

# ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

Vol. XII

AUGUST, 1938

No. 2

## 1—GENERAL AND PHYSICAL CHEMISTRY

92. **The equilibrium of the system  $\text{TiO}_2$ - $\text{SO}_3$ - $\text{H}_2\text{O}$  at  $150^\circ\text{C}$ .** T. Sagawa. *J. Soc. Chem. Ind. Japan*, 41, 52-56 (1938).—In his previous papers the author reported his exptl. results of the system in question at  $100^\circ\text{C}$ . The present report concerns with the results of experiment on the system at  $150^\circ\text{C}$  performed with the object to see how much the reaction would be accelerated and what compounds might exist at  $150^\circ\text{C}$ . Experiments were carried out in almost the same way as at  $100^\circ\text{C}$ . But at  $150^\circ\text{C}$ , owing to the boiling of the soln., the bottle used could not be opened in the thermostat when the concn. of sulphuric acid was less than 52.5 %  $\text{SO}_3$ , whose concentration corresponded to the acid having the boiling point just at  $150^\circ\text{C}$ . Fortunately, most of the sulphates of titanium, especially basic sulphates, are less reactive, so the samples can be taken after cooling the bottle. In these cases, from the result of calculation, care has been taken to minimise the error due to the vaporisation and condensation of water in the dead space of the vessel within the exptl. error.

As the result, it has been found that in this system  $\text{TiO}_2$  and four kinds of sulphates of titanium, whose molecular ratios  $\text{TiO}_2$ : $\text{SO}_3$ : $\text{H}_2\text{O}$  are 6:5:4, 1:1:1, 1:1:0 and 2:5:5 resp., are present as the solid phase at  $150^\circ\text{C}$ . Among those four sulphates, the two-6:5:4 and 2:5:5—have been found for the first time in the present investigation.

The range of concentration which pptes.  $\text{TiO}_2$  by hydrolysis, was widened to 36.2 % at  $150^\circ\text{C}$  by 1.7 % of  $\text{SO}_3$  compared with that

at  $100^\circ\text{C}$ . And in the range of hydrolysis the solubility of  $\text{TiO}_2$  was lowered. The pptd.  $\text{TiO}_2$  contd. 1~3.3 % of  $\text{SO}_3$ , which was about one half of that at  $100^\circ\text{C}$  at the corresponding concn. of sulphuric acid, changing according to the concn. of sulphuric acid in the mother liquor. The purity of the pptd.  $\text{TiO}_2$  was 95~93 %, which was a little higher than that at  $100^\circ\text{C}$  (92~93 %).

Among these sulphates the sulphate whose molecular ratio  $\text{TiO}_2$ : $\text{SO}_3$ : $\text{H}_2\text{O}$  was 2:5:5 was easily soluble in water.

Generally speaking, the more basic the sulphate is, the less easy to dissolve. The time required before equilibrium is established is considerably shortened and only about one tenth of that at  $100^\circ\text{C}$  is necessary in the whole range.

Author.

93. **On the differential equation of ultracentrifuging.** S. Oka. *Proc. Phys.-Math. Soc. Japan*, 19, 1094-1104 (1937).—Lamm's differential equation of ultracentrifuging.

$$\frac{\partial c}{\partial t} = k \left( \frac{\partial^2 c}{\partial x^2} + \frac{1}{x} \frac{\partial c}{\partial x} \right) - s\omega^2 \left( \frac{\partial c}{\partial x} + 2c \right),$$

has been solved, satisfying certain boundary and initial conditions. The applicability of the soln. has been confirmed by performing numerical calculations.

Author.

94. **Studies on the aqueous solutions of some chromic salts. II. Modified green chromic sulphate, ol-green chromic chloride and green chromic**

**sulphate.** H. Sueda. *Bull. Chem. Soc. Japan*, **12**, 524-536 (1937).—For the modified green chromic sulphate, the formula of  $\mu$ -ol-mono- or di-sulphato-di-chromic sulphate is deduced (i) from its absorption spectra, (ii) from the quantities of sulphuric acid produced when this salt is formed from violet chromic sulphate, and (iii) from the sulphate ions which is pptd. by barium chloride in various dilutions. When hydroxo-pentaquo chromic chloride soln. was heated, the author recognized the production of ol-compound, to which the formula of di-ol-octaquo-di-chromic chloride was given. The modification of the green chromic sulphate in aqueous soln., produced on standing, on heating, or on adding sodium hydroxide, is discussed.

Author.

**95. On the kinetic theory of monatomic liquid.** A. Harashima. *Proc. Phys.-Math. Soc. Japan*, **III**, **20**, 120-124 (1938).—In order to investigate the behavior of atoms in monatomic liquids the author proposed a simple model, and regarded each atom as composed of a massless solid sphere and an oscillator in it, which having the mass of the atom were bound to the centre by a force proportional to the distance from it. The atoms were considered to collide with each other in so dense an aggregation as almost in the solid state and the oscillator was incessantly deviating from the centre of the sphere. By this model it is shown that the specific heat obeys Dulong-Petit's law. The thermal pressure was calcd. as follows:

$$P = (2ekT)^{1/2} / 2\pi^2 a^2,$$

where  $P$  is the thermal pressure,  $e$  the proportional const. for the force acting on the oscillator,  $k$  the Boltzmann's const., and  $a$  what is obtained by the formulae  $(4/3)\pi a^3 = M/Ld$ , where  $M$  is the atomic weight,  $L$  Loschmidt's number, and  $d$  the density. The results for A, K, Na and Hg were compared with those obtained from thermodynamical data, that is, with those calcd. by the formulae  $P = T(a/x)$  or  $P = (c_p - c_v)/Vd$ , where  $a$  is the expansion coeff. and  $x$  is the compressibility. The agreement is satisfactory considering the

simplifications made in the theory. Author.

**96. Studies on the ignition of explosive gas by heated wire.** K. Hadome. *Hokkai-Tanko*, **282**, 1-12 (1938).—As the causes inducing explosion of gas in the coal-mine, the combustion of Tungsten filament by breakage of electric bulb and the red-heated surface formed by short on cords of electric safety lamp, leading wire, electric cord, signing wire etc. are considered. The present expts. were carried out to examine these causes, and the results obtained as the temp. of ignition of gases by heated wire are given.

J. C. L.

**97. The Faraday effect of strong electrolytes in aqueous solutions. VI.** A. Okazaki. *Mem. Ryogun Coll. Eng.*, **10**, 89-113 (1937).—By the use of the data for the magneto-optical rotation of a number of electrolytes in aqueous soln. obtained by other investigators, the variation with concn. of the corrected molecular rotation  $M[D_2]$  was studied. It was found that the  $M[D_2]$ -values of HCl, HBr, HI, CdCl<sub>2</sub>, AlCl<sub>3</sub>, CsBr, CdBr<sub>2</sub>, NH<sub>4</sub>Br, CdI<sub>2</sub> and CH<sub>3</sub>COOLi decrease with increasing concn., while those of HNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, LiClO<sub>3</sub>, HIO<sub>3</sub> and LiIO<sub>3</sub> increase and that of CH<sub>3</sub>COOH is practically independent of the concn.

The  $M[D_2]$ -values at infinite dilution were detd. by graphical extrapolation. Most of them proved to be given by the sum of the corrected ionic rotations.

Author.

**98. Magneto-optical molecular rotations of electrolytes in undissociated states.** A. Okazaki. *Mem. Ryogun Coll. Eng.*, **10**, 115-119 (1937).—The corrected molecular rotations  $M[D]$  of some electrolytes in undissociated states, i.e. HCl, HBr and HI in liquid state, and NaCl, KCl, CaF<sub>2</sub> and NaClO<sub>3</sub> in solid state, were calcd. by the use of the data for the magneto-optical rotations which had been obtained for D-lines by other investigators. From comparison with the values of  $M[D]$  at dissociated states, it was found that for HCl, HBr, HI, NaCl and KCl a decrease in the corrected molecular

rotation takes place upon formation of molecules from free ions as in the case of the molecular refraction.

Author.

99. **A study of carbon tetrachloride ethyl alcohol system.** F. Ishikawa and T. Yamaguchi. *Bull. Inst. Phys. Chem. Research*, **17**, 246-255 (1938).—The vapour pressure of  $\text{CCl}_4$ - $\text{C}_2\text{H}_5\text{OH}$  system was measured at  $25^\circ$  by the ebullioscopic method, and the partial pressure curves of the liquids, and each component were detd. This system presented a great positive deviation from Raoult's law. The max. vapour pressure was about 144 mm. and corresponded to the mol fraction of  $\text{CCl}_4$ , 0.74. Applying Duhem-Margules formula to these results, the following equations were obtained:  $p_1 = P_1 x e^{5.2593(1-x)^2 - 7.8664(1-x)^3 + 4.0732(1-x)^4}$ , and  $p_2 = P_2(1-x) e^{1.6061x^2 - 2.9988x^3 + 4.0732x^4}$ , where  $p_1$  and  $p_2$  are the partial pressure of  $\text{CCl}_4$  and  $\text{C}_2\text{H}_5\text{OH}$  resp.,  $P_1$  and  $P_2$  the vapour pressures of each pure phase, and  $x$  the mol fraction of  $\text{CCl}_4$ . From the above-mentioned results, the activity of each component, coeff. and other thermodynamical numerical values were calcd.

J. C. L.

100. **The production of carbon monoxide and hydrogen by methane-steam reaction. I. Action of a nickel catalyst upon the water gas reaction.** S. Tutumi. *J. Chem. Soc. Japan*, **58**, 379-390 (1937).—The water gas reaction at  $700^\circ$  and  $800^\circ\text{C}$ . in the presence of a nickel catalyst, adding 10%  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{ThO}_2$ ,  $\text{CuO}$ ,  $\text{MnO}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  as promoters was examined. The results of the comparison between these promoters are as follows: Ni + 10%  $\text{MgO}$  catalyst has the highest catalytic ability for the oxidation of CO. So long as the promoters added do not so much promote the sintering of Ni catalyst, the larger ability to oxidize CO a promoter has, the more effective it is.

J. C. L.

101. **Oxygen exchange reaction between water and carbonic acid ion.** T. Titani, T. Morita and K. Goto. *Bull. Chem. Soc. Japan*, **13**, 329-330 (1938).—Though repeated

dissoln. and separation was done at room temp. with heavy water whose heavy oxygen was concd. and fully dried  $\text{K}_2\text{CO}_3$ , the concn. of heavy water seldom decreased. No exchange of the oxygen atoms between water and carbonic acid ion took place. J. C. L.

102. **Condensation of styrol in heavy water and heavy alcohol.** M. Koizumi and T. Titani. *Bull. Chem. Soc. Japan*, **13**, 304-305 (1938).—In condensation (at  $100^\circ\text{C}$ ) of styrol in heavy water and heavy alcohol ( $\text{C}_2\text{H}_5\text{OD}$ ), no exchange reaction was observed. J. C. L.

103. **Concentration of heavy hydrogen in hydrocarbon.** T. Morita, K. Goto and T. Titani. *Bull. Chem. Soc. Japan*, **13**, 99-110 (1938).—Water formed by burning carbohydrates (cane sugar and cotton) in the air had a higher density than the ordinary water due to the abundance of heavy isotopes of oxygen in the water formed. The hydrogen contained in the water formed by the said combustion was heavier than the ordinary hydrogen by about 17. J. C. L.

104. **A study of hydrogen anode electric current by means of oscillograph.** G. Okamoto and T. Iijima. *Bull. Inst. Phys. Chem. Research*, **16**, 1426-1436 (1937).—When Ni hydrogen electrode which has been polarised into anode reaches a const. state, the electric current decreases rapidly at first and then gradually. To investigate this phenomenon quantitatively, the current was photographed. The results are as follows: sudden decrease in the electric current means the decrease in the number of the hydrogen atoms adsorbed on the surface of the electrode, and the gradual decrease at the later period is due to the diffusion of the hydrogen atoms in the interior of the electrode to the surface; the number of the adsorption points of the hydrogen molecules is  $10^{13}$  per  $\text{cm}^2$ ; the heat of activation for the ionisation of the adsorbed hydrogen atoms is 16.6 cal. J. C. L.

105. **Hydrogen exchange reaction between nitrophenol and water. (I) Ex-**

**change reaction and hydrogen bond.** M. Koizumi and T. Titani. *Bull. Chem. Soc. Japan*, **13**, 318-328 (1938).—Hydrogen exchange reaction between *p*-, *m*- and *o*-nitrophenol and heavy water was studied at 100°C. H in OH radical enters immediately into exchange reaction. When heavy water is adequately acidified, two hydrogen nuclei of *o*- and *p*-form and three hydrogen nuclei of *m*-form gradually begin exchanging. In this case, the reaction velocity of alkali soln. is larger than that of acid soln. Of the three kinds of alkali heavy water, the exchange velocity of *p*-form is almost equal to that of *m*-form, and that of *o*-form is remarkably small. From the fact that the exchange velocities of those two forms are almost equal, it is seen that acceleration by OH radical for the exchange reaction is far greater than retardation by NO<sub>2</sub> radical. That the exchange reaction of *o*-compound is small is considered to be due to hydrogen bond of OH radical with O of NO<sub>2</sub>. The rest of the hydrogen atoms also gradually enter into exchange-reaction at a velocity smaller than the above-mentioned velocity. J. C. L.

**106. Relation between the configuration of the metallic complex salts and their absorption spectra.** III. *cis*-[Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>]. H. Sueda. *J. Chem. Soc. Japan*, **59**, 47-48 (1938).—Under the assumption of the existence of the *cis*-type in [Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>], the H<sub>2</sub>O molecules of *cis*-[Co(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>](NO<sub>2</sub>)<sub>3</sub> was exchanged for the NO<sub>2</sub> radical and *cis*-[Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>] made. The spectrum taken proved to be of the same type as [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub> and *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl. It coincides with the absorption which was expected from the assumption in the previous paper. J. C. L.

**107. Hydrogen exchange reaction between water and pyrrol, indol and their CH<sub>3</sub> derivatives. I. Exchange of hydrogen between pyrrol and water.** M. Koizumi and T. Titani. *Bull. Chem. Soc. Japan*, **13**, 85-94 (1938).—The hydrogen molecules were exchanged at room temperature between

pyrrol and neutral heavy water. When heavy water was acidified to the pH value larger than 2, H combined to C did not undergo exchange-reaction even after shaking for 10 hours at 30°; when the pH value was made smaller than 2, the exchange took place slowly; when it was smaller than 1, equilibrium was soon established. In the exchange due to H of C-H bond all the H atoms in a pyrrol molecule underwent the reaction simultaneously. If heavy hydrogen distribution coeff. between heavy water and H of N-H bond is taken to be 0.88, that between heavy water and H of C-H bond will be 0.70.

**II. Hydrogen exchange reaction between heavy water and thiophen or furan.** *ibid.*, 95-98.—Exchange of hydrogen did not occur between heavy water and thiophen even under such a condition as it would take place between pyrrol and heavy water. From this fact the secondary exchange reaction between pyrrol and heavy water is ascribed to NH radical.

**III. Exchange reaction of hydrogen between water and N-methyl-pyrrol.** *ibid.*, 298-304.—Though *N*-methyl-pyrrol and neutral heavy water were shaken together for a long time at room temperature, no exchange reaction took place. This is because *N*-methyl-pyrrol has no dissociated H. When heavy water acidified by HCl to pH smaller than 3 was employed, an exchange similar to the secondary one of pyrrol took place, and its reaction velocity became remarkably large with decreasing pH value. All the hydrogen atoms in the *N*-methyl-indol molecule partake in the reaction, and distribution coeff. of heavy hydrogen is 0.68.

**IV. Hydrogen exchange reaction between indol and water.** *ibid.*, 307-318.—When indol and neutral heavy water were shaken at 60°, hydrogen combined with N of the indol molecule quickly underwent exchange reaction. In the case of heavy water acidified by HCl to the pH value 2.5, there was no difference from the case of neutral heavy water; when the pH value was 2.5-0.5, one of the H of C-H bond (perhaps H at the β position) was exchanged (the second-

dary exchange reaction); when the pH value was below 0.5, H at the  $\alpha$  position also underwent exchange reaction (the tertiary exchange reaction). Condensation of indol took place parallel with those secondary and tertiary exchange reactions. The distribution coeffs.

of heavy hydrogen between water and indol in the case of the primary, secondary and tertiary exchange reactions are as follows:  $k_1 = k(\text{NH}/\text{H}_2\text{O}) = 1.07$ ,  $k_2 = k(\beta\text{-CH}/\text{H}_2\text{O}) = 0.69$ ,  $k_3 = k(\alpha\text{-CH}/\text{H}_2\text{O}) = 0.45$ .

J. C. L.

## 2-ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

108. **Spectroscopic Studies of the Extreme Ultra-Violet.** T. Suga. *Sci. Papers Inst. Phys. Chem. Research*, 34, 7-31 (1937).—Using a 1 metre vacuum spectrograph of Siegbahn type, the extreme ultra-violet spectra of hydrogen, helium and neon were investigated, special attention being paid on the influence of a trace of one gas mixed with another gas. Extension of the series was achieved for the following series: Lyman series of hydrogen (formerly  $n=15$  now to  $n=22$ ), HeI,  $1'S_0-m^1P_1$ ; HeII,  $1^2S_{1/2}-m^2P_{3/2}$ ; and NeI,  $1'S_0-m^1P_1$ ,  $1'S_0-m^3P_1$ ,  $1'S_0-md_5$ ,  $1'S_0-md_3$ , and  $1'S_0-ms'$ .

Various methods of excitation were tried: D. C. arc with a hollow cathode, or with a water-cooled cathode, A. C. excitation giving disruptive discharge, etc. Among various features presented, the following may be mentioned: i) The particular enhancement of the intercombination line of HeI,  $\lambda 591 \text{ \AA}$ ,  $\nu = 1'S_0-2^3P_1$ , in a D. C. discharge; ii) The appearance of many forbidden HeI lines violating the  $\Delta L$ -rule in a disruptive discharge; iii) Change in the relative intensity of HeI and HeII spectra, according to difference in the condition of excitation; iv) The change in the relative intensities of NeI lines  $1'S_0-4^1P_1$ ,  $1'S_0-4^3P_1$ ,  $1'S_0-5^1P_1$  and  $1'S_0-5^3P_1$ , when a trace of neon was mixed in helium, as compared with the case of pure neon.

Author.

109. **The cathodo-luminescence of luminescent calcium silicate.** E. Iwase and

S. Iimori. *Sci. Papers Inst. Phys. Chem. Research*, 34, 173-179 (1938).—It was confirmed that the intense yellow cathodo-luminescence exhibited by some specimens of Japanese wollastonite and pectolite, whose main constituent is calcium silicate, is to be ascribed to a small amount of manganese contained in these minerals. The content of manganese in natural wollastonite and pectolite was determined. Comparisons were made on the cathodo-luminescence bands as well as the manganese contents between the natural specimens and synthesized materials. Authors.

110. **A note on the excitation of electrons by neutrons.** E. Takeda. *Proc. Phys.-Math. Soc. Japan*, III, 19, 835-838 (1937).—A new phenomenon, which can be explained by assuming that electrons are emitted from atoms when they interact with neutrons, was found by Kikuchi and his co-workers. Gibson, Seaborg, and Grahame, however, did not admit the necessity of the above assumption in studying the emissions of gamma-rays from lead and iron, bombarded with  $\text{Bn} + \text{Be}$  fast neutrons. More exact estimation of the effect was made by using  $\text{Ra} + \text{Be}$  neutron source. Attention was paid for diminishing the wall effect. The results obtained confirmed the existence of the effect discovered by Kikuchi and others.

Author.

111. **Vibrational analysis of ultraviolet bands of lithium, sodium and potassium molecules.** H. Yoshinaga. *Proc. Phys.-Math.*

*Soc. Japan*, III, 19, 1073-1083 (1937).—More than one hundred band heads were already found in the observation of six ultraviolet band systems of  $\text{Na}_2$  molecule. The molecular const. of these band systems, together with those one band system of  $\text{Na}_2$  molecule and five band systems of  $\text{K}_2$  molecule which were newly found by the author, were calcd. in the vibrational analysis. The disson. products, the disson. energy and the symbol of the upper state of all ultraviolet band systems of  $\text{Li}_2$ ,  $\text{Na}_2$  and  $\text{K}_2$  molecules, could be detd. by comparing the corresponding band systems from the following three facts. i) The intensity distribution and the molecular consts. of the corresponding band systems of these three molecules are similar to one another. ii) The disson. energy  $D$  calcd. by Birge-Sponer's method is greater than the true value of  $D_0$ , so there holds the relation:  $\nu_{00} + D' - D_0'' > \text{excitation energy of disson. products } \nu_{00} + D' - D''$ . iii) All the upper states of these band systems are single.

Author.

**112. On the interaction of elementary particles. II.** H. Yukawa and S. Sakata. *Proc. Phys. Math. Soc. Japan*, 19, 1084-1093 (1938).—In the previous papers, (Yukawa, *Proc. Phys.-Math. Soc. Japan*, 17, 48 (1935)) one of the authors introduced a new field, which was responsible for the short range exchange force between the neutron and the proton as well as for the  $\beta$ -disintegration. This field turned out to be accompanied by quanta each with the charge either  $+e$  or  $-e$ , the mass about  $1/10$  of that of the proton and zero or integer spin, obeying the Bose statistics. In this paper, the quantization of the new field was performed which was represented by two scalar functions complex conjugate to each other. The interaction of this field with the heavy particle was dealt with as that of the electromagnetic field with the charged particle. The exchange force of the Heisenberg type between the neutron and the proton, can be obtained, but with wrong sign. The interaction between two neutrons or two protons, which is deduced as higher order effect is too small by a factor 10. Thus, the intro-

duction of non-scalar field seems to be necessitated. The problem of passage of high energy-heavy quanta through matter was considered and the cross sections for typical processes were calcd.

Authors.

**113. On the molecular spectrum of hydrogen emitted by an arc discharge.** H. Hasunuma. *Proc. Phys.-Math. Soc. Japan*, 20, 125 (1938).—The spectrum of an arc run in  $\text{H}_2$  at about 1 atm. pressure and of a current strength of 2.6 amp. was investigated with a  $3.2 \text{ \AA/mm}$  dispersion in the region from green to red. The spectrum was very much different in relative intensity of lines from the ordinary one. There was also a large number of intense new lines. The latter belonged mostly to higher rotational numbers of the  $0-0$  or  $1-1$  bands of  $3p^3\pi-2s\sigma$  ( $\alpha$ -bands), and  $3d^3\Sigma$ ,  $\pi$ ,  $d-2p^3\pi$ . Each rotational branch has been extended very far, for example, in the R-branch of  $3d^3\Sigma-2p^3\pi$ ,  $0-0$  band, beyond the 20th member. The maximum intensity lies at the 6th or 7th member for each branch. For some bands the series stopped abruptly at a certain member. This was ascribed to perturbations among various upper levels.

Author.

**114. Absorption spectrum and molecular structure. I Aromatic amines.** S. Kato and F. Someno. *Sci. Papers Inst. Phys. Research*, 33, 206-230 (1937).—A strong diffuse absorption starting at about  $\lambda \ 2500 \text{ \AA}$  due to every aromatic amine seem to correspond definitely to far ultra-violet bands of  $\text{NH}_3$ , whose absorption represents the convergence point of Rydberg series involving the excitation of the normal  $[\text{Za}]$  to the lowest excited state ( $3s$ ) of a non-bonding  $2p(z)$  electron of the single bonded trivalent nitrogen. Since the excited orbital ( $3s$ ) partly overlapped the phenyl radical or around an atom group, the authors considered the electronic interactions between the amino and the phenyl radicals containing both loose bonds. Taking cognizance of the observed spectra, the authors concluded that the pairing of  $2p(z)$  electron is not destroyed by the effect of strong interac-

tion. The salt formation should probably be caused by the destruction of the electron pairing of  $2p(z)$ . Investigation on the complicated aromatic amines suggests that the excited orbitals ( $3s$ ) should be nearly the same as in aniline as well as in normal orbitals ( $Z$ ), in order that the compounds may give a spectrum in the gaseous state or in ether and conc.  $H_2SO_4$  solns., having a close resemblance to that of aniline. Some specific characters were found in their spectra according to the number or nature of the substituents replaced in the N atom of the amino radical.

Authors.

**115. Application of interference spectro-scope to a study of the fine structure of a molecular spectrum.** N. Imanishi. *Bull. Chem. Soc. Japan*, **13**, 77-84 (1938).—By means of a crossed spectroscope which consisted of Michelson échelon lattice or Lummer-Gehrcke interference plate, the fine structure of  $\lambda$  6400 Å,  $3s^2\ ^3\Sigma \rightarrow 2p\pi^3\ ^3\Pi$ ,  $o \rightarrow o$  of the helium band spectrum was studied. The effect of the isotope of Au was also studied from the molecular spectrum of AuII.

J. C. L.

**116. Dissociation of molecules in the carbon stars.** Y. Fujita. *Proc. Phys.-Math. Soc. Japan*, **III**, 20, 149-159 (1938).—As to the carbon stars whose redness may have some influence on the interpretation of their physical character, the author tried to calc. the molecular abundance and to discuss the intensity variation in the molecular band. He applied new formulae to the electron pressure and the surface gravity, taking the luminosity of T and N stars into account. He explained

the scattering of CN and  $C_2$  band intensities in these stars as due to the difference in the sequences of luminosity, mass and temp.

Author.

**117. The spin angular momentum of the electron.** U. Kakinuma. *Sci. Papers Inst. Chem. Research*, **34**, 189-193 (1938).—The author proposes a theory which is different from the predecessors' in the fact that the classical formula for the density of the angular momentum of a light wave,  $m=[rS]/c^2$ , is applied to the spherical electron as discussed in the previous papers (*This Abstracts*, No. 40), and a plausible physical interpretation of the spin is given by taking a special set of the quantum numbers  $(n, l, m)=(\frac{1}{2}, 0, \frac{1}{2})$ . Thus it is concluded that the intrinsic angular momentum of the electron is  $\frac{1}{2}h$ . Author.

**118. The near infra-red spectrum of HgI.** T. Suga, M. Kamiyama and T. Sugiura. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 32-49 (1937).—Using a 30 amp. mercury arc as the source of light, and in such a long exposure as 100 hrs., HgI spectrum in the near infra-red region was investigated. Compared with the previous expt. by the authors, the accuracy of the measurement was considerably improved (error  $\pm 0.01$  Å) by the use of a plane grating and a 1 metre objective lens, instead of the prism spectrograph. Among the 214 lines in the region between  $\lambda$  6700 and  $\lambda$  13700 Å, about 50 line were newly found, of which 24 lines were designated into different series. Although rather narrow in the range, remarkably high sensitivity of the "Sakura" 950 film was noticed in the region near  $\lambda$  10000 Å.

Authors.

### 3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

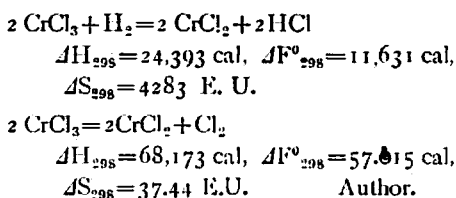
**119. Magneto-optical molecular rotations of electrolytes in undissociated States.** A. Okazaki. *Mem. Ryojun Coll. Eng.*, **10**, 115 (1937).—The corrected molecular rotations  $M[D]$  of some electrolytes in

undissocd. states, i.e. HCl, HBr and HI in liquid state, and NaCl, KCl,  $CaF_2$  and  $NaClO_3$  in solid state, have been calc. from the data for the magneto-optical rotations which had been obtained for D-lines by some investigators.

From comparison with the values of  $M[D]$  in dissociated states, it is found that for HCl, HBr, HI, NaCl and KCl, decrease in the corrected molecular rotation takes place in formation of molecules from free ions as in the case of the molecular refraction. Author.

120. On the reduction equilibrium of chromic chloride by hydrogen. K. Sano. *J. Chem. Soc. Japan*, 59, 17-19 (1938).—The reduction equil. of chromic chloride by hydrogen was studied by the static method at 627°~696° K and the following relation was obtained,  $\log K_p = \frac{-4,871.043}{T} + 8.3457$ .

From the result obtained some thermodynamical values were calcd. as follows:



121. The Faraday effect of strong electrolytes in aqueous solutions. VI. (Utilization of the data of other investigators) A. Okazaki. *Mem. of Ryōjun Coll. of Eng.*, 10, 89 (1937).—From the data for the magneto-optical rotation of a number of electrolytes in aqueous solns. obtained by other investigators, variation with concentration of the corrected molecular rotation  $M[D_2]$  was studied. It was found that the  $M[D_2]$ —values of HCl, HBr, HI, CdCl<sub>2</sub>, AlCl<sub>3</sub>, CsBr, CdBr<sub>2</sub>, NH<sub>4</sub>Br, CdI<sub>2</sub> and CH<sub>3</sub>COOLi decrease with increasing concn, while those of HNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, LiClO<sub>4</sub>, HIO<sub>3</sub>, LiIO<sub>3</sub> increase and that of CH<sub>3</sub>COOH is, in practice, independent of the concentration.

The  $M[D_2]$ —values at infinite dilution were determined by graphical extrapolation. Most of them have proved to be given by the sum of the corrected ionic rotations.

Author.

122. On Bjerrum's theory of strong electrolytes. S. Kaneko. *J. Chem. Soc.*

*Japan*, 58-62 (1938).—Concerning the activity coeff. of strong electrolytes in the dilute soln., the following formula was obtained both from Bjerrum's theory and the author's theory (Researches of the Electrotechnical Laboratory No. 403):

$$\ln \gamma = -4\pi n \int_a^b c - \frac{\epsilon^2 z^2}{DkT} r^2 dr - \frac{\epsilon^2 z^2}{2DkT} \frac{x}{xb}$$

$$b = \frac{\epsilon^2 z^2}{2DkT}$$

where  $\gamma$  is the mean activity coeff.,  $n$  the number of molecules in unit volume,  $a$  the mean diameter of ions,  $\epsilon$  the charge of electron,  $z$  the valency of ions,  $r$  the distance from the centre of the ion,  $D$  the dielectric const. of the solvent, and  $x$  the reciprocal of the thickness of ionic atm. Author.

123. The charge of an electron and the equivalent conductivity of strong electrolytes. S. Kaneko. *Bull. Electrotechn. Laboratory*, 1, 436-437 (1937).—From the data of the equivalent conductivity of KCl soln. at 25°C measured by Shedrovsky, the charge of an electron was calcd. by Onsager's theory and the value  $4.793 \times 10^{-10}$  e.s.u. was obtained. Author.

124. The foundation of the theory of strong electrolytes. S. Kaneko. *J. Chem. Soc. Japan*, 59, 299-303 (1938).—The foundation of Debye-Hückel's theory of strong electrolytes was verified from a statistical mechanics, and the exact formulae of activity coeff., osmotic coeff. and heat of dilution were deduced. Author.

125. The individual activity coefficient of ions and the velocity of reactions. S. Kaneko. *J. Chem. Soc. Japan*, 59, 295-298 (1938).—The author proved that there was no contradiction between Brönsted's theory about the velocity of reactions and the theory that the author proposed about the individual activity coeff. of ions in the mixture of electrolytes in his previous paper, and gave a few examples to make the meaning of the individual activity coeff. clearer.

J. C. L.



126. **The adsorption of helium on charcoal below 78°K., and production and thermometry of low temperatures.** E. Kanda. *Bull. Chem. Soc. Japan*, **13**, 241-246 (1938).—The adsorption of helium on charcoal below 78°K. was measured and the heat of sorption was detd. Systematical trials of the desorption method for the purpose of obtaining low temp. without liquid helium were described. Resistance thermometers of manganin and of constantan were calibrated

with the helium gas thermometer down to 6°K. Author.

127. **On the hydrogen peroxide electrode.** K. Kodama and T. Onizuka. *Inst. of Biochem., Kyushu Imp. Univ., Fukuoka*.—In the cell Pt.  $\text{H}_2\text{O}_2\text{H}^+/\text{satd. KCl}/\text{satd. KCl, HgCl, Hg}$ , the effects of the concn. of hydrogen peroxide and hydrogen ion were studied. It was found that the equation  $E = E_0 - 51.8 \times \text{pH}$  held at 20°C. Between pH 0.117 and pH 6.97 Authors.

#### 4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

128. **On the Liesegang phenomena under the electric field.** T. Okaya. *Japan. J. Phys.*, **12**, 9-25 (1937).—When a capillary tube filled with gelatine impregnated with a soln. of potassium bichromate is put in contact with a soln. of silver nitrate at one end, the silver ions begin to diffuse through the gelatine and form discrete and separate pptn. layers of silver bichromate at such a place  $l_n$  from the contact end and at a moment  $t_n$  as satisfy the relation:  $\beta_0 = l_n / \sqrt{t_n}$ ,  $\beta_0$  being a const. The author observed that this relation held even when an electric potential difference  $V$  was applied between both end of the capillary tube. In this case, the const.  $\beta$  was related linearly to  $V$  in such a way as  $\beta = \beta_0 (1 - \gamma V)$ . He also investigated both theoretically and exptly. the relation which held between  $l_n$  or  $t_n$  and the order number  $n$  of the pptn. layers. He studied theoretically the cases of rhythmic pptn. and obtained the expression for the pptn. energy which must be const. for every pptn. layer and for each system of expts. From the exptl. data, he confirmed that  $\omega$  was really const. and nearly equal to 17.8 kcal. per ion-molecule of silver even under the electric field. He also found that the diffusion const.  $a$  and the mobility  $x$  of silver ions can be given approximately by  $a = a_0 (1 + mV)^{-\frac{1}{2}}$ ,  $x = x_0 (1 - mV)$ , provided that  $V$  is not large. The temp. effects on these const.

$\beta$ ,  $a$  and  $x$  were also investigated.

Author.

129. **Studies on the physico-chemical properties and the constitution of thermoreversible gel. I, II and III.** F. Hirata. *J. Chem. Soc. Japan*, **58**, 1156-1162 (1937).—The measurements made by the author on sol and gel of gelatine on their scattering of light, electrolytic conductivity, ultrafiltration, refractive index and the rigidity of gelatine gel are given. The following empirical equation was obtained:  $X_0 \cdot P = \frac{a \cdot \varepsilon}{1 - \beta \cdot \varepsilon^2}$ , where  $a$  and  $\beta$  are const.,  $X_0 \cdot P$  the displacement of gel, produced by a const. pressure  $P$  on the axis of capillary tube of the special app. for measurement of rigidity of gel used by the author and  $\varepsilon$  the dielectric const. of the intermicellar liquid of the gel. In the case when  $P = 6 \times 10^4$  (dyne/cm<sup>2</sup>), the numerical values of  $a$  and  $\beta$  were computed as  $2.082 \times 10^{-6}$ ,  $+1.602 \times 10^{-4}$ , resp. By the aid of these results, the constitution of thermoreversible gel of gelatine is discussed and the conclusion is reached that the cause of the change of rigidity of gel due to temp. can be ascribed to the change of dielectric const. of intermicellar liquid of the gel due to temp. and that the nature of the intermicellar forces which cause the rigidity of gel may be an electric dipolar one. Author.

130. **A new theory of wetting-out action.** K. Hishiyama and M. Sekido. *J. Soc. Textile Industry, Japan*, 3, 545-565 (1937).—The authors have studied on the theory of wetting-out action of solns. against textile materials, containing wetting-out agent, and the results obtained are as follows:

1) The essential force of wetting-out action is an interfacial expansion, and not a tension, which occurs on the interface of a liquid against a solid. The surface tension of a liquid against air and the interfacial expansion of the liquid against a solid have important relations to wetting. The interfacial expansion coincides vectorically with the adhesion tension (Haftspannung), which is assumed to be the difference between the interfacial tensions of the solid.

2) Let  $\sigma$  be the surface tension of a liquid against air, and  $\varepsilon$  its interfacial expansion against a solid. If a drop of the liquid lies upon the solid surface, two forces act at the point O. When the drop remains lying in equilibrium condition upon the solid surface with formation of angle of contact  $\theta$ , the cosine of the contact angle indicates the ratio of  $\varepsilon$  to  $\sigma$ , namely,

$$\cos \theta = \varepsilon / \sigma \quad \text{or} \quad \varepsilon = \sigma \cdot \cos \theta.$$

If the contact angle is smaller than  $90^\circ$ , as in the case of a drop of quicksilver lying on the surface of a glass plate, an interfacial tension occurs on the interface of the liquid against the solid.

3) The surface tension which acts in the case of wetting is dynamic, and not static, and the dynamic tension is always not so small. The dynamic surface tension, which acts in the case of high rate of wetting, is nearly equal to that of pure water. It is recognised that the surface tensions of a pure liquid, such as water, has in most cases the

same magnitude either in the static state or in the dynamic.

4) Although the static surface tension of water is remarkably lowered by the presence of wetting-out agent, its substantial action is to enlarge the contact angle without noticeably depressing the dynamic tension. The wetting power of a soln. against a textile material is represented by the product of the dynamic surface tension and the cosine of the contact angle.

5) The wetting-out action is a dynamic phenomenon. Therefore, in testing the wetting power of a soln., the rate of wetting must be measured at its various stages. Authors.

131. **The catalytic action of colloidal constituents of soils on the conversion of cyanamide.** S. Yoneda. *Dōjyo-hiryō*, 11, 446-454 (1937).—To study the relative ability of some colloidal constituents of ordinary soils on the conversion of cyanamide, various substances were added to its aqueous soln. at  $50^\circ\text{C}$ . At certain intervals the content of cyanamide-, urea- and dicyandiamide-nitrogen was determined. The results may be summarized as follows. Of the greatest catalytic activity to form urea was manganese dioxide hydrate; next to it were manganese dioxide and iron hydroxide. Manganese hydroxide showed catalytic ability to form dicyandiamide. Iron oxide, aluminium hydroxide, colloidal silica gel, fuller's earth, humic acid and activated charcoal had a very slight ability to convert cyanamide. As some investigators showed, most of cyanamide was transformed to dicyandiamide in the alkaline soln. of pH 9.2, but this reaction was modified to form urea and dicyandiamide simultaneously, when iron hydroxide or manganese dioxide hydrate was added to this soln.

Author.