-449 (1936).—The phase boundary potential of oils and solns. of various electrolytes were measured with a quadrant electrometer. J. C. L.

The lyophile property of celluloses. VIII. IX. K. Kanamaru and S. Ueno. *J. Soc. Chem. Ind. Japan*, 40, 178-187 (1937). VIII.—The swelling in org. solvent of nitro cellulose. As the swelling of cellulose in water is primarily considered to be due to

its hydration, it is reasonable to consider that the swelling and dissolving of cellulose derivatives in org. solvents is also primarily caused by the action by which the polar molecules of the solvents are electrostatically adsorbed, arranged and settled towards the polar group in these derivatives, that is, by the phenomenon of solvation. The exptl. results by the authors also showed that ζ potential gives some suggestions to this swelling and dissolving. First, the ζ potential in various org. solvents for indicating the swelling (or solvent) degree of nitro cellulose of higher degree of nitration, was measured with time. As the org. solvents, absolute alcohol, ether, benzene, acetone and ethyl acetate were chosen, and they were used individually or mixed. Further, the variation due to the time of measuring was obtained, and in order to help the consideration of the standpoint of the polar theory for the above exptl. results, the total porosity was obtained by the Debye formula, using the density and the dielectric const. of the single and the mixed solvent. IX. The meaning of ζ potential for the lyophile property of cellulose derivatives. The swelling degree and ζ potential in single solvents of alcohol, ether and benzol of nitro cellulose and those in binary mixed solvents of alcohol ether system, ether benzene system, acetone benzene system and other acetate benzene system, were

measured and the results of the researches of their variation were considered as follows: (1) The stronger nitro cellulose were swollen, the higher became its ζ potential. (2) ζ potential of nitro cellulose in the organic solvents were once lowered immediately after it was immersed, and the higher ζ potential is, and, accordingly nitro cellulose being strongly swollen, the more rapid the velocity of its swelling, the greater the velocity of lowering. (3) After elapsing of longer hrs. the ζ potential once raised up to a certain max. point from which again it descended, reached the equil. at last and approached the const. value (ζ_{∞}). (4) The difference $\Delta\zeta_0 - \zeta_{\infty}$ of the value ζ_0 , measured immediately after the immersion from the value ζ_{∞} in the equil. state of solvation, or the value $\Delta\zeta/\zeta_0$ ran parallel to that of the swelling degree in the org. solvent of nitrocellulose. And the lower the ζ potential became, the stronger the solvent was swollen. Thus, the above exptl. facts are considered theoretically; from the interesting dependency accepted between ζ potential and its state of variation with time, and from the swelling degree and the swelling velocity, it is deduced that $-(d\zeta/dt)t=0$ denotes the velocity of solvation measured immediately after the immersion, and $\zeta_0 - \zeta_{\infty} = \Delta\zeta$ or $\Delta\zeta/\zeta_0$ is correlated to the degree of solvation. J. C. L.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

Studies on the sorption of gases by titania gel. III.—Relation between the vapour pressure and the sorbed amount of ammonia. I. Higuti. *Bull. Inst. Phys. Chem. Research*, 16, 42–52 (1937).—In this report sorption, desorption and resorption isotherms for ammonia have been studied over a range of temp. from -50° to 40°C with the same gel as that used in the sorption of sulphur dioxide. In the high temp. region (20° and 40°C) sorption isotherms

have an ordinary form to which Freundlich's formula is applicable, but isotherms at lower temps. (below -33°C), where sorption measurements have been carried on to the satd. vapour pressure of ammonia, have two inflexion points and a hysteresis loop. This hysteresis phenomena may be attributed to the capillary condensation as in the case of sulphur dioxide and the probable existence of the latter at least in the hysteresis region has been discussed from the following points of

view: that at the beginning point of the hysteresis loop the radius of the mean capillary pore calcd. by Thomson and Anderson's formula is about $9.5\text{\AA}$ and independent of the temp., this value being large enough for the condensation of the vapour as compared with the molecular diameter of ammonia ($2.85\text{\AA}$); that the liquid volumes calcd. from the sorbed amts. are approximately the same for the equal radius notwithstanding the temp. and the nature of the sorptive, the max. value being 0.36 cc per gram of gel: that the differential heat of sorption at high pressure range is const. and ca. 6070 cal. per mole which is close to the heat of condensation of ammonia (5670 cal. per mole at -40°C.).

Author.

Electrophoresis of foams. S. Komagata. *J. Electrochem. Assoc. Japan*, 4, 380-385 (1936).—Electrophoresis of air foams with the diameter of $0.008\sim 0.100\text{ cm}$ in $10^{-4}\sim 10^{-6}\text{N}$ aqueous solns. of H_2O , NaOH , HCl , CaCl_2 and AlCl_3 was measured with the rotational cylindrical app. for foam cataphoresis by the McTaggart method. (1) The velocity of electrophoresis in the dilute soln., when the particles are small, is approximately const., independent of electric potential and the time of measuring. As for larger particles, the greater the electric potential and the time, the less becomes the velocity. (2) The electrophoresis of smaller particles with the diameter of $0.008\sim 0.100\text{ cm}$ in concd. aqueous soln. is similar to that in (1). The dimension and the electrophoresis velocity of the particles reach the max. at a certain length of the diameter, and this max. generally migrates towards the smaller diameter with the increase of the concn. (4) The relation between ζ electric potential and concn. in these electrolytic solns. is on the whole approximate to that in oil or glass. J. C. L.

A theory of surface tension of ternary solutions. K. Ariyama. *Bull. Chem. Soc. Japan*, 12, 38-43 (1937).—The theories of surface tension of Debye-Hückel electrolyte can be divided into two main

groups; one which is based on the assumption of the existence of the 'image force' near the boundary between water and air, and the other based on the calcn. of surface free energy caused by the electrostatic force of ions. On the basis of expl. evidence on the surface tension of ternary soln., the theories of former category are shown to be unacceptable. Theories of Oka and also of Ariyama which belong to the latter category are applied to explain the surface tension of ternary solns. Agreement with expt. is satisfactory.

Author.

Electroendosmose in collodium membrane. J. Nozaki. *Acta Med. Hokkaido-nensia*, 14, 2629-2643; 2644-2656 (1935).

I. Effect of diameter of pore and electric charge in membrane.—In electroendosmose with a diaphragm of collodium membrane the direction of water migration varies according to the quality of membrane; in the neg. membrane water migrates to the neg. pole, while in the pos. to the pos. pole. The quantity of migrating water is proportional to the diameter of the pore and the power of electric charge of membrane, and it increases when the membrane is heated to $20^\circ\sim 40^\circ\text{C.}$, but decreases when heated over 50°C. II. Effect of electrolytic neutralized salts, acid and base on electric charge of membrane.—Concerning the collodium membrane (neg.) and the satd. methyl violet collodium membrane (pos.), dried incompletely, the relation of the electroendosmose was investigated. The neutralized salt gives a cation to the negative membrane, and neutralizes the electric charge of the membrane, but electrifies the membrane when the concn. of neutralized salt is great. The neutralization of anion to the pos. membrane is weaker, and does not electrify the membrane by giving an anion to it. The greater the value of the ion, the stronger becomes the neutralization of the cation. Both acid and base do not change the quality of the electric charge of membrane in the concns below 10^{-3}N , but electrify the membrane in the high concn. over 10^{-2}N .

J. C. L.

On the catalytic action of Japanese acid clay on mixed vapour of aniline and methyl alcohol. K. Kobayashi and M. Mizushima. *Waseda Appld. Chem. Soc. Bull.*, 14, 17-22; 23-27 (1937).—It has already been reported by Harushige Inoue that methyl aniline formed by the direct condensation of methyl alcohol and aniline was transformed into p-toluidine by contact action of Japanese acid clay at higher temp., with the formation of methyl aniline and dimethyl aniline, and the mechanism of the reaction for the formation of p-toluidine and dimethyl aniline by the interaction of aniline and methyl alcohol in presence of the catalyst will be explained by the following Hoffmann's rearrangement; $\text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{-NHCH}_3 \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ (*Bull. Chem. Soc. Japan*, I, 157-162 (1916)).—We have studied the catalytic action of Japanese acid clay on mix. of aniline and methyl alcohol. In our first report we have described the exptl. app. and operation and the results of the preliminary exptl. test. We have confirmed that we can obtain d-toluidine as chief product by using Japanese acid clay. In our second report we have described the influence of the reaction temp. to the yield of p-toluidine and methylaniline, and the mechanism of the catalytic reaction. A mix. 61.5g of aniline and methyl alcohol (1 mol; 1.2 mol) was passed over 80g of Japanese acid clay, dried at 130°C for five hrs., duration of reaction being seven hrs. and reaction temps. being 220°C, 250°C, 300°C, 350°C and 400°C. Each of the reaction products obtained at each of the above mentioned reaction temps. were fractionated by distillation. We have examd. the phys. consts. and the melting points of the acetates of each fraction. Both methylaniline and p-toluidine were obtained as main reaction products at 250°C, but methylaniline decreases in quantity at higher reaction temp. and p-toluidine increases in quantity. The mechanism of the catalytic reaction may be considered as follows; When a equimolecular mix. of methylalcohol and aniline is passed over Japanese acid clay at 250°-350°C, the clay strongly absorbs the

$[\text{NH}_2]$ radical of aniline and then $[\text{H}]$ on para position of benzene ring directly combines to $[\text{OH}]$ radical of methyl alcohol. Thus p-toluidine is obtained from aniline by simple dehydration by the action of Japanese acid clay. Japanese acid clay is not a mere mix. of silica and alumina. It may be considered that the principal compn. is an intimate mix. of hydrated aluminium silicate such as montmorillonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O} + \text{aq.}$) and amorphous silica ($\text{SiO}_2 \cdot \text{NH}_2\text{O}$).

Authors.

On the stability of foam. T. Sasaki. *Bull. Chem. Soc. Japan*, 11, 797 (1937).—It is a known fact that the foam of a liquid, for example the soap soln. or beer, vanishes by adding a small quantity of an org. substance such as ethyl alcohol or ether. However there is no plausible explanation of this phenomenon yet. So I started the following expts. When we shake the test tubes contg. equal volumes of the liquids made from various proportions of butyl alcohol and water, and compare the heights of foam produced in them, the following fact is observed. The height of foam produced increases rapidly from zero by an addn. of a minute quantity of butyl alcohol to water. On further addn. of the alcohol, however, the height reaches a max. and then falls again, finally tending to zero at the concn. at which the water is satd. with the alcohol. Further increase of the alcohol in water makes the system heterogeneous, from which, as well as from the homogeneous soln. of water in butyl alcohol, no foam can be produced on shaking. The same phenomenon is observed in some ternary systems. For example, when we shake a soap soln., a stable foam can be obtained. This foam vanishes instantaneously on adding a small quantity of butyl alcohol, but it can be reproduced when the soln. is shaken again. If we continue to add butyl alcohol, a condition will be arrived at which the water is satd. with the alcohol and no foam can be produced on shaking. It may be considered probable, from the above facts, that the homogeneity of a film plays an important rôle for the stability of the foam which it

forms. That is to say, the foam of a homogeneous liquid mixt. will be destroyed by adding one of the components, for the film of the foam becomes heterogeneous, being made of patches of the excessive component. In this case, the surface tension differs naturally in the different parts of a film. So the film, and accordingly the foam, will collapse. It can also be shown that a soap film made on a wire frame is torn off by touching with a drop of a liquid of low surface tension, alcohols for example. In general, such foam-depressant may be considered effective when it has a small solubility in water as well as a high surface activity. A quantitative study is now being made on these phenomena.

Author.

Studies of the oiliness of the liquids. II. Friction coefficients of the films of mono- and poly-molecular layers. H. Akamatsu and J. Sameshima. *Bull. Chem. Soc. Japan*, **11**, 791-796 (1936).—The static friction coeffs. have been measured by the balance method when the mono- and poly-molecular films of some fatty acids (such as stearic, palmitic, oleic acid etc.) are deposited on glass surface by Langmuir-Blodgett's method. The friction coeff. of the clean glass surface is about unity, and the presence of only one-molecular layer of one of these substances reduces the friction coeff. to about one tenth, but no further reduction takes place by the increase of the thickness of film. There are little differences of the friction coeffs. among these substances, but the effect of "piston oil" is detected. In the present expt., oleic acid and castor oil have been used as "piston oil". When castor oil is used the friction is somewhat larger than that when oleic acid is used. This may be explained by the fact that oleic acid has greater surface pressure than castor oil, so the former deposits the film in more compressed state than the latter. Relatively large difference of friction coeff. is detected by the change of "piston oil" in the case of myristic acid, since this acid makes an expanded film. It seems possible that a regular arrangement of

molecules favours the lubricating power more than the irregular arrangement. We can deposit the film on glass surface by means of the condensation of vapour or the evaporation of solvent from the soln. These methods, however, give less regular arrangement of molecules than Blodgett's method, and the friction of such a film is larger. Authors.

Studies on the surface-activity and adsorption of aminoacids. V. VI. T. Ito, *J. Agr. Chem. Soc. Japan*, **12, 204-208 (1936).**—V. Diaminoacids such as Lysin, Arginin and Histidin were found to exert at a concn. of 0.05M and in a region of pH=1 to 13 practically no influence on the surface tension of water as measured by the stalagmometric method. On the other hand, they showed appreciable adsorbability on active charcoal (*Carbo animalis pur. sicc.*, Merck). Thus the adsorption curves (x/m , pH) for Histidin and Lysin showed a marked max. at pH=7.5 and 9.5 resp., which coincides approximately with the resp. isoelectric points (pH 1) of the aminoacids under consideration. The adsorption of Arginin (pH=10.76 at 25°) rose rapidly between pH=6.5 and 9.5, and then remained approximately const. with decreasing hydrogen ion-activity up to pH=13. VI. The surface tension of the aqueous solns. of α -, γ - and δ -aminovaleric acid and of α - and ϵ -aminocaproic acid up to the concn. of 0.04M was measured; and thus it was shown that the surface-activity decreases as the distance separating the amino and carboxyl group in these aminoacids increases. δ -aminovaleric acid, for example, was found to be completely surface-inactive. The similar tendency was also observed when the surface tension of 0.05 molar solns of the aminoacids in question was measured at varying pH. As regards the adsorption by the active charcoal, the x/m , pH-curves for α -aminoacids showed all a flat max. extending over a range of pH=about 3 to 9, whereas those for γ -, δ - and ϵ -aminoacids ran approximately parallel to the pH-axis in the region of pH from 1.5 to 9.5, to fall down subsequently with increasing pH. α -aminoacids

are, therefore, in the form of electroneutral molecules the most adsorbable on active charcoal, while in the case of γ -, δ - and ϵ -aminoacids the adsorbability of the electroneutral molecules cannot exceed that of the corresponding cations. The author tried to interpret the obtained results on the basis of the zwitterion theory.

Author.

Preparation of colloid by vapour explosion and a colloidal chemical study of dispersion system. N. Sata. *Bull. Chem. Soc. Japan*, 11, 443-455; 481-503; 598-627 (1935).—A new method of preparing colloid dispersion by system was elaborately studied. The stability of the colloid formed has much relation to the app., dispersoid, and stabilisers. A substance to be dispersed was tightly enclosed in a vessel, and was made to explode by heating. The vapour was led directly to the dispersion medium to prepare sols of Hg, Se and S. The results obtained are as follows: (a) Hg sol. In examn. of the influences of natural impurities, such as dust, Na_2S , Na_2SO_3 , and the ultraviolet ray on the Hg sol, it was found that increased the stability, the solns. of Na_2S and Na_2SO_3 were adequate to the stabilization and the exposure to the X-ray decrease the stability. (b) The stabilization of stirring, shaking and blowing in of air. (c) S sol is not stable because of its solubility in dispersion phase and of its chemical change. Besides, as for sols of Hg, S and Se, (i) the change of their appearances with time in various concns., (ii) observations by means of a microscope, (iii) measurement of the viscosity and the surface tension, (iv) the study of their electrophoresis, (v) the process of coagulation by NaCl , CaCl_2 , and AlCl_3 were investigated.

J. C. L.

On the interfacial characteristics of titanium oxide which has a high dielectric constant. S. Komagata and K. Hiruma. *J. Electrochem. Assoc. Japan*, 5, 91-93 (1937).—The authors measured the interfacial kinetic potentials of the titanium oxide for water and aqueous solns. of HCl

and KOH , in which the sample of TiO_2 has a dielectric const. as high as that of water, namely 80. The results of the expts. are not affected by Coehn's rule on the relation between the interfacial kinetic potential and the dielectric const. of the materials which form the interface.

Author.

Studies on the surface-activity and adsorption of aminoacids. VII. and VIII. T. Ito. *J. Agr. Chem. Soc. Japan*, 12, 990 (1936); 13, 172-176 (1937). VII. Adsorption of a few representative aminoacids, such as arginin, α -aminovaleric, α - and ϵ -aminocaproic acids by charcoal purified by Miller's HF-HCl method was investigated. On comparing the results obtained with those of the previous work with untreated charcoal, it is seen that such a purification of the charcoal has no influence upon the shape of the adsorption curves (x/m , pH). The purified charcoal, however, showed a stronger adsorptive power for the aminoacids than the one not purified. VIII. Sodiumsalts of n -butyric, isovaleric and n -caproic acids were found at a concn. of 0.05M to reduce slightly the surface tension of water, the influence being the greater, the higher the molecular weight of the fatty acid. Moreover, the surface tension remained approximately constant when the pH was varied from about 7 to 13 by adding various quantities of NaOH to the solutions. One is thus led to the conclusion that the fatty acids under consideration are also in the form of surface active ions, although in slight degree. In the same way, n -amylamine and isohexylamine ions were presumed to be surface active. The adsorption of the amins by charcoal from strong acid solns. was found to be stronger than that of the fatty acids from strong alkaline solns.; this is comparable with the case of mono-amino-acids which are adsorbed better from acid solns. than from alkaline ones.

Author.

On the interfacial characteristics of titanium oxide which has a high dielectric constant. S. Komagata and K.

Hiruma. *J. Electrochem. Assoc. Japan*, 5, 91-93 (1937).—The authors measured the interfacial kinetic potentials of the titanium oxide for water and aqueous solns. of HCl and KOH, in which the sample of TiO_2 has a dielectric const. as high as that of water, namely 80. The results of the expts. are not effected by the Coehn's rule on the relation between the interfacial kinetic potential and the dielectric consts. of the materials which form the interface. Authors.

Comparison of the methods for measuring specific surface tension. II. H. Takahashi. *Kyoto Furitu Ika Daigaku Zasshi*, 15, 523-528 (1935).—By the drop-counting method, the capillary tube method and the ring method the specific surface tension of $M/2 \sim M/80$ solns. of KCl, NaCl and LiCl contg. 25% of alcohol was measured. It was found that the numerical value obtained by these three methods did not agree, and that the value by the ring method was the largest and that by the dropping method the smallest. Generally, the greater the concn. of the salt, the more the surface tension decreases. The decrease is more remarkable in KCl and NaCl than in LiCl. J. C. L.

Adsorption of ion of glycocholl and white of an egg. S. Muramoto. *Kyoto Furitu Ika Daigaku Zasshi*, 16, 1264-1270 (1936).—When $M/2$ glycocholl and 1% white of an egg were added to $N/20 \sim N/1.280$ NaCl and NaOH, the potential difference migrated to the direction where the activity of Cl^- and OH^- decreased, and where it increased with respect to Na^+ . But the increase of Na^+ activity could not be concluded with respect to the migration of this potential difference, because the amalgam electrode was influenced by the admixed substances.

J. C. L.

Abnormal diffusion. G. Harada. *Acta Med. Hokkaidonensia*, 15, 779-806 (1937).—Considering the so-called Loeb's abnormal osmosis and its mechanism, the existence of abnormal diffusion was proved

by using collodium membrane. The abnormal diffusion occurred at the point of the concn. $4^{-1}N \sim 256^{-1}N$ of neutralized soln., and, as for the positively charged membrane, it was done more remarkably in salts of 3-valent pos. ion than in those of 2-valent metal. As for the negatively charged membrane, the abnormal diffusion occurred more remarkably in salts of 4 or 3-valent ion than in those of 2 or 1-valent ion. Abnormal diffusion had the relation with the degree of permeability of membrane, and it did not occur at the membrane which had high potential difference of standard membrane and whose pores were small in diameter. And it did not take place in the membrane, lower in its electric charge. The similar fact to the above could be observed when the animal membrane was used. J. C. L.

Electrolyte effect of collodium membrane on permeability. G. Harada and T. Isida. *Acta Med. Hokkaidonensia*, 15, 814-824 (1937).—By putting the collodium membrane swollen by alcohol between salt soln. and water, the diffusion quantity (v) was measured. After the membrane was immersed in $1-N$ solns. of various salts for 24 hrs., it was washed as clean as possible. By using the same salt soln. the quantity of diffusion (N) was measured. Then, N/v was obtained. The salts used were NaCl, NH_4Cl , KCl, BaCl_2 , CuCl_2 , MgCl_2 , CaCl_2 , AlCl_3 , KNO_3 , KBr, K_2CrO_4 , K_2CO_3 , K_2SO_4 , $\text{K}_3\text{Fe}(\text{CN})_6$, and $\text{K}_4\text{Fe}(\text{CN})_6$. Generally, $(N/v) > 1.0$ in the diffusion of $1-N$ NaCl soln. with some exceptions. $(N/v) < 1.0$ in the diffusion of $16^{-1}N$ NaCl soln. with a few exceptions. Even in the case of exceptions, (N/v) in $1-N$ NaCl soln. was generally greater than that in $16^{-1}N$ NaCl with the exception of K_2SO_4 and the salts of 3-valent metals. It is concluded that the electrolyte causes some changes to the diameter of pores of the membrane and its electric charge. J. C. L.

Effects of short waves and super-short waves on permeability of collodium membrane. G. Harada. *Acta Med.*

Hokkaidonensia, 15, 807-813 (1937).—Super-short waves and short waves act diminishingly on potential difference of KCl standard membrane of collodium membrane swollen with alcohol. They sometimes give change to the condition of the diffusion. Any selective action between waves could not be proved.

J. C. L.

Adsorbabilities of various kinds of adsorbents. T. Matui. *Kyoto Furui Ika Daigaku Zasshi*, 18, 1391-1394 (1936).—Adsorbabilities of various kinds of adsorbents were examd. by benzoic acid method and methylene-blue method. The results of their order obtained by comparison were as follows: ligcarbon, *Sankyo* charcoal > ados, alsilin, adsorbin > carbonian, kaolin.

J. C. L.

A note on the theory of surface tension of ternary solutions. K. Ariyama. *Bull. Chem. Soc. Japan*, 12, 114-116 (1937).—The surface tension of the mixed solutions of inorg. salt and inorg. acid is not additive. The expl. fact that the ratio of the neg. adsorption of the inorg. salt decreased by the addn. of inorg. acid, could be acctd. for by the assumption that the dielectric const. of adsorption layer was smaller than that of pure water, when the hydrogen ions from org. acid were positively adsorbed at the surface of the solns.

J. C. L.

"Zonal effect" in the slow coagulation of colloid arsenious sulphide. S. S. Joshi and S. S. Kulkarni. *Bull. Chem. Soc. Japan*, 12, 145-147 (1937).—The slow coagulation of dilute colloid arsenious sulphide was measured by means of a Pulfrich refractometer. And it was observed that the variation of the refractive index was not time-continuous, but zonal. Thus, the zonal effect in the slow coagulation is accepted, and Smoluchowski's theory rejected.

J. C. L.

A theory of surface tension of aqueous solutions of inorganic acids. K. Ariyama. *Bull. Chem. Soc. Japan*, 12, 109-113 (1937).—In contrast to all the other

general electrolytes inorg. acid added to water decreased its surface tension. This phenomenon can be acctd. for by the assumption that water molecules are arranged with H atoms turned upwards on the surface of water, and that hydrogen ions are combined closely with water molecules by hydrogen bond to form oxonium ions, namely, that hydrogen ions are positively adsorbed on the surface of water.

J. C. L.

Liesegang phenomenon at electric field. I. Effect of light. S. Miyamoto. *J. Chem. Soc. Japan*, 58, 37-41 (1937).—Also see *Gakujitu Kyoho*, 12, 221-223 (1937). By filling a quartz tube with gelatine gel, Ag-NO₃ aq. was dispersed from one end of the tube, and K₂Cr₂O₇ aq. from the other, and the Liesegang layer was made by using the electric field of 100/12.4 V/cm. The effects of illumination by electric light or ultra-violet rays on the layer were examd., and it was found that the ultra-violet rays decreased the thickness and interval of the ppn. layers, and that its effects were continued after the light was intercepted. Considering the fact that, when the part of K₂Cr₂O₇ was illuminated before the pptn. was formed, the effect appeared in the part not illuminated, it seems that ultra-violet rays give some changes to gelatine and K₂Cr₂O₇.

J. C. L.

A colloid chemical study of ternary solutions. (II). C₆H₆-H₂O-C₂H₅OH system and CCl₄-H₂O-CH₃OH system. N. Sata and Y. Niwase. *Bull. Chem. Soc. Japan*, 12, 86-95 (1937).—The apps. with C₆H₆-H₂O-CH₃OH and CCl₄-H₂O-CH₃OH similar to that in the previous study of C₆H₆-H₂O-C₂H₅OH system were constructed. The states of the two systems at the critical point of ternary solns. changing from the homogeneous mix. solns. to the white emulsion through the range where fluorescence is produced were observed. The results obtained are as follows: (1) no relation between specific gravity and dispersion degree of the component is maintained, and (2) such symmetrical molecules as C₆H₆ and CCl₄ are

different from such chain molecules as pentane and hexane. J. C. L.

The thin collodium membrane. K. Ituzi. *Kyoto Furitu Ika Daigaku Zasshi*, 17, 492-498 (1935).—Standard membrane potential differences of a great number of thin collodium membranes were measured to be 29.4~59.8mV, and it was found that most of them were at the range of 35~36mV. J. C. L.

Effects of collodium membrane immersed in various salt solutions on standard membrane potential difference. J. Nozaki. *Acta Med. Hokkaido-nensia*, 15, 832-838 (1937).—By immersing for 24 hours incompletely dry collodium membrane and methyl violet collodium membrane in 1N solutions of various neutralized salts, and by measuring the standard membrane potential differences before and after the immersion, the changes due to the adsorption of ion and the action of membrane imbibition were compared. In this result the order of strength of cation which acted on the negatively charged membrane and lowered the potential difference, was as follows: $\text{Li}^+ < \text{Zn}^{++}, \text{Ca}^{++}, \text{Mg}^{++}, \text{Na}^+ < \text{Cu}^{++} < \text{Ba}^{++}, \text{K}^+$. This is in good agreement with the so-called Hofmeister order in swelling of gelatine-gel. And the order of the strength of anion which acted on positively charged membrane and lowered the potential difference was as follows: $\text{B}^- < \text{J}^- < \text{CrO}_4^{--}, \text{NO}_3^-, \text{F}^- < \text{Cl}^- < \text{SO}_4^{--} < \text{CO}_3^{--}$. This order was almost contrary to the Hofmeister order. Anion acting on the neg. membrane, and cation on the pos., the greater the valency of ion was, the stronger the action which heightened the potential difference. J. C. L.

Sedimentation velocity of Japanese acid clay suspension and concentration of hydrogen ion. (I) Y. Shibata. *J. Chem. Soc. Japan*, 57, 1079-1085 (1936).—With the commercial Japanese acid clay suspended in water, six kinds of suspensions whose particle sizes were made nearly uniform by

fractional sedimentation were formed. To these suspensions were added N/10 HCl and NaOH. Thus, P_H of the suspensions being varied, the variation of the sedimentation velocity of the particles was observed. And it was found that when the P_H was made greater than 7, the sedimentation velocity decreased, while, greater than 12, it increased. Further when the P_H was decreased below 7, the velocity was increased too. This is due to coagulation of the particles by the excess of acids and bases. J. C. L.

The dimension of pores in diaphragm and electroendosmosis. (I) H. Muraoka. *J. Electrochem. Assoc. Japan*, 5, 85-87 (1937).—The distribution of the dimension of pores in glass filter plane and the av. radius were obtained by the flowing method. With these results the velocity of electroendosmosis of KCl and H_2O was measured. The results obtained showed that the velocity of the electroendosmosis increased nearly proportional to the av. radius, but at last it ran parallel with the axis of radius, as its variation decreased slowly. In this case the conc. which marked the highest electroendosmosis had the max. with respect to the axis of dimension of pores. And using the above diaphragm, the electroendosmosis of two kinds of mixed solns. with respect to KCl, $\text{Al}_2(\text{SO}_4)_3$ and CuSO_4 was measured, and compared with that measured when the solns were not mixed. And there appeared the variation of the curve by the strength of adsorption of ions, especially of Al. J. C. L.

Quantity of Cl diffused from KCl-agar-agar-bridge into water. T. Matunaga. *Kyoto Furitu Ika Daigaku Zasshi*, 17, 371-376 (1936).—The relation between the quantity of Cl diffused in 1 hour from satd. 3% KCl agar-agar gel and the cross section of the capillary tube was examd. The following empirical equation is deduced: $y = 0.0084x + 0.00061$, where y shows millimol of the diffused KCl, and x the cross section of the bridge, mm^2 . J. C. L.