

ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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1—GENERAL AND PHYSICAL CHEMISTRY

132. **Discontinuous change in magnetization in ferromagnetic substances.** K. Murakawa. *Proc. Phys.-Math. Soc. Japan*, 18, 380—401 (1936) and 19, 715—733 (1937).—When a coil is wound around a ferromagnetic wire and is connected to a Braun tube or an electromagnetic oscillograph through an amplifier, the transient voltage induced in the coil can be recorded when the magnetic field, in which the ferromagnetic wire is placed, is varied. If the rate of change of the magnetic field is sufficiently slow, the oscillogram consists of isolated peaks or isolated groups of peaks. The peak or the group of peaks corresponds to a path in the ferromagnetic wire along which the reversal of magnetization takes place, starting from a reversal nucleus. The reversal nuclei are produced not simultaneously but one after another when the strength of the applied field increases; the ferromagnetic wire is thus gradually filled with the paths of reversed magnetization, until the direction of magnetization of each part of the wire coincides with that of the easiest magnetization. The velocity of propagation of reversal was measured from the oscillogram. The velocity of propagation depends on the radius of the ferromagnetic wire examd.

Author.

133. **On the inner potentials of graphite and molybdenite.** R. Ueda. *Proc. Phys.-Math. Soc. Japan*, 20, 280—287 (1938).—The values of the mean inner potential of graphite and molybdenite were precisely detd. by analysing cathode ray reflection spectra. They

were found to be 13.0 volts for graphite and 19.5 volts for molybdenite. The apparent decrease of inner potential in low order reflections, which was first observed by Yamaguti, was studied exptl. in detail and compared with the theoretical values calcd. by Bethe's theory.

Author.

134. **Constitution and viscosity association of high-molecular-weight hydrocarbons.** B. Yamaguchi. *Bull. Chem. Soc. Japan*, 13, 61—77 (1938).—The relation between the chem. structure and the viscosity assn. of high-molecular-weight hydrocarbons, such as those present in lubricating oil fractions was studied. An equation expressing the relation in lubricating oils between viscosity assn. and viscosity-temp. coeff. was established, and, in order to study their viscosity assn. in relation to their chem. structure, calcs. of viscosity assn. were made with the aid of the equation for a number of high-molecular-weight hydrocarbons whose viscosity-temp. coeff. and chem. structure are known. Interesting conclusions were drawn for these hydrocarbons in connection with the effect of chem. structure on the viscosity-temp. coeff.

Author.

135. **Studies on lubricating oils. III. Viscosities of hydroaromatic hydrocarbons.** I. Kagehira. *Report of the Imp. Naval Fuel Depot*, 97, 35—43 (1935).—In the previous paper (I), the writer stated that hydroacenaphthenes were more viscous than hydrodiphenyls and that partially hydrogenated

acenaphthene or pyrene which contd. the benzene ring in the molecule was more viscous than its saturated compound, but in the case of partially hydrogenated compd. of naphthalene or diphenyl, a different phenomenon was observed. In this paper, the writer discussed these phenomena from the standpoint of the molecular assocn. Dr. T. Ishikawa has proposed the following viscosity formula for binary mix., taking the assocn. degrees of constituents into consideration, $\eta =$

$\eta_1 + (\eta_2 - \eta_1) \frac{k_2 a_2 Z_m}{k_1 a_1 (1 - Z_m) + k_2 a_2 Z_m}$, where η_1 , η_2 and η are viscosities of the components—1, 2 and their mixture resp.; Z_m , a molar fraction of the component 2; k_1 and k_2 , field consts. of the components 1 and 2; a_1 and a_2 , assocn. degrees of components 1 and 2 resp. By putting in this formula, the values of viscosities of benzene solns. of hydroaromatic hydrocarbons from 0.1 to 0.9 molar fraction and by calcg.

for every molar fraction, $\left(\frac{k_2 a_2}{k_1 a_1}\right) Z_m = 0$ and $\left(\frac{k_2 a_2}{k_1 a_1}\right) Z_m = 1$ are obtained. If k_1 , k_2 and the assocn. degree of benzene are assumed to be const. for all cases and, in the case of $\left(\frac{k_2 a_2}{k_1 a_1}\right) Z_m = 0$, assocd. molecules are to be almost completely dissocd. to single molecules, then the assocn. degrees of hydroaromatic compds. will be obtained from the following equation:

$$\left(\frac{k_2 a_2}{k_1 a_1}\right) Z_m = 1$$

$$\left(\frac{k_2 a_2}{k_1 a_1}\right) Z_m = 0$$

From the results obtained, the writer concluded that: (i) viscosities of hydroacenaphthenes higher than those of hydro-diphenyls seem to depend on their higher degrees of molecular assocn. and (ii) that tetrahydronaphthalene or phenylcyclohexane is less viscous than decahydronaphthalene or dicyclohexyl seems to depend on the fact that the benzene ring in the molecules of the former compounds decreases the degrees of their molecular assocn., but, (iii) the benzene ring in the tetrahydroacenaphthene- or decahydro-pyrene-molecule increases its degree of

molecular assocn. and thus the viscosity of the unstd. compound becomes higher than the std. compound. J.C.L.

136. Decomposition rate of tetralin peroxide. V. Effect of prooxygens on the rate of decomposition of peroxyde. T. Yamada. *J. Soc. Chem. Ind. Japan*, 40, 907—909 (1937).—In the continued study concerning the effect of antioxidant on the rate of decompn. of tetralin peroxide, the effect of prooxygens was studied. Prooxygens used are Mn-, Co-, and Pb-oleates. Other exptl. conditions were the same as in the preceding reports. The result obtained was this: these prooxygens elevated the reaction order from the first, which was observed when no catalyzer was added, to the second or the third. Some explanations were given from the rate of diminution of activity of prooxygens for the decompn. of tetralin peroxide. Author.

137. Expansion and pressure coefficients of nitrogen, hydrogen, helium and neon, and the absolute temperature of 0°C. J. Ôishi. *Bull. Inst. Phys. Chem. Research*, 16, 241—257 (1937).—By means of a gas thermometer, vital parts of which were made of Jena glass 1565^{III}, the mean expansion coefficient α_N and the mean pressure coefficient β_N of the gases for the temp. range of 0°—100°C and for the ice-point press. of 1000 mm Hg were found as follows:

	$\alpha_N \cdot 10^7$	$\beta_N \cdot 10^7$
N ₂	36729	36745
H ₂	36586	36619
He	36580	36604
Ne	36598	36616

Using the values $\left(\frac{d(pv)}{dp}\right)_0$ and $\left(\frac{p(pv)}{dp}\right)_{100}$ given by Holbom and Otto and others for the gases, the values of τ_α and τ_β , which are the expansion and the pressure coeff. resp. at the Avogadro state, were calcd. The results are as follows: The results for nitrogen, hy-

and c and d are the concn. (mol/l.) and the thickness (cm.) of layer of the soln. resp. For substances whose circular dichroism is unknown the following relation may be used :

$$2\theta = 2\sqrt{\frac{I}{I_0}} e^{\frac{1}{2}\epsilon cd},$$

where I and I_0 are intensities of the light before and after traversing the soln. and ϵ is the molar extinction coeff. of the racemic substance. Applying the latter equation for colourless substances, the most suitable angle for half-shadow polarimetry was found to be 7.5° to 8° , which coincides with usual practice.

Author.

141. **X-ray diffraction haloes appearing wire on Laue-photographs taken with drawn wire of aluminium.** Y. Seiki. *J. Sci. Hiroshima Univ.*, 8, 99—102 (1938).—X-ray diffraction haloes appearing on Laue-photographs, of end-on view, of aluminium wire prepd. by drawing always in the same direction were studied minutely in the present expt. Author.

142. **On the interaction of elementary particles. III.** H. Yukawa, S. Sakata and M. Taketani. *Proc. Phys.-Math. Soc. Japan*, 20, 319—340 (1938).—The linear equations for the new field, which was considered in the first and second parts of this paper, are constructed as a generalization of Maxwell's equation for the electromagnetic field. The field is thus described by two four vectors and two six vectors, which are conjugate complex to each other resp. The quantization of this field is performed and it is shown that the quanta accompanying it have each spin 1. The interaction of these quanta with the electromagnetic field is discussed and it is found that each of them has the magnetic moment of the magnitude $e\frac{h}{2\pi} m_0 c$ approximately.

Thus, the anomalous magnetic moments of the neutron and the proton can be attributed to the virtual presence of the heavy quanta. As a consequence of the interaction between this field with the heavy particle, the exchange forces of Majorana and Heisenberg types, are obtained which are correct both in sign and

magnitude. Finally, the probability of annihilation of the heavy quantum in free space by emitting a pos. or neg. electron and a neutrino or an antineutrino is calcd. and its bearing on the problem of the hard component of the cosmic ray is discussed. Authors.

143. **Specific gravities of aqueous solutions of inorganic neutral salts and fatty acid salts.** E. Kin and K. Ri. *Chosen Kagakukai Kaihō*, 9, 1—6 (1938).—The specific gravities of aqueous solns. of various concns. of the salts mentioned below were measured at 20°C by means of a pycnometer holding 5 cc: NaCl, KCl, $\text{MgCl} \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, NaBr, NaNO_3 , KNO_3 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, Na_2SO_4 , K_2SO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, KSCN, etc. J. C. I.

144. **On the rhythmic precipitation in the electric field. Note III.** T. Okaya. *Proc. Phys.-Math. Soc. Japan*, 20, 110—119 (1938).—The rhythmic pptn. of the silver bichromate in gelatin in the electric field was studied both theoretically and exptl. 1) The pptn. energy of a molecule-ion of silver for the formation of silver bichromate is quite const. even in the case where the electric field is applied and is independent of the order number of pptn. layer. Its numerical value is 17.8 kil. cal. 2) If the applied electric field V is not strong ($-6 < V < +6$ volts), the diffusion coeff. a of silver ions which move through the gelatin may be expressed by $a = a_0(1 + mV)^{-\frac{1}{2}}$. 3) The mobility of ions x may also be given by $x = x_0(1 - mV)$ with the same numerical factor m as in 2). 4) The ratio $\beta = \ln \sqrt{t_m}$ of the position $\ln$ to the square root of time of formation t of the n -th. pptn. layer is approximately independent of the order number n . It may be expressed by $\beta = \beta_0(1 - \gamma V)$, where γ is a certain numerical factor. These coeffs. a , x , β as well as m and γ were measured or deduced for the exptl. systems taken into consideration by the author. Author.

145. An investigation on oxidation of crystal surfaces with electron diffraction method. II. Copper single crystals.

T. Yamaguti. *Proc. Phys.-Math. Soc. Japan*, III, 20, 230—241 (1938).—Electron diffractions from mineral cuprite and single crystals of cuprous oxide, the latter being obtained by oxidizing single crystals of copper at high temps., were investigated. In the spot patterns, some spots corresponding to diffractions forbidden from the structure factor were observed, to which an interpretation was given. Orientations of the oxide single crystals to their mother copper single crystals are detd. by the analysis of the spot patterns from the crystals of both kinds, and three different relative orientations are observed, the presence of which is to be attributed to the presence of three different modes of transpositions, and is not due to recrystallizations of copper atoms in forming the cuprous oxide lattice from the copper lattice. Lattice consts. of cuprous oxide formed under different conditions and mineral cuprite are detd. from the spot patterns, knowing the wave-lengths of electrons from the diffraction rings of magnesium oxide powder, which was pptd. on the surfaces of the specimens. Author.

146. The effect of the high tension electrical discharge on the contact-catalytic reaction. I. Seto and M. Ozaki.

Gakujitu Kyōhō, 13, 420—422 (1938).—The authors have studied such catalytic reactions under the influence of the high tension electrical discharge, as the hydrogenation of soya bean oil (*J. Soc. Chem. Ind., Japan*, 38, 197, (1935); 40, 418, (1937)), the reduction of nitrobenzene (*ibid.*, 40, 189, (1937)), and that of menthone. In these expts., the reacting liquid was mixed with a nickel catalyst on kieselguhr in suspended state and placed in a ozoniser-type reaction vessel which was kept at a cons. t. temp. In case the reacting liquid had poor insulating power, it was dissolved in a suitable solvent, paraffin oil, in order that a sufficiently high electrical tension could be applied on the reaction system. The reaction was carried out

by blowing hydrogen through the reacting mixt. from the bottom of the vessel and at the same time applying the high electrical tension on the electrodes placed inside and outside the vessel. As the result of the expts., it was found that the effect of the electrical discharge was remarkable in promoting the rate of the catalytic reaction, especially when the insulating power of the reacting mixt. and accordingly the discharging voltage was high, but the increase of the intensity of the discharging current had unfavourable effect on promotion of the reaction. Therefore, it seems to the authors that, in these expts., the statical electrical tension may play some important rôles in the heterogeneous reaction proceeding on the surface of the catalyst. Authors.

147. The motion of ethylene halide molecules in crystals as revealed by the Raman effect. S. Mizushima and Y. Morino.

Bull. Chem. Soc. Japan, 13, 182—189 (1938).—In the region of the unmodified line there have been observed for crystalline ethylene halides some Raman lines which correspond to motions of molecule as a whole, but not to internal normal vibrations. For ethylene bromide a considerable change in these low frequency lines was observed between the spectrum at -40°C . and that at 0°C . and it is highly probable that this change is caused at the transition temp. (-24°C .) observed in the thermal measurement. An explanation for these exptl. results was suggested to identify these lines with lattice frequencies and to regard the transition point as the temp. at which the one dimensional molecular rotation sets in.

Authors.

148. The normal vibrations of ethylene halides. Y. Morino.

Bull. Chem. Soc. Japan, 13, 180—197 (1938).—To treat mathematically C—H vibrations as well as their effects on chain frequencies, the 18 normal modes of vibration were treated assuming the ethylene halide molecule $\text{C}_2\text{H}_4\text{X}_2$ to be a system of a particles. The conclusion is that there is as much lower frequencies as those of the four

body problem $\text{N}-(\text{CH}_3)-(\text{CH}_2)-\text{X}$, even though the motion of hydrogen atoms is taken into consideration. Author.

149. **Dipole moments of benzil and stilbene dichloride.** K. Higashi. *Bull. Chem. Soc. Japan*, **13**, 158—166 (1938).—The dipole moments of benzil and stilbene dichloride were measured with the following results.

Benzil 3.62 D (25°) and 3.62 (50°) in benzene, 3.52 D (25°) and 3.46 D (50°) in carbon tetrachloride. α -Stilbene dichloride at 25° 1.45 D in benzene and 1.32 D in carbon tetrachloride. The results lead to the conclusion that the C-C bond in a benzil molecule should be a hybrid of single and double bonds.

Author.

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

150. **γ -ray activity induced in cadmium by slow neutron bombardment.** S. Nakagawa and I. Sumoto. *Proc. Imp. Acad.*, **14**, 106—107 (1938).—Activities induced in cadmium by bombarding neutrons were investigated. It was especially noted that the 45 minute period of activity was observed only by γ -rays. β -rays of the corresponding product is supposed to be either very weak or entirely suppressed. Authors.

151. **Infra-red absorption spectra and hydrogen bridge. I. Near infra-red spectra of inorganic oxyacids.** T. Sidei and K. Imahori. *Proc. Phys.-Math. Soc. Japan*, **III**, **20**, 304—311 (1938).—The near infra-red absorption spectrum of sulphuric acid at various concns. and temps. together with some preliminary accounts for nitric acid is presented in this paper. In the case of sulphuric acid at room temp. a broad band with a max. at 1.81μ was observed, and it was ascribed to the vibration characteristic of the motion of hydrogen against oxygen in the acid OH group. A similar band was observed in acid solns. When temp. rose the band at 1.81μ was weakened in its intensity and a new band at 1.5μ which was in the overtone region characteristic of the OH radical appeared increasing its intensity with temp. For fuming sulphuric acid and fuming nitric acid at room temp. the characteristic OH absorption bands lie at 1.5μ and 1.55μ resp. From

these facts the structures of these acids and their solns. together with the nature of the hydrogen bond were discussed. Author.

152. **Absorption bands of metallic complexes. I. The third bands.** R. Tsuchida. *J. Chem. Soc. Japan*, **59**, 586—596 (1938).—Absorption spectra of complex compds. usually consist of the first, the second and the third bands as well as those due to co-ordinated groups themselves. The origins of these absorption bands have been discussed in this series of papers. Postulating that, by absorption of a quant. $h\nu_3$ (ν_3 =the frequency of the third band), a kind of neutralization takes place between the central ion and one of the co-ordinated anion to produce an excited ionogen in the original seat of co-ordination, the following relation was derived: $h\nu_3 = S + P + E - J$, where E is the electron affinity of the anion, J the ionization energy of the central ion, S the co-ordination energy, and P the work of approach of the anion to the seat of co-ordination. The ultra-violet absorption band of solid alkali halide was explained as a special case of the third band. Examples of special bands, i.e., bands ascribed to co-ordinated groups themselves, were given and the end absorption explained. **II. The first bands.** *Ibid.*, 731—743 (1938).—The first band is ascribed to electron transitions in the unsatd. transition-shell of the central ion. The band, therefore, appears only when the

central ion is of a transition element. The shift of the first band by substitution of co-ordinated groups or ions may be explained by postulating that the electron transitions are more or less depressed by the negative field of the co-ordinated groups or ions. The depression may conveniently be represented by P , the energy of approach of the co-ordinated group or ion, i.e., the work done by the ligand, if it were to approach from infinity to the seat of co-ordination. The ascending order of P , i.e., the sequence of hypsochromic effect on the first band, is theoretically NH_3 , H_2O , F^- , Cl^- , Br^- , and I^- . The empirically obtained order of hypsochromic effect on the first band is NO_2^- , NH_3 , ONO^- , H_2O , NCS^- , NO_3^- , SO_4^{2-} , OH^- , $\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, Cl^- , CrO_4^{2-} , and Br^- . All the exper. rules so far obtained of the shifts of the first bands may be explained by the hypothesis. Careful observation of the first bands of nitro-ammine and nitrito-ammine cobaltic compds. led to the following conclusion. In $\text{Na}_3\text{Co}(\text{NO}_2)_6$, so-called sodium cobaltic nitrite or hexanitro-cobaltate, the NO_2^- ion is co-ordinated to the central cobaltic ion not by N, but by O. The complex should, therefore, be correctly called sodium hexanitrito-cobaltate. Author.

153. On the electronic structure of alloys. T. Muto. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 377—390 (1938).—From the rigorous point of view, Jones and Mott's method of attack of alloy-properties may be considered to be based on some ambiguous assumptions, although their theory was successful in explaining some of the phys. properties of alloys. In order to remove the ambiguities, the author worked theoretically the alloy problem by means of the ordinary perturbation theory in quant. mechs. combined with Nordheim's virtual system, and it was found that Jones and Mott's theory is approximately valid as far as the form and size of the Brillouin zone are concerned, but the amt. of energy discontinuity across the boundary planes can not be derived correctly from their

theory. By his general method of treatment mentioned above, the author was able to explain satisfactorily the abnormal change of a diamagnetic susceptibility of AuCu_3 -alloy in the order-disorder transition, which could not be accounted for by the Jones' theory of alloy. The fine structure of X-rays absorption edge of alloy and its electrical conductivity was theoretically discussed in accordance with the exper. observations. Author.

154. On the decomposition voltage of fused magnesium chloride. K. Sano. *Sci. Repts. Tohoku Imp. Univ.*, **I**, 26, 604—610 (1938).—The decompn. voltage of fused magnesium chloride was calcd. from the thermodynamical values of the chloride in the solid state detd. by the present writer in his previous report, and it was compared with those of other investigators. Author.

155. Electric conductivity of glasses and fused salts. S. Kaneko. *J. Chem. Soc. Japan*, **59**, 673—674 (1938).—Assuming that the ions in the soln. are vibrating incessantly and occasionally jumping from one place to another, the following relation between the specific conductivity κ of glasses or fused salts and absolute temp. T was found: $\log \kappa = -\frac{A}{T} + B$ where A and B are consts. Author.

156. Absorption spectra of thiocyanate compounds of metals. I. Y. Uzumasa, H. Okuno and K. Doi. *J. Chem. Soc. Japan*, **59**, 655—661 (1938).—The absorption spectra of thiocyanates of NH_4 , K, Ca, Ba, Mg, Zn, Cd, Be, Al, Hg(II) , Bi, Fe(III) , Ti (III, IV) and V (II, III, IV, V) were studied and their absorption curves were mapped after Hartley and Baly for the visible as well as the ultra-violet regions. For NH_4 , K, Ca, Ba, Mg, Zn, Cd, Be, Al and V (V), no selective absorption was observed, while for Hg , Bi, Fe, Ti and V (II, III, IV) there was found a characteristic band at wave number 3500 mm^{-1} . This band is possibly due, as Y. Shibata once suggested, to the complex ion

formed by the metallic and thiocyanate ions. Of the coloured thiocyanate complexes examd., bathochromic action of thiocyanate radical was in general observed. The aqueous soln. of free thiocyanic acid has also shown a band at 3500 mm^{-1} , for which some polymerization products of the acid are considered to be responsible. It is suggested that the characteristic band at 3500 mm^{-1} should be used for testing the purity of free thiocyanic acid or of thiocyanates which do not develop any selective band in the pure state.

Authors.

157. Researches on the concentration of hydrogen ions contained in the aqueous solutions of complex cobaltamines and their absorption spectra. IV. Aqueous solutions containing ethylene diamine. T. Uemura and N. Hirasawa. *Bull. Chem. Soc. Japan*, **13**, 377—387 (1938).—One of the writers (Uemura) has already discussed with H. Sueda on the spectrochem. effects given by the solns. of various cobaltamines. In the present research some complex cobaltamines that contain the ethylene diamine (abbreviation: en) molecules in their complex radicals were selected. 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 ions concn. Both configurations, cis- and trans-, of the three complex salts, $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{Cl}_2$, $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}_3$ and $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, show similar absorption curves in their alkali solns., 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 alkali 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.

158. The kinetic energy of an atom nucleus in Hartree-Fock's model. S. Tomonaga. *Sci. Papers Inst. Phys. Chem. Research*, **32**, 229—232 (1937).—In the calculation of the efficiency of an atom nucleus by the single body model it is difficult to separate the kinetic energy of the centre of gravity from the whole kinetic energy of the nucleus. Bathe and Rose studied the influence of the sepn. in a special case of the vibration model. The method is to use the wave function turning x_1 , the coordinate of the position of the material point, into

$$\xi_1 = x_1 - \frac{1}{\lambda(Z+N)} \sum_{j=1}^{N+Z} x_j, \text{ where } \lambda, \text{ the parameter,}$$

is taken as 1 to satisfy the condition of the minimum energy after integrating Hamilton's function.

J. C. L.

159. A Note on the Stark-effect of secondary spectrum of hydrogen. M. Kiuti and H. Hasunuma. *Proc. Phys.-Math. Soc. Japan*, **III**, **20**, 160—161 (1938).—The detached Stark-effect component observed in the P (2) and R (0) lines of the $\text{O}-4$, $\text{O}-3$ and $\text{O}-1$ bands of $3'\text{N}-2\text{p}'\Sigma$ is interpreted as due to forbidden transitions from $3\text{p}'\pi$, $v=0$, $K=1$ α to the respective end states of these lines. The $3\text{p}'\pi$, $v=0$, $K=1$ α term, having been newly ascertained by Richardson in the analysis of $3\text{p}'\pi-2\text{s}'Z$ bands, just falls close to the common upper level of the lines, $3'\text{N}$, $v=0$, $K=1$ α , and is to interact with the same in the presence of electric field.

Authors.

160. On the application of the vector model method to calculation of nuclear energy. T. Shimose. *Proc. Phys.-Math. Soc. Japan*, **III**, **20**, 83—84 (1938).—The vector model method, which has been used for the calcn. of electronic energy by Dirac and van Vleck, is also applicable for the calcn. of the 1st order energies of Wigner and Majorana in (2p)ⁿ. The author obtained the expressions of the first order energies and confirmed the formulae in Hund's papers by the vector model method.

J. C. L.

161. **Slowing down of neutrons by thin layers of paraffin.** S. Nishikawa, S. Nakagawa and I. Sumoto. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 1—6 (1937), with 6 figs.—An analysis of neutron groups which activate elements was made by the method of slowing down of neutrons by paraffin layers. Using comparatively thin plates of paraffin for a small successive variation of thickness, curves connecting the detected activity and paraffin thickness with and without absorbers were obtained for Ag, I and Br detectors. It is shown that these curves have some inflexions which indicate the existence of effective groups for the detectors used. Authors.

162. **On the energy loss of fast charged particles by pair creation.** M. Kobayashi and S. Ozaki. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 321—331 (1938).—A fast charged particle passing through matter can lose its energy by creating electron pairs directly in the field of an atom. According to the method of Williams and Weizsäcker, the authors have estimated the order of magnitude of the av. energy loss of a charged particle per collision with an atom in this way, and obtained the following results. The total energy loss of a fast electron due to pair creation is proportional to and smaller approximately by a factor α (the fine-structure const.) than that due to 'Bremsstrahlung'. A heavy particle with an elementary charge loses the equal amount of energy by pair creation as that of an electron of the same velocity. The greater part of the energy lost in this way is carried away by high energy pos. and neg. electrons. Since the energy of electrons produced by ionization is comparatively small, and the energy loss due to 'Bremsstrahlung' of a heavy charged particle with mass M is smaller by a factor $\left(\frac{m}{M}\right)^2$ than that for an electron with mass m of the same velocity, the energy transfer to fast light particles by a heavy particle with mass M , which is much greater than $\sqrt{\frac{1}{\alpha}}m$, will be almost entirely due to pair creation. And the greater part of cosmic ray

showers at depths in matter may be initiated by these pos. and neg. electrons created by heavy charged particles in this way. The energy loss due to pair creation increases rapidly with increasing energy of incident particles, and for sufficiently high energy ($\geq 10^4 Me^2$) it will be greater than the energy loss due to ionization which increases very slowly. Authors.

163. **On $3d^84s$ configuration of Ni. II.** T. Yamauchi. *Proc. Phys.-Math. Soc. Japan*, **III**, 20, 242—244 (1937).—The configuration of $3d^84s$ of NiII, analysed by Shenstone, is very near to LS coupling case, as is shown by the validity of Landé's g -formula except for few terms. Nevertheless, 4P terms are partly inverted, and the interval of two 2D terms, which is to be zero according to the LS formula, is larger than that of 2P . These suggest strong perturbation between 3P and 2D . In this note, these static energies of these two terms were very close by. They were indeed nearer than the values calcd. according to the first order theory, which might be attributed to the perturbation on 2D from $3d^9$ configuration. The anomalies of intervals and g -values were then satisfactorily accounted for. Author.

164. **On the thermo-luminescence of quartz exposed to X-rays.** T. Futagami. *Proc. Phys.-Math. Soc. Japan*, **III**, 20, 458—466 (1938).—Quartz, exposed to X rays, obtains a smoky colour, and if the crystal is heated, the colour will fade away, emitting thereby a blue thermo-luminescence. The absorption spectrum of coloured quartz was examd., and it was found that it extends all over the regions of infra-red, visible and ultra-violet spectra, and that there exist two flat maxima at $390 m\mu$ and $302 m\mu$. The intensity variations of the thermo-luminescence with respect to time and temp. were investigated by a rotating film app. The spectrum of the thermo-luminescence was obtained by a quartz spectrograph, and it was found to be a continuous one ranging from $610 m\mu$ to $385 m\mu$ with a maximum at $469 m\mu$. The

intensity distribution of the spectrum was also detd.
Author.

165. On the relation between the configuration of metallic complex salts and their absorption spectra. III. *cis*-trinitro-triammine-cobalt. H. Sueda. *J. Chem. Soc. Japan*, 59, 47—48 (1938).—*Cis*-trinitro-triammine-cobalt was prepd. and its absorption band proved to be identical with that expected from author's assumption given in the first paper.
Author.

166. Absorption bands of metallic complexes. III. The second bands. R. Tsuchida. *J. Chem. Soc. Japan*, 59, 819—832 (1938).—The absorption spectra of co-ordination compds. consist of the first, the second and the third bands as well as those due to ligands themselves. Some of the compds. may lack the first or the third band, but none of them the second. Postulating that by absorption of a quantum $h\nu_2$ (ν_2 =frequency of the second band) the co-ordinate linkage is temporarily broken to produce an excited metastable ligand in the original seat of co-

ordination, the following relations have been derived: $Q = P - R + S + \frac{\phi - \sum \phi_i}{n}$, and $S =$

$h\nu_2$, where Q is the heat formation per co-ordination, R the activation energy, S the co-ordination energy, ϕ the lattice energy of the co-ordination compd., ϕ_i 's the lattice energies of the component compds. of first order, and N the co-ordination number. The co-ordination energy, S ($h\nu_2$), may be taken as the measure of stability of the co-ordination compd. The order of hypsochromic effect of ligands on the second band gives the order of strength of the co-ordinate linkages between the central ion and the ligands. The order of stability has been detd. spectrochemically, viz., NH_3 , NO_2^- , ONO^- , H_2O , NCS^- , OH^- , NO_3^- , Cl^- , CO_3^{--} , Br^- . The substitution of ligands which proceeds naturally takes place in the direction, in which the value S increases, or in other words, the second band is displaced towards the shorter wave-lengths; whereas the stability of co-ordination compds. may be defined by S the photochemical stability should be given by $P - R$. Both the stabilities are compared with illustrations.
Author.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

167. On the additive properties of the strong electrolyte solution. S. Kaneko. *Bull. Electrotechn. Laboratory*, 2, 156—157 (1938).—The method of the least squares is applied to the calcn. of the most probable values when the additivity law holds on various properties of the strong electrolyte soln.
Author.

168. Determination of the vapour pressures of solid salts. II. Vapour pressure of alkali halides and their thermodynamic calculations K. Niwa. *J. Chem. Soc. Japan*, 59, 637—649 (1938).—In the previous work of this series the vapour pressure of solid mercuric halides was

detd. by Knudsen's effusion method applying a microbalance, and sufficiently accurate results were obtained. The present paper is concerned with a detn. of the vapour pressure of solid salts at higher temps. using a similar app. which was somewhat improved for this purpose. The vapour pressure of solid alkali halides was detd. between 500° and 840°C, and from those results obtained thermodynamic values, such as heat of sublimation, molecule energy, chem. const., free energy change of sublimation, entropy change of sublimation and entropy of salt vapour, were calcd., and a certain regularity was found to exist between the values obtained

and the crystallochemical consts. Author.

169. On the determination of surface conductivities in glass diaphragm for aqueous solutions of electrolytes. M. Nishikawa. *J. Electrochem. Assoc., Japan*, 6, 174—177 (1938).—In the expts. of electro-osmosis, streaming potential and the like, dilute solns. are often treated, and the surface conductance becomes important in the interstices of capillary or diaphragm materials. The scale of surface conductivity is expressed as x_s/x_o , that is the ratio of surface conductance to bulk conductance, and is calcd. as follows:

$$\frac{x_s - x_o}{x_o} = \frac{1 - x_o/k_e}{x_o/x_e - K/k_e}, \text{ where } x_o \text{ represents}$$

the specific conductivity in the inner part of liquid, x_o the effective conductivity, K the cell const. between both electrodes of the cell, and k_e the cell const. between diaphragm and electrode. The surface conductivity can be calcd. from this equation by the measurement of x_o and x_e . The author detd. the surface conductivities in hard glass diaphragm for dilute aqueous solns. of HCl, KOH, KCl, KNO₃, KH₂PO₄, K₂SO₄, K₂CO₃, K₃PO₄ and K₄Fe(CN)₆ and it was concluded that the ratio of surface conductance to bulk conductance increases remarkably as the concn. decreases. The surface conductivities were generally similar in salt solns. of the same concn. and increased slightly with the valencies of anion. In the case of acid or alkali, however, they showed far smaller values than those of the salts of the same concn. The surface conductivity also increases as the temp. decreases.

Author.

170. On the two-component system sulphur dioxide and potassium iodide. I. Mori. *Bull. Inst. Phys. Chem. Research*, 17, 342—354 (1938).—The vapour pressure depression of solns. of potassium iodide in liquid sulphur dioxide at various concns. was measured by the static method at 0°, 10° and 20°C. The relation between vapour pressures and concns. of the solns. may be represented satisfactorily by the following equations:

$$\begin{aligned} \text{at } 0^\circ\text{C } \left(\frac{0.1532 - N}{p - 889.5} \right) &= 0.00057443 \\ &- 0.0031203N + 0.0034265 e^{-\frac{0.58770}{N}} \\ &\quad (N = 0.1532 \sim 0.0214) \end{aligned}$$

$$\begin{aligned} \text{at } 10^\circ\text{C } \left(\frac{0.1892 - N}{p - 1018.7} \right) &= 0.00027500 \\ &- 0.0012775N + 0.0015914 e^{-\frac{0.60022}{N}} \\ &\quad (N = 0.1892 \sim 0.0229) \end{aligned}$$

$$\begin{aligned} \text{at } 20^\circ\text{C } \left(\frac{0.1546 - N}{p - 1943.3} \right) &= 0.00031095 \\ &- 0.0016670N + 0.0033262 e^{-\frac{0.67101}{N}} \\ &\quad (N = 0.1546 \sim 0.0150) \end{aligned}$$

where p is the vapour pressure in mm.Hg and N the mol fraction of KI. The composition of the molecular compd. formed between SO₂ and KI at 0° and -10°C was detd. by measuring the change in vapour pressure in varying the mol ratio of SO₂ to KI. The conclusion was drawn that the molecular compd. must have the compn. KI₂SO₂ at those temps., though Walden and Centnerszwer, and Foote and Fleischer had reported the existence of KI₄SO₂. Using the data obtained the free energy of formation of the molecular compd. and other thermodynamic quantities were calcd. Author.

171. The equilibrium diagram of the system — CaO·MgO·2SiO₂·MnO·TiO₂. U. Nishioka. *Metals*, 14, 138—140 (1938).—The equil. of diopside-pyrophanite system has been studied by means of the microscopic examn. of the quenched specimens under the metallurgical microscope, and a diagram has been proposed. The system is a simple eutectic type having an eutectic point at 1183° with 48 w. per cent of MnO·TiO₂. Author.

172. The equilibrium diagrams of the three binary systems (1) CaO·SiO₂·TiO₂·MgO·TiO₂, (2) CaO·MgO·2SiO₂·MnO·TiO₂ and (3) CaO·SiO₂·2CaO·Fe₂O₃. K. Iwase and U. Nishioka. *Sci. Repts. Tohoku Imp. Univ.*, 1, 26, 592—603 (1938).—The equil. diagrams of the three binary systems, CaO·SiO₂·TiO₂·MgO·TiO₂, CaO·MgO·2SiO₂·MnO·TiO₂ and CaO·SiO₂·2CaO·Fe₂O₃ were detd. by

means of microscopic examn. of specimens quenched from various temps. with a metalurgical microscope and in the case of $\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ system also by thermal analysis. These three binary systems are all of a simple eutectic type, having neither solid soln. nor compd. Authors.

173. Measurement of P_H considered from the theoretical stand-point of activity coefficients. S. Yoshida. *Shikisen*, 8, 147—155 (1937).—In the study of hydrogen ion concn., whether the soln. to be used is a weak electrolyte or a strong electrolyte soln. must be considered. In the case of weak electrolyte soln., Ostwald's dilution law is employed, but in the case of strong electrolyte soln. Debye-Hückel's or Ghosh's law is. The author's exptl. results show a bitter agreement with Ghosh's theory than with Debye-Hückel's. When the normal electrode potential of a calomel electrode is detd., the $N/100$ binary electrolyte soln., such as hydrochloric acid, is usually used to measure the activity of hydrogen ion according to Ghosh's theory.

Author.

174. The heat of formation and specific heat of tantalum nitride. S. Satoh. *Sci. Papers Inst. Phys. Chem. Research*, 34, 477—486 (1938).—Since the specific heat of tantalum nitride is not yet known, the mean specific heat of it was measured by means of the ice calorimeter over the three temp. ranges: 0° — 99.5°C , 0° — 305.3°C , 0° — 500.4°C , and the equation of the true specific heat was obtained: $C = 0.04785 + 7.068 \times 10^{-5}t - 5.808 \times 10^{-8}t^2$. By using these values, the heat of formation of tantalum nitride at 25°C was computed from the dissocn. press. of it at high temps. The result obtained is as follows: $\text{Ta} + \text{N} = \text{TaN} + 58650$. The relationship between the heats of formation of nitrides of the elements belonging to the fifth series, the fifth and sixth groups of the periodic table of the elements, and their atomic numbers is discussed.

Author.

175. The heat of formation and specific heat of calcium nitride. S. Satoh. *Sci. Papers Inst. Phys. Chem. Research*, 34, 584—595 (1938). As the specific heat of calcium nitride is not yet known, the mean specific heat of it was measured by the ice calorimeter over the three temp. ranges: 0° — 99.7°C , 0° — 304.3°C , and 0° — 500.3°C , and the equation of the true specific heat was obtained within the limit over the above temp. ranges: $C = 0.1817 + 1.273 \times 10^{-4}t + 1.388 \times 10^{-8}t^2$. By using these values, the heat of formation of calcium nitride was computed from the dissocn. pressure measured at high temps. The result obtained is as follows: $3\text{Ca} + \text{N}_2 = \text{Ca}_3\text{N}_2 + 108,200$. The relationship between the heats of formation of the nitrides of the elements belonging to the second group of periodic table and their atomic numbers is discussed.

Author.

176. Vapour pressure of the corrosive substances. IV. K. Arai and M. Kawabata. *Bull. Inst. Phys. Chem. Research*, 17, 229—308 (1938).—I. The vapour press. of phosphorus tribromide. The vapour press. of phosphorus tribromide was measured by the statical method in an all-glass app. (Jackson's glass-spring manometer). The expts. were made over temps. ranging from 40° to its boiling point, and the following equations, relating the vapour press. (p) with the absolute temp. (T), were calcd. from the results: $\log p = 7.67865 - \frac{2137.0}{T}$, $\log p = 7.5030 - \frac{2672.6}{T + 0.04286}$, and $\log p = -\frac{2131.4}{T} + 1.75 \log T - 0.0018752 T + 3.8611$. The boiling point obtained by the vapour press.-temp. curve is 172.8° . The latent heat of evaporation at the boiling point and the mean heat of evaporation over the temp. range studied were calcd. from the Clausius-Clapeyron formula, as follows: $\Delta H_{172.8} = 9704$ cal. $\Delta H_{\text{mean}} = 9789$ cal. The values of Trouton's const. indicate that phosphorus tribromide is a normal liquid.

II. The vapour press. of phosphorus trichloride. The vapour press. of phosphorus

trichloride was measured over temps. ranging from -20° to 70° , by the same method as in the previous case, and the following results were obtained. Three empirical equations relating vapour press. and absolute temp. were obtained: $\log p = 7.6455 - \frac{1657.3}{T}$, $\log p = 7.5030 - \frac{1959.0}{T + 0.338}$, and $\log p = -\frac{7157.1}{T} + 1.75 \log T + 0.0034216 T + 4.67002$. The boiling point was read as 74.7 at 760 mm from the p - T curve, and the latent heat of evaporation at the boiling point and the mean value the temp. range studied were calcd., as follows:— $\Delta H_{4.7} = 7414$ cal. $\Delta H_{\text{mean}} = 7584$ cal. From the values of Trouton's const. it must be concluded that phosphorus trichloride is a normal liquid. The freezing point was found to be 93.6° by the cooling curve method. Authors.

177. Atomic heat of nitrogen in various nitrides. I. S. Satoh. *Sci. Papers Inst. Phys. Chem. Research*, 34, 751–760 (1938).—The atomic heat of nitrogen was deduced from the molecular heats of various nitrides in order to find it for the purpose of applying Neumann-Kopp's law. It was found that the atomic heat of nitrogen is about 2.4 in case nitrogen forms nitrides with elements of small atomic numbers and is about 4 in case nitrogen forms nitrides with elements of large atomic numbers; and that, as a whole, it ranges between 2 and 5, considerably smaller than the value 6.2. The variation of atomic heats of nitrogen in some nitrides with temp. is also discussed. Author.

178. The specific heats of beryllium nitride, phosphorus nitride, and titanium nitride. S. Satoh. *Sci. Papers Inst. Phys. Chem. Research*, 34, 888–896 (1938).—The mean specific heat of beryllium nitride was measured by the ice calorimeter over three

temp. ranges $0^{\circ} \sim 99.5^{\circ}\text{C}$, $0^{\circ} \sim 303.3^{\circ}\text{C}$, and $0^{\circ} \sim 500.3^{\circ}\text{C}$, and the equation of the true specific heat within the limit stated by the above temp. ranges is obtained: $C = 0.2726 + 7.884 \times 10^{-4}t - 5.163 \times 10^{-7}t^2$. The mean specific heat of phosphorus nitride was detd. by the same method over two temp. ranges: $0^{\circ} \sim 99.6^{\circ}\text{C}$ and $0^{\circ} \sim 305.3^{\circ}\text{C}$, and the equation of the true specific heat within the limit stated is obtained: $C = 0.2027 + 6.252 \times 10^{-4}t$. The mean specific heat of titanium nitride was also detd. by the same method over three temp. ranges: $0^{\circ} \sim 99.6^{\circ}\text{C}$, $0^{\circ} \sim 305.3^{\circ}\text{C}$, and $0^{\circ}\text{C} \sim 500.5^{\circ}\text{C}$, and the equation of the true specific heat within the limit stated is obtained: $C = 0.1410 + 1.9818 \times 10^{-4}t - 1.27 \times 10^{-7}t^2$.

Author.

179. Studies of selenious acid. F. Ishikawa and H. Abe. *Sci. Papers Inst. Phys. Chem. Research*, 34, 775–786 (1938).—The dissociation press. of H_2SeO_3 have been measured by the statical method in the temp. range, $20^{\circ} \sim 150^{\circ}$. The results may be represented by the following eqs.: (Below 70°) $\log p$ (mm) $= -3517.94/T + 11.9024$ for H_2SeO_3 (s) $\rightleftharpoons \text{SeO}_2$ (s) + H_2O (g) and (Above 70°) $\log p$ (mm) $= -1886.5/T + 7.1520$ for the system: satd. soln. of $\text{SeO}_2 \rightleftharpoons \text{SeO}_2$ (s) + H_2O (g). The vapour press. of satd. solns. of H_2SeO_3 have also been measured, and the vapour press. curve intersects at about 70° with the curves corresponding to the above two equation. Therefore, H_2SeO_3 and its satd. soln. do not exist above 70° , the solid phase being SeO_2 . This conclusion was confirmed by the detn. of solubility at various temps. The solubility curves intersect with one another at 72° . The result of analysis of the solid phase in equil. with satd. soln. above 70° shows that the composition of the solid phase is SeO_2 instead of H_2SeO_3 . Authors.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

180. Sorption of vapour by silica gel. I. Sano. *J. Chem. Soc. Japan*, 59, 883–892

(1938).—The sorption velocities and amts. by silica gel of the following vapours have been

measured at 25°C under 50 mm Hg by a static method: n-hexane, n-heptane, methyl alcohol, ethyl alcohol, ethyl acetate, ethyl ether, acetone, propyl amine, chloroform, carbon tetrachloride, methyl iodide, ethyl iodide, carbon disulphide, benzene, and cyclohexane. The following results were obtained: 1. The velocities can be expressed by the formulae proposed by Prof. Sameshima (*Bull. Chem. Soc. Japan*, 7, 177, (1932)) $s \log (s/s-x) - x = kt$ and $x = k \log t + a$, where x denotes the sorption amt. at time t , s , k and a being consis. 2. There holds approximately a linear relationship between the satn. amt. and the molecular volume. Author.

181. On the adsorption of hydrogen on reduced nickel. S. Iijima. *This Journal*, 12, 1—14 (1938).

182. On the peptisation of ferric hydroxide by means of super-sonic waves. S. Watanabe. *J. Chem. Soc. Japan*, 58, 463—475 (1937).—When super-sonic wave acts on the ppts. of ferric hydroxide, the volume of the ppts. increases. This phenomenon seems to be an action particular to super-sonic wave: super-sonic wave urges water to occlusion in the interior of a gel, and, even when the gel seems to be solidified by washing, it peptised. That the phenomenon of peptisation was different in the case of heated ppts. was ascribed to variation in the combination between the particles of ferric hydroxide caused not only by the emission of NH_4 but by crystallisation

of amorphous ppts.

J. C. L.

183. On the interfaical characteristics of diatomaceous. S. Komagata and K. Hiruma. *J. Electrochem. Assoc. Japan*, 6, 195—198 (1938).—Applying Freundlich's formula the adsorption of dye-stuff upon 12 kinds of diatomaceous produced in Japan is measured, and influences of calcinating temp. and electro-dialysing treatment upon the adsorption are examd. The relation of the electrokinetic potential to the adsorption of dye-stuff is also discussed. Authors.

184. On the adsorption of deuterium on reduced nickel. S. Iijima. *This Journal*, 12, 83—89 (1938).

185. A study of the energy distribution of the active centres of catalysts by the adsorption of poisonous substances. M. Kubokawa. *This Journal*, 11, 452—466 (1937).

186. A note on "The decomposition of methane on the surface of platinum." M. Kubokawa. *This Journal*, 11, 467—469 (1937).

187. The decomposition of methane on reduced nickel. M. Kubokawa. *This Journal*, 12, 90—104 (1938).

188. The activated adsorption of methane on reduced nickel. M. Kubokawa. *Proc. Imp. Acad.*, 14, 61—66 (1938), and *This Journal*, 12, 149—159 (1938).