ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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1—GENERAL

(STRUCTURE—PROPERTIES—REACTIONS)

The relation between double refraction and crystal structure of the KH_2PO_4 type. T. Oda. *J. Chem. Soc. Japan*, **63**, 154—161 (1942).—By applying Ewald's atomistic theory of crystal optics, the double refraction of the four ionic crystals, KH_2PO_4, KH_2AsO_4, $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ was calcd. They belong to the tetragonal system and have the same $H2_2$ type structure. It was assumed that an isotropic dipole corresponds to the M^+ ion (K^+, NH_4^+), while an anisotropic dipole corresponds to the $(H_2AX_4)^-$ ion [viz. $(H_2PO_4)^-$, $(H_2AsO_4)^-$]. It was also assumed here that the principal axes of polarisability ellipsoid of the $(H_2AX_4)^-$ ion were parallel to the crystal axes (a, a, c) and at the same time to the coordinated axes (x, y, z). Then, from the optical and the X-ray data of the respective crystal and the known value of polarisability of the free M^+ ion (0.88 A^3 for K^+, 1.62 A^3 for NH_4^+), there were obtained the principal polarisabilities of $(H_2AX_4)^-$: viz. $a_x(=a_y)=5.92$ A^3, $a_z=5.43$ A^3 for $(H_2PO_4)^-$ in KH_2PO_4; $a_x(=a_y)=7.20$ A^3, $a_z=6.81$ A^3 for $(H_2AsO_4)^-$ in KH_2AsO_4; $a_x(=a_y)=6.19$ A^3, $a_z=5.34$ A^3 for $(H_2PO_4)^-$ in $NH_4H_2PO_4$; $a_x(=a_y)=7.30$ A^3, $a_z=6.41$ A^3 for $(H_2AsO_4)^-$ in $NH_4H_2AsO_4$. Further, the eqs. obtained of the principal refractive indices were examd. and it was concluded that such anisotropy of polarisability of $(H_2AX_4)^-$ ion played an important role in the birefringence of these crystals. This may be caused by the optical interaction between two oxygen atoms which are linked together by the hydrogen bond almost nearly parallel to the axes of these crystals. In confirmation of this point, there was treated the case of KH_2PO_4 crystal by the method of W.H. Bragg and results obtained fairly consistent with the above discussion. Author.

A liquid model of atomic nuclei. T. Nagamiya and T. Noguti. *Proc. Phys.-Math. Soc. Japan*, **24**, 4, 306—312 (1942).—Heavy atomic nuclei are treated under the assumption that each particle in them is vibrating in a cell formed by its neighbours. An average interaction potential similar to that acting between atoms or molecules, was assumed to exist between any two nuclear particles, and the liquid theory of Lennard-Jones and Devonshire was used to calc. the binding energy and the radius of the nucleus, the thermal motions of atoms in the case of Lennard-Jones and Devonshire being replaced by the quantum mech. zero-point motions of the nuclear particles. It was found that, as far as the order of magnitude is concerned, the results are in good agreement with the expt. and do not contradict with the data usually obtained from light nuclei. Authors.

Raman effect and dipole moment in relation to free rotation. XIV. Chlorobromoethane, chloroiodoethane, and bromoiodoethane. S. Mizusima, Y. Morino, Y. Miyahara, M. Tomura and Y. Okamura. *Sc. P.*, **39**, 387—395 (1942).—The Raman spectra of CH_2C-CH_2Br and

ClH_2C–CH_2I in the liquid and solid states and that of BrH_2C–CH_2I in the solid state were observed. The values of dipole moment of ClH_2C–CH_2I and BrH_2C–CH_2I were measured in hexane, heptane, and benzene sols. From these exptl. results it is concluded that the molecules of these dihalogenoethanes take the trans and gauche forms in the liquid state and only the trans form in the solid state. The assignment of the skeletal frequencies of both of the trans and gauche molecules is discussed and the frequency of the Raman-inactive deformation vibration of the trans molecule of ClH_2C–CH_2Cl is estimated. Authors.

Raman effect and dipole moment in relation to free rotation. XV. Raman spectrum of gaseous 1, 2-dichloroethane. Y. Morino, I. Watanabe and S. Mizusima. *Sc. P.*, **39**, 396—400 (1942).—By observing the Raman spectrum of the vapour of 1, 2-dichloroethane the authors show the coexistense of the trans and gauche molecules in the gaseous state. The equil. ratio of these two molecular species in this state is, however, found to be different from that in the liquid state. This is due to the intermolecular forces. These forces play so important a part in the solid state that practically all the molecules assume the trans form. **XVI. Dielectric constant of gaseous 1, 2-dichloroethane and the equilibrium ratio of rotational isomers.** I. Watanabe, S. Mizusima, and Y. Morino. *ibid.*, **39**, 401—409 (1942).—Dielectric consts. of gaseous 1, 2-dichloroethane were measured at different temps. under various press. From this result the equil. ratio and the energy difference between the trans and gauche isomers are calcd. The partition function used in this calcn. are obtained from the molecular data of previous expt. Taking into account the result of the intensity measurement of Raman lines, the equil. ratio in the liquid state is also detd. This is discussed in relation to the value of dielectric const. of the pure liquid. Authors.

Viscosity and expansion coefficient. T. Takeuti. *Bull. Tokyo Univ. Eng.*, **11**, **4**, 93—96 (1942).—Coeffs. of viscosity and of thermal expansion of solid and of liquid are calcd. from the view point of atomistics. Author.

On the mass of isotopes. Y. Kato and T. Takeuti. *Bull. Tokyo Univ. Eng.*, **11**, 7, 250—251 (1942).—Packing fraction and relative abundance of isotopes are charted with some remarks. Authors.

Determination of intermolecular forces from transport phenomena in gases. Calculation of viscosity and isotopic thermal diffusion according to the Sutherland model. M. Kotani. *Proc. Phys.-Math. Soc. Japan*, **24**, **1**, 76—95 (1942).—Coeff. of viscosity η of the simple gas and the thermal diffusion ratio of the gaseous isotope mixt. are calcd. as functions of temp., according to the theories of Enskog and Chapman, assuming the intermolecular interaction potential of Sutherland's type

$$U(r)=\infty,\ r<a\ ;\ U(r)=-\frac{\mu}{r^6},\ r>a.$$

The assumption usually made that μ is small is not introduced, and $\frac{a^2}{\sqrt{MkT}}\eta$ and k_T (thermal diffusion ratio) are obtained as numerical functions of $\zeta=\frac{\mu}{2kTa^6}$. Quantum correction is not taken into account in the present paper, so that the results are not directly applicable to He and H_2. The results are tentatively applied to discussions of viscosity of N_2, CH_4, Ne and to isotopic thermal diffusion of CH_4 and Ne. Temp. dependence of viscosity of N_2 and CH_4 is represented fairly well by the formula, with suitable choice of values of force parameters *a* and μ. These parameter values are in satisfactory agreement with those obtained from the second virial coeff., the agreement being much improved by the use of the "exact" formula instead of the usual approximate one (Sutherland formula) for the viscosity coeff. In case of Ne, the result is less satisfactory, and the possibility of explaining the data for heavier inert gases by taking repusion of finite softness is discussed. Finally, the temp. dependence of isotopic thermal diffusion ratio of Ne and CH_4 is calcd. with the use of parameter values detd. from viscosity and is compared with exptl. results of Nier. Author.

On the dissociation of silver oxide at low temperatures. S. Iijima. *Bull. Inst. Phys. Chem. Research*, **21**, 737—743 (1942).—By means of a thermobalance, to which a mercury manometer was attached, the following reactions occurring at various temps. between 170° and 350° have been studied: $Ag_2O \rightarrow 2Ag+\frac{1}{2}O_2$ and $2Ag+\frac{1}{2}O_2=Ag_2O$. It was observed (1) that the decompn. of Ag_2O begins at a temp. above 230° and is completed at about 270° within a few days, (2) that the influence of press. of oxygen on the decompn. temp. is insignificant, and (3) that the oxidation of silver does not take place when the press. of oxygen is lower than 760 mm, irrespective of both the temp. of the system and the form of silver which may differ according to the method of preparation. Hence, it is clear that a reverse action hardly occurs in the system, $Ag_2O \rightleftarrows 2Ag+\frac{1}{2}O_2$, under the press. mentioned above. And the conclusion reached by Benton and Drake that the decompn. of Ag_2O is reversible at temps. even as low as 170°～190° is surmised to have been erroneously deduced from the press. change brought about by some other causes such as adsorption and desorption.

Author.

On the mechanism of the thermal dehydration of boric acid. I. Thermal analysis of orthoboric acid. N. Takatori. *Mazda-Kenkyu-Jiho*, **17**, **9**, 497—502 (1942).—The author tried the process of the well-known thermal analysis upon boric acid, for the first time. One g. of the sample was heated in a small platinum crucible. The hot junction of the pyrometer was kept bare and in direct contact with the sample, and the readings of the rising temp. were plotted every 20 seconds. It took 3 hours to raise the temp. of the sample to 700°C. from room temp. As the results of expts. for 4 samples of boric acid, such as "Kahlbaum" "Kahlbaum zur Analyse," "Merck" and "extremely pure (in Nippon)," the heating curves agreed very satisfactorily with each other, and 4 halting and 6 breaking points were obtained on the curves; namely the mean values were 134±1, 143±, 154± and 173±°C. for the former, and 105±1, 116±1, 128±1, 148±1, 183±1 and 226—245°C. for the latter, resp. It may be seen, therefore, that there is some more polyboric acid outside so-called meta- or pyroboric acid. This will be discussed in the forthcoming papers. **II. Determinations of the dissociated water from boric acid.** *ibid.*, **17**, 563—568 (1942).—Boric acid was heated in the dry air current of 10 cc./min., and dissocd. water was absorbed in P_2O_5 tube. The results of this expt. are shown by 4 kinds of curves. (1) The dissocn. of boric acid increases rapidly with the rise of temp. from 95° to 150°; then it occasionally ceases between 150° and 170°; and finally the complete anhydride is given above 577°. (2) The sublimation curve is found to take almost the similar course as the dehydration curve, although the measuring points were scattered more particularly in the region of the higher temp. It is seen that the sublimation of boric acid does not practically occur below 100°, and it does not exceed 3% at the greatest. (3) The composition curve of the residues is drawn by the indirect calcn. (4) The vapour press. curve is derived from the quantities of dissocd. water, and show that the vapour press. arises to 1 atm. nearly at 130°. **III. Observations on the thermal behaviour of boric acid.** *ibid.*, 621—625, (1942).—The changes during the heating of boric acid were carefully observed from both the upper

and lower sides using the platinum crucible and the transparent quartz tube. The facts observed are noted in detail on each thermal analytic curve. **IV. Discussion of exptl. results.** *ibid.*, 626—632, (1942).—The mech. of the thermal dehydration of boric acid is discussed on the basis of the thermal analysis under due consideration of the expts. of the dehydration and of the external observations. It is concluded that boric acid begins to lose its combined water at 105°, and changes into HBO_2 at 134±1°. Those obtained at 143±1° and 154±1° may be seen to correspond to $H_4B_6O_{11}$ ($4HBO_2 \cdot B_2O_3$) and $H_3B_5O_9$ ($3HBO_2 \cdot B_2O_3$), but nothing is found in the literature about these two substances. The melting point of $H_3B_5O_9$ is 173±1°. Those of $H_2B_4O_7$ and HB_3O_5 occur at 227±1° and 243±1°, resp. Lastly boric anhydride, B_2O_3, 13 obtained above 577°.
Author.

On explosive reaction of gases. I. Explosive reaction of oxyhydrogen gas induced by a heated platinum ribbon. R. Goto. *This Journal*, **16**, 101—118 (1942).
II. An experiment which shows the heterogeneity of the thermal explosion of oxyhydrogen gas. R. Goto. *This Journal*, **16**, 141—151 (1942).
III. Theoretical consideration on explosive reactions of gases. R. Goto. *This Journal*, **16**, 152—168 (1942).

Compressional force of magnetized iron. T. Takeuti. *Bull. Tokyo Univ. Eng.*, **11**, 8, 267—268 (1942).—Thermal dilatation of magnetized iron is calcd. according to Honda—Hironé's theory.
Author.

The absorption spectrum of Si I in the extreme ultra-violet. T. Takamine, Y. Tanaka and H. Nakayama. *Sc. P.*, **39**, 423—426 (1942).—When a disruptive discharge is passed through a quartz capillary in rarefied gases, the Lyman continuum in the extreme ultra-violet is seen intercepted by many absorption lines. A beautiful Rydberg series composed of several of those absorption lines is found to be due to Si I. It is most likely that the excited silicon atoms exploded from the capillary wall are rich in the aureole at the mouth of the capillary, and the aureole acts as an absorbing layer.
Authors.

2—SUB-ATOMICS, RADIOCHEMISTRY AND PHOTOCHEMISTRY

Vibrational structure of the ${}^2\Sigma_g^+ \leftarrow {}^1\Sigma_g^+$ Rydberg series of N_2. Y. Tanaka and T. Takamine. *Sc. P.*, **39**, 427—436 (1942).—The (1.0) bands of the Worley-Jenkins series of N_2 (${}^2\Sigma_g^+ \rightarrow {}^1\Sigma_g^+$) were newly found in absorption. The limit of this new (1.0) Rydberg series is found to be 127.834 cm^{-1} (λ 782.26 A), or at 15.770 volts, whereas that of Worley-Jenkins series (0.0) bands lies at 125.670 cm^{-1} (λ 795.74 A), or at 15.503 volts. The expt. was carried out using a 3 metre grazing incidence vacuum spectrograph.
Authors.

Vibrational structure of the ${}^4\Sigma_g^-$ $(O_2^+) \leftarrow {}^3\Sigma_g^-$ Rydberg series of O_2. Y. Tanaka and T. Takamine. *Sc. P.*, **39**, 437—446 (1942).—Using a 3 metre grazing incidence vacuum spectrograph the extreme ultra-violet O_2 absorption band was investigated. Whereas the results of Price and Collins were confirmed in the main, certain modifications in their classification seem necessary. Their Q progression, together with some of their V and W bands, can be arranged into three different series, each forming a Rydberg series and converging resp. to the normal (v=0), and the vibrational (v=1, and v=2) states of an excited O_2^+ electronic state which Mulliken first tentatively called $b\,{}^4\Sigma_g^-$ and was later confirmed by Nevin, thus constituting the (0.0), (1.0), and (2.0) bands of $a\,{}^4\Sigma_g^- - {}^3\Sigma_g^-$ Rydberg series of O_2. The ionization potential corresponding to the O_2^+ $b\,{}^4\Sigma_g^-$ state comes out as 18.079±0.004 volts, agreeing closely with the values 18.1± 0.1 volts obtained by combining the data for the $b\,{}^4\Sigma_g^- \rightarrow a\,{}^4\Pi_u$ bands of O_2^+ together with the electron impact data for the $a\,{}^4\Pi_u$ state. Beside these, there was found another Rydberg type absorption band series in the region of shorter wave-lengths, that converge at λ 620 A (20.21 volts), for which the corresponding electronic state in O_2^+ has not so far been known. Apart from the Rydberg type bands, there were also found a considerable number of absorption bands forming several different progressions (non-Rydberg type) in the region extending from λ 700 A to 1000 A. Authors.

CO absorption spectra in the extreme ultra-violet. Y. Tanaka. *Sc. P.*, **39**, 447—455 (1942).—Using a 3 metre grazing incidence vacuum spectrograph the absorption spectra of CO molecules in the extreme ultra-violet were investigated. Two sets of CO absorption bands each forming a Rydberg series (one sharp, and the other diffuse) were found. They show the vibrational structure similar to the N_2 and O_2 absorption series recently reported. Both the sharp and the diffuse Rydberg series converge to an approximately common limit 158700 cm^{-1} or at 19.58 volts. This value of ionization potential obtained for the (0.0) bands agrees closely with the calcd. value obtained by combining the data of electron impact expt. and that of the analysis of CO^+ bands. Author.

The extreme ultra-violet absorption spectra of nitric oxide. Y. Tanaka. *Sc. P.*, **39**, 456—464 (1942).—The absorption band spectra of nitric oxide molecules were investigated in the extreme ultra-violet region with 1 m normal incidence type vacuum spectrograph using the helium continuum as a background. Among a large number of the discrete absorption bands, three Rydberg type series converging at 677 A, 749 A and 872 A resp. were classified. The relative positions of these three limits are identical to those of the energy states of the ionized nitric oxide molecules (NO^+). Applying the general rule for the relative positions of the electronic states of isoelectronic molecule, the term characters of the newly found NO^+ electronic states were investigated, and the positions of the (0.0) bands of NO^+ band systems are anticipated. Author.

On the helium continuum. Y. Tanaka. *Sc. P.*, **39**, 465—474 (1942).—The properties of the helium continuum (600 A—1000 A) were investigated under various exptl. conditions. One of the most important results has been that the helium continuum has two max. intensity regions at 818 A and 674 A, and one min. intensity region at about 717 A. A possible explanation for this fact was attempted by using the Franck-Condon principle obtaining the potential curves of the upper $1s\sigma\,2s\sigma\,'\Sigma_u^+$, $1s\sigma\,2s\sigma\,{}^3\Sigma_u^+$ and the lower unstable $(\sigma_u 1s)^2\,'\Sigma_g^+$ states. It was also observed that this continuum was much intensified either by increasing the helium press. in the discharge tube, or by decreasing the length of the spark gap. At a press. higher than 50 mm of mercury, this continuum appeared intensely. When, however, the helium press. became greater, the resonance line (584 A) of helium atom decreased in intensity, and finally it turned to an absorption band having its sharp head at the long wave-length side. At a low or medium press. (from 1 mm to 3 mm of mercury) there could be obtained a still intense continuum by decreasing the length of spark gap down to 0.5 mm, but in a silent discharge the continuum diminished in intensity to nearly zero, whereas, on the other hand, the helium resonance line (584 A) and 600 A diffuse band appeared very intensively. These facts suggest not only the difference between the origin of helium continuum and that of 600 A diffuse band, but also a close correlation between 600 A band and helium resonance line (584 A). Author.

On the energy states of the valency electrons in some metals. I, 14. The nature of the activation energy of Zn in its self-diffusion. M. Satô. *Sc. Repts. Tohoku Imp. Univ.*, **31**, **1**, 38—40 (1942).—The activation energy of Zn in its selfdiffusion, Q=19600 cal./mol. [F. R. Banks, *Phys. Rev.*, **59**, 376 (1941)], corresponding to $\nu/R = 0.063$ per atom, is explained as the energy of the dissocn. in which the molecule of Zn$_2$ in the state, $E_2 \equiv (4s, 4p)(4s, 4d)\,^5F$ or $E_1 \equiv (4s, 4p)(4s, 5p)\,^5D$, dissociates into two atoms in the states, $(4s, 4p)\,^1P_1$ and $(4s, 4p)\,^3P$, the probabilities of the occurrence in E_2 and E_1 being in ratio 1 : 0.06. Author.

Contribution to the technique of the manufacture of the secondary-electron emissive surface. K. Takayanagi and T. Horii. *J. Inst. Elec. Eng. Japan*, 2, **10**, 355—359, (1941).—Expts. were made with Cs—Cs$_2$O—Ag targets to investigate the effect of various factors on the multiplication ratio, R, of these targets. For a lower velocity of the impinging primary electrons, the max. of the ratio R was found at which the colour of the silver oxide assumed the first yellow of the interference orders, and the amount of caesium distilled upon the oxidized layer was relatively small. For a higher primary electron velocity, the max. of the ratio R was found at a thicker oxidized layer (in terms of interference colour: blue violet) which has slightly more caesium in its composition. The similar results were observed during the heat-treatment or activation of the targets. In an earlier stage of the treatment, where the target possesses a relatively high photo-sensitivity, the multiplication ratio R attains its max. value at a higher primary electron velocity and the ratio R varies slowly with the electron velocity near the max. As the treatment proceeds on, a secondary emission increases, and then remains practically const. while the photo-sensitivity diminishes, in which the sharply defined max. of the ratio R is observed at a lower primary electron velocity. It appears from these characteristics that the secondary emission proceeds from the Cs$_2$O layer while the caesium adsorbed upon the surface diffuses the impinging primary electrons. With regard to the manufacture of targets, it seems preferable that the oxidization of silver should be discontinued when the first yellow of the interference order appears, and that caesium in excess may be distilled upon the oxidized layers, followed by a thorough heat-treatment. Authors.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

(THERMODYNAMICS)

Mechanism of stepped discharge. H. Nomoto. *J. Inst. Elec. Eng. Japan*, **5**, 10—12, 142—145 (1941).—Stepped discharge appears when the electrode is not heated but it vanishes in a tube with an indirectly heated electrode. From this fact, it can be deduced that the energy consumed during the stepped discharge in the tube is transformed to heat energy in the process of spark discharge or electric breakdown of gas. The energy consumed in the H$_2$ discharge tube was studied with a number of electrode materials such as Hg, Zn, Pb, Al, Cu, etc. The results of various expts. reveal that the consumption of energy is mostly confined to the cathode in the form of heat which causes a local heating at a point on the surface of the cathode to form cathode spot where the cathode material begins to vapourize, and that when its vapour press. reaches a certain value, arc discharge starts to occur rapidly. In a H_2 discharge stepped discharge vanishes when the gas press. becomes equal to the vapour press., but it is not necessary that the vapour press. should be equal to the gas press. in the whole tube, if the vapour press. near the cathode spot reaches a sufficient value. At a const. temp., as press. becomes higher, ionization becomes intense in the space around the cathode fall to balance the vapour press. of cathode metal, so that the energy is greatly reduced. The voltage current characteristic curve of stepped discharge shows a similar form to that of low current glow. In the stepped discharge, the physical meaning of the characteristic curve should be interpreted as follows: If the current is smaller than the normal total current, the glow spreads over the electrode surface. This condition is referred to as normal discharge. When current increases beyond the normal total current, the glow concentrates into a small point on the electrode surface and forms a sufficient cathode spot to turn into arc discharge. This is defined as abnormal discharge. Author.

Stepped discharge in argon and helium. H. Nomoto. *J. Inst. Elec. Eng. Japan*, 5, 4, 72—74 (1941).—In stepped discharge the slope of abnormal discharge of the voltage current characteristic curve is largely dependent on the kind of electrode material, and, more or less, on the press. and electrode distance in the tube. The voltage current characteristic curve of stepped discharge is also influenced by the kind of gas, and its slope in the abnormal discharge region shows a similar tendency to that of low current discharge curve. The stepped discharge of He shows a remarkable peculiarity of its own, and, unlike in other gasses, its step slopes down, the first potential drop being not very rapid. The difference between normal cathode falls of dynamic and static glow is about 10 V, which is approximately 10% of the voltage of other gases. The difference between the normal cathode fall of low current glow and electric breakdown voltage is also about the same. The normal cathode fall of both glows of stepped discharge in He has the same characteristics as in other gases. The normal total current becomes max. at p_0d_0 which is pd of minimum electric breakdown voltage. Below p_0d_0 it increases in proportion to $(p_0d_0)^2$, and above p_0d_0 it decreases in proportion to pd. Where pd is large, normal glow discharge vanishes. The characteristic curve of abnormal discharge has the smallest inclination at p_0d_0. The inclination of stepped discharge is affected by the kind of gas, its press. electrode distance, and electrode material, but in the case of low current glow, it is not influenced by electrode material. Author.

The mechanism of electrical breakdown of insulating liquids. S. Sawa. *J. Inst. Elec. Eng. Japan*, 2, 234—238 (1941).—In this paper, the author intends to clarify the mech. of electrical breakdown of insulating liquids by investigations of dust figures and Lichtenberg's figures. The exptl. results are summarized as follows: 1. Electrical breakdown of liquid insulators is caused by neg. and pos. "twig-like" streamers. 2. Pos. and neg. "twig-like" streamers are of entirely different characteristics; and the breakdown of insulation is not effected until spark discharge is completed, which is caused by the neg. streamer stretching out to reach the pos. electrode after the meeting of the two streamers. 3. Both pos. and neg. streamers are the phenomena of purely local electrical breakdown which is caused by the ionization by collision of electrons. Therefore, the breakdown of insulation caused by these streamers is purely electrical. The electron stream after the meeting of the two streamers is probably supplied mainly by the neg. electrode. 4. In a void the same "twig-like" streamers occur independently, and they are likewise caused by the ionization by collision of electrons. 5. "Treeing" obtained by the carbonization of the discharge path on the surface of a solid in an insulating liquid bears a striking resemblance to the "twig-like" figures obtained by residual charge or Lichtenberg's figures on photographic plates, but they are different in causes and characteristics. 6. "Treeing" and "twig-like" figures are similar in the final process leading to insulation breakdown, though the former is due to the thermal action of the streamer. Author.

Diffusion of ions and deionization time of low pressure mercury-vapor discharge tubes. S. Ariga. *J. Inst. Elec. Eng. Japan*, **62**, **3**, 131 (1942).—In the study of mercury-arc rectifiers and inverters, the deionization time becomes an important problem, and the diffusion of ions through the arc guide and buffer of the mercury-arc rectifier has an important effect upon the operation of these apparatus. In the study of these phenomena, the condition of the deionization at the tube wall should be taken into account, but it was formerly entirely neglected. The ions diffuse towards the wall and are there deionized and disappear. Therefore, when the vapor density is high and the diffusion const. of the ion is small, there is an enormous gradient of ion density towards the wall, so that the ion density before the wall is nearly zero. On the contrary, when the vapor density is low the condition is entirely different. If this effect is taken into account, the condition of the diffusion of ions and deionization is entirely different according as the vapor density is high or low, and this is mathematically treated and solved. From the result of this soln., when the vapor density is lower than 0.1 mm, the quantity of ions that diffuse through a tube, for example, varies strikingly with the vapor density, and this fact is entirely different from that expected from Schottky's formula heretofore used and even a difference of nearly one hundredfold occurs and this fact is proved by expts. Author.

The electric conductivity of the semi-conductors. T. Hibi. *Denkigaku-kaishi*, **63**, 83 (1943).—In the electric conductivity of the semi-conductors such as ZnO, Al_2O_3 and etc., it is well known that the active energy varies by the different manner of treatment. But it is not possible to interprete these phenomena according to Wilson's theory, since it considers only one active energy which does not depend on the treatment. Nijboer has attempted to remove this difficulity by assumption of the existence of the impurity centres and of 'frozen-in' vacant lattice points. In the present paper the electric conductivity of ZnO and Al_2O_3 is calcd. by the following three eqs.; (i) the equation derived without approximation in Wilson's calcn.; (ii) the eq. replacing the Maxwell-distribution by the Fermi-Dirae statistics in Eq. (i); (iii) the eq. computed without approximation in Nijboer's calcn. As the result, it is recognized that the variation of active energy due to the treatment can be explained qualitatively by all the three eqs. Further, the qualities of the three eqs. are also discussed by comparing some exptl. results hitherto obtained. Author.

On the thermionic emission of the semi-conductors. T. Hibi. *Denkigaku-kaishi*, **63**, 84 (1943).—Following the equation replacing the Maxwell-distribution by the Fermi-Dirac statistics in Wilson's calcn., a new thermionic emission formula for the semi-conductors is derived. For the purpose of comparing the calcd. values with the exptl. results, the thermionic emission of the semi-conductor BaO is evaluated by this formula. From the results of this calcn., it is found that the proportional factor varies from n_0 to $n_0^{\frac{1}{2}}$ and from e^{-K} to $e^{-K/2}$ when the temp. is increasing. Accordingly, it is suggested that the positive temp. coeff. of work function exists in the oxide coated cathode

similar as in the pure metal. Some considerations are made with respect to the facts that work function differs by the methods of measurements and that there exists a parallelism between electric conductivity and thermionic emission of the same semi-conductor.
Author.

Studies on magnetochemistry. I. Diamagnetic susceptibility of selenophene. 1. G. Hazato. *J. Chem. Soc. Japan*, **63**, 1685—1688 (1942).—Measuring the magnetic susceptibility of selenophene, by means of modified Weiss-Foex method, the author obtained the value: $\chi_M = -66.82 \times 10^{-6}$. This value is compared with those of furan, pyrrole, and thiophene measured by Bonino and others. Everyone of these exptl. values shows, however, some deviation from the result calcd. from Pascal's additive law and the amts. of these deviations increase systematically from furan to selenophene. From this tendency, the author presumes that there should be some quantitative relationship between these deviations and the corresponding atomic sizes of the heteroatoms in these molecules. Some quantitative details will soon be published.
Author.

The activity and osmotic coefficient of the concentrated 1—1 salt solutions. S. Kaneko. *Bull. Electrotechn. Lab.*, **6**, 493—496 (1942).—The activity and osmotic coeff. of the concd. 1—1 salt solns. are calcd. by the following formulas and compared with the observed values:—

$$\ln\gamma = -\frac{\varepsilon^2}{2\mathrm{DkT}}\frac{\mathrm{k}}{1+\varkappa\mathrm{a}} + \frac{8}{3}\pi\mathrm{Na}^3\mathrm{c} + \frac{5}{3}\pi^2\mathrm{N}^2\mathrm{a}^3\mathrm{c}^2 + \frac{256}{81} \times 0.2689\pi^3\mathrm{N}^3\mathrm{a}^9\mathrm{c}^3 - \mathrm{gV_{II}c} + \ln\frac{1000\mathrm{c}}{\mathrm{m}\delta}$$

$$\mathrm{g} = 1 - \frac{\varepsilon^2}{2\mathrm{DkTa}}\left[\frac{1}{\varkappa\mathrm{a}} - \frac{1}{1+\varkappa\mathrm{a}} - \frac{2}{\mathrm{k}^2\mathrm{a}^2}\ln(1+\varkappa\mathrm{a})\right] + \frac{4}{3}\mathrm{Na}^3\mathrm{c} + \frac{10}{9}\pi^2\mathrm{N}^2\mathrm{a}^6\mathrm{c}^2 + \frac{64}{27}\times 0.2689\,\pi^3\mathrm{N}^3\mathrm{a}^9\mathrm{c}^3$$

where γ is the activity coeff., g the osmotic coeff. ε the charge of an electron, D the dielectric const. of the solvent, *k* the reciprocal of the thickness of the ionic atm., a the mean diameter of the ions, N Avogadro number, c concn. of the soln. in mol/cm³, g the osmotic coeff.
Author.

The Wien effect of the weak electrolyte. S. Kaneko. *Bull. Electrotechn. Lab.*, **6**, 551—553 (1942).—The relation between Onsager's theory of the Wien effect of the weak electrolyte and Bjerrum's theory of assocd. ion pair is made clear in this report.
Author.

On Debye-Hückel's theory of strong electrolytes. S. Kaneko. *Fiftieth anniversary papers of the Electrotechn. Lab.*, 148—149 (1942).—Inconsistency of the Debye-Hückel's theory of strong electrolytes is discussed.
Author.

The equivalent conductivity of the concentrated 1—1 salt solution. S. Kaneko. *Bull. Electrotech. Lab.*, **6**, 571—572 (1942).—The equivalent conductivity of concd. 1—1 salt soln. is calcd. by the equation

$$\Lambda = \Lambda_0 - \frac{\varepsilon^2}{3\mathrm{DkT}}\Lambda_0\left(e^{-\varkappa\mathrm{a}/\sqrt{2}} - e^{-\varkappa\mathrm{a}}\right) - \frac{\mathrm{N}\varepsilon^2}{3\pi\eta}\varkappa e^{-\varkappa\mathrm{a}} \times \frac{10^{-11}}{9} \tag{1}$$

or

$$\Lambda = \Lambda_0 - \frac{\varepsilon^2}{3\mathrm{DkT}}\Lambda_0\frac{e^{\sigma\mathrm{a}}-1}{1+\varkappa\mathrm{a}} - \frac{\mathrm{N}\varepsilon^2}{3\pi\eta}\frac{\varkappa}{1+\varkappa a}\times\frac{10^{-11}}{9} \tag{2}$$

$$\sigma = \left(1 - \frac{1}{\sqrt{2}}\right)\varkappa \tag{3}$$

where Λ_0 is the limit of the equivalent conductivity, ε the charge of an electron, D the dielectric const. of the solvent, k Boltzmann's const., T the absolute temp., a diameter of the ions, $\varkappa$ reciprocal of the ionic atm., N Avogadro's number viscosity of the solvent and these values are compared with the observed value. Author.

The nearest distance between ions in the electrolyte solution. S. Kaneko. *Bull. Electrotech. Lab.*, **6**, 596—597 (1942). —Assuming the potential energy E between ions is expressed by the following equation:

$$E=\frac{e_1e_2}{Dr}-\frac{\mu}{r^6}-\frac{\lambda}{r^9},$$

where e_1 and e_2 are the charge of positive and negative ion, D dielectric const., r the distance between ions, μ and λ consts., the nearest distance between ions in vapour or in the soln. is calcd. Author.

The Faraday effect of strong electrolytes in aqueous solutions. VIII. KF, RbCl, CsCl, $MgCl_2$, $CaCl_2$ and $SrCl_2$. A. Okazaki. *Proc. Phys.-Math. Soc. Japan*, **III, 24**, 40—48 (1942).—The relation between the magnetooptical rotation and the concn. of the aqueous solns. of KF, RbCl, CsCl, $MgCl_2$, $CaCl_2$ and $SrCl_2$ was studied for D-lines. It was found that the values of the molecular rotations M[D] of KF, RbCl CsCl tend to decrease slightly with increasing concn., while those of $MgCl_2$, $CaCl_2$ and $SrCl_2$ decrease remarkably. The values of M[D] of these electrolytes in dissocd. states were detd. by extrapolation to infinite dilution. Author.

The Faraday effect of ions in aqueous solutions. A. Okazaki. *Proc. Phys.-Math. Soc. Japan*, **III, 24**, 357—361 (1942).—The molecular rotation const. $\Phi=M[D]$ and the molecular refraction R of diamagnetic gaseous atoms are related to each other by the formula $\Phi=-\frac{\pi}{2eN}\frac{R^2}{p}$, where N is Avogadro's number and p the number of dispersion electrons per molecule. The values Φ of many strong electrolytes for D-lines were detd. in aqueous solns. and it is shown that these values at infinite dilution are given by the sums of the rotation consts. of the component ions, i.e. $\Phi=\Phi_{+}+\Phi_{-}$ (for reference, *Proc. Phys.-Math. Soc. Japan*, **III, 24**, 40—48 (1942)). For gaseous atomic ions one can evaluate the value of Φ by assuming the values of R and p. Assuming that the Φ-value of a small ion such as Li^+, Na^+, F^- in aqueous soln. differs, due to remarkable hydration effect, from that in the gaseous state, while a large ion such as K^+, Rb^+, Cs^+, Cl^-, Br^-, I^- shows little hydration effect, the following formula is obtained for the molecular rotation const. Φ of a molecule consisting of two large ions,

$$\begin{aligned}\Phi_{\text{solution}}&=(\Phi_{+}+\Phi_{-})_{\text{gas}}\\&=-\frac{\pi}{2eN}\left(\frac{R_+^2}{p_+}+\frac{R_-^2}{p_-}\right)_{\text{gas}}.\end{aligned}$$

By applying the above relation to KCl molecule, one can determine the ionic rotation consts. of K^+ and Cl^-, and hence those of many other ions in aqueous solns.

Author.

The Faraday effect and refraction of rare gases and rare-gas-like ions. A. Okazaki. *Proc. Phys.-Math. Soc. Japan*, **III, 24**, 361—367 (1942).—The values of molecular rotation consts. Φ of rare gases can be calcd. from the data for their natural dispersion. For atoms having similar electronic configurations, for example Cl^-, A and K^+, the Φ-values as well as the values of molecular refraction decrease remarkably as their nuclear charges increase by unity.

Author.

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY
(CONTACT CATALYSIS)

On the irregular series of the coagulation of colloidal solutions by electrolytes. III. Studies of the coagulation of various HgS-sols, prepared from different mercuric salts as starting material. N. Sata and K. Môri: *Bull. Chem. Soc. Japan*, **16**, **5**, 139—143 (1941).—Each of HgS-sols prepared from $Hg(CN)_2$, $HgSO_4$, or $Hg(No_3)_2$, has shown by $AgNO_3$ almost the same coagulation curve of irregular series such as those starting from $HgCl_2$. That is to say, for irregular series, there is no influence of electrolytes existing in sols. **IV. On the rôle of H_2S for irregular series of HgS-sol.** N. Sata and S. Itô. *Bull. Chem. Soc. Japan*. **17**, **1**, 4—9 (1942).—It has been observed that H_2S is indispensable peptising and stabilising agent for HgS-sol and that, although it contains certain amounts of coagulating electrolytes, stable sol is obtained if there exists as much H_2S as corresponds to it. The irregular series have been already found independent of stability of sols. Such a HgS-suspension as has been prepared from the ppts. purified by boiling and decantation over one year in a fused quartz apparatas still shows irregular series, although it is very unstable. **V. On the conditions of coagulation experiments, especially on the actions of supersonic waves.** N. Sata and S. Itô. *Bull. Chem. Soc. Japan*, **17**, **2**, 56—61 (1942).—In order to obtain the results of coagulation expts. quantitatively and reproducibly, it is necessary to arrange carefully the conditions of expts., namely the method of shaking and mixing sols with electrolyte-solns. Too much shaking leads to flocculation. The use of super-sonics has been favourable under suitable conditions. **VI. Comparative studies on the coagulation curves of various sols.** N. Sata and S. Itô. *Bull, Chem. Soc. Japan*, **17**, **7**, 309—313 (1942).—The coagulation curves by $AgNO_3$ of several sulfide sols, such as ZnS, CdS and As_2S_3, which have been prepared by the same method and stabilized equally by H_2S as HgS sol, are compared. In spite of analogous surface structures and stabilizing mechs. of colloidal particles of these sols with those of HgS-sol, neither of them shows. the irregular series. Authors.

Moisture absorption coefficient of paper. S. Sima. *Proc. Phys.-Math. Soc. Japan*, **16**, 152—154 (1942).—In the present investigation, the formula $m/M=k_t P$ has been established, where m is the amount of moisture absorbed in paper, M the mass of paper, and P the vapour press. in the state balancing the above conditions. In the above relation, k_t, which is called moisture absorption coeff., is an important const. number detd. by temp. and quality of the paper. The change of k_t for different kinds of paper due to temp. has been measured by the balanced vapour press. method, and it was ascertained that the moisture absorption can be explained consistently by the function of capillary contraction. Author.

The absorption of hydrogen sulfide in contact with aqueous solutions. II. O. Kamiike and S. Kataoka. *J. Chem. Soc. Japan*, **63**, 1075—1077 (1942).—An expression applicable to the water-sodium chloride-hydrogen sulfide systems, in terms of the diffusion distance, diffusion coeff. and time, derived theoretically in (I) (O. Kamiike, S. Kataoka, and S. Inaba, *ibid.*, **63**, 1007—1014 (1942)) has been applied to the water-glycerine-hydrogen sulfide systems. As in (I) the indicator method has been used to det. the rates of absorption and diffusion coeff. at various concns. The results are discussed briefly. Authors.

The monomolecular film of "Buna-

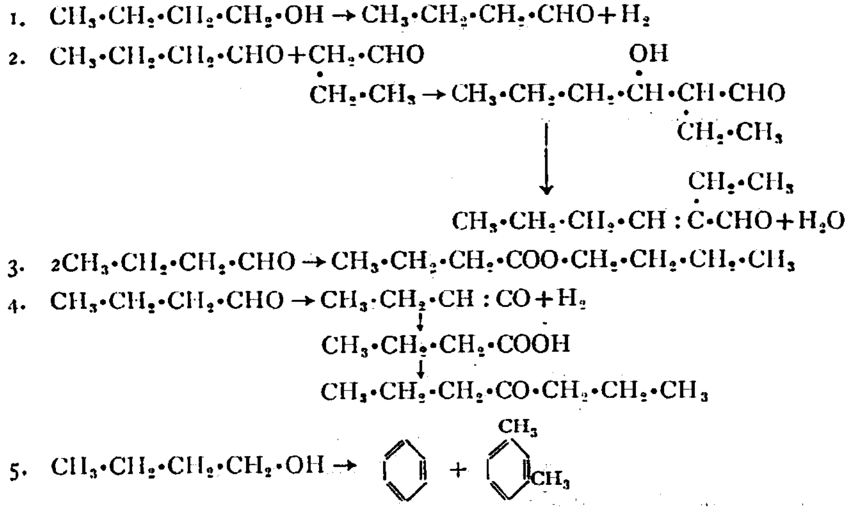
N". K. Suzuki. *J. Chem. Soc. Japan*, **63**, 1058—1060 (1942).—Buna-N, the copolymer of butadiene and acrylnitrile can spread on water and form the monolayer owing to the hydrophilic nature of its nitrile groups. The monolayer was formed from the benzene soln. and the surface press. f was detd. changing the area a and the temp. T (3°—32°C). The f-a-T relation is of a new type. The f-a curves are S-shaped. The limiting area at zero press. is 1.5 sq. m/mg, or 47 sq. Å per CN, independent of T. The film shows a high compressibility (e.g. 0.30 cm/dyne at $a=0.7$ sq. m/mg and $T=10°C$), which is completely reversible after a compression to one fifth of the area. Temp. coeffs. of surface press. and of compressibility are neg. (e. g. for the former −0.052 dyne/cm. deg. at $a=0.7$ sq.m/mg, $T=10°C$). These extraordinary properties are attributed to the rubber-like nature of Buna-N. Author.

Dehydrogenation of methane I. H. Kuraku. *J. Chem. Soc. Japan*, **63**, 1147—1150 (1942).—The catalysts, Mg-, Zn-, Fe-, Ni- chromite, were prepared by calcining the complex salts of ammonium chromates containing the crystaline water. With these catalysts the dehydrogenation reactions of CH_4 with steam were studied. By comparing the rate of decomposition of CH_4 at 900°, the following data were obtained:

Chromite	Mg,	Zn,	Fe,	Ni
Decomp. rate %	31	34	68	84

It is shown that the Fe catalyst is available for this reaction. Author.

Catalytic action of MgO on n-butyl alcohol. T. Mizosita. *Report of the Institute of Scientific Research, Manchoukuo*, **6**, **2**, 13—26. The catalytic action of MgO on butyl alcohol under the temp. of 500 and 550°C resp. was investigated as to the components in the gaseous and liquid products. In the gas produced, H_2 was the main component and the presence of CO and CO_2 indicated the decompn. of aldehyde produced by dehydrogenation of alcohol. In the liquid products, aldehyde, n-dipropylketone, 3-methylalheptene-3, butyl ester, benzene and m-xylene were identified by chemical and absorption spectrum method. These substances are considered to be formed by the dehydrogenation, condensation and cyclization of alcohol or aldehyde produced, and the reaction may be represented as follows.



1. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO + H_2$

2. $$\begin{array}{l} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO + \underset{CH_2{\cdot}CH_3}{CH_2{\cdot}CHO} \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{OH}{CH}{\cdot}\underset{CH_2{\cdot}CH_3}{CH}{\cdot}CHO \\ \downarrow \\ CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH:\overset{CH_2{\cdot}CH_3}{C}{\cdot}CHO + H_2O \end{array}$$

3. $2CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$

4. $$\begin{array}{l} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO \rightarrow CH_3{\cdot}CH_2{\cdot}CH:CO + H_2 \\ \qquad\qquad\qquad\downarrow \\ \qquad\qquad CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \\ \qquad\qquad\qquad\downarrow \\ \qquad\qquad CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \end{array}$$

5. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \rightarrow$

Hydrogenation and hydrogenolysis of diphenyl ethers over platinic oxide catalyst under mild conditions. M. Tomita and S. Uyeo. *J. Chem. Soc. Japan*, **63**, 1189—1193 (1942).—It has been found that diphenyl ethers, which are in general very stable against the ordinary reagents for effecting the scission of carbonoxygen linkage, react comparatively rapidly with hydrogen over Adams' platinic oxide catalyst under the normal press. at room temp. Diphenyl ether itself undergoes under these conditions hydrogenation and hydrogenolysis yielding cyclohexan and cyclohexanol as the end products. Methyl 2, 3-dimethoxydiphenyl ether tricarboxylate- (5, 6, 4′) and methyl 3, 4-dimethoxydiphenyl ether tricarboxylate- (5, 6, 4′) absorb 4.5—5.7 mol equivalents of hydrogen, resulting in methyl 3-hydroxy-4, 5-dimethoxyphthalate (m.p. 112°) and methyl 3-hydroxy-5, 6-dimethoxy-phthalate (m.p. 87—88°) resp. Methyl 2-methoxy-diphenyl ether dicarboxylate- (5, 4′) and 2, 3-dimethoxy-2′-methyldiphenyl ether dicarboxylic acid- (5, 4′) react with approximately 7—9 mol equivalents of hydrogen to form mixts. of completely and incompletely hydrogenated benzene derivatives. The above reaction occurs perhaps over three stages: first, the hydrogenation of the less stable benzene nucleus takes place to form cyclohexyl or cyclohexenyl phenyl ether, which then undergoes hydrogenolysis resulting in cyclohexan and phenolic benzene derivatives. Further hydrogenation of the latter products also yields as an end product a cyclohexan derivative, but in special cases, when it is very stable toward hydrogenation, the reaction stands still at the second stage. For example, the presence of two carbomethoxy groups in a benzene nucleus prevents further hydrogenation, yielding hydroxyphthalate as the end products. Authors.

A consideration of mechanism of reduction of silver chloride by hydrogen and deuterium on the basis of the absolute reaction rate. I. Higuti. *Bull. Inst. Phys. Chem. Research*, **21**, 8, 743—748 (1942).—(Prof. F. Isikawa and K. Yosimura *Bull. I.P.C.R.*, **20**, 11 (1941)).—Previously showed that the velocity of reduction of silver chloride by hydrogen and deuterium might be expressed by $\frac{dp}{dt}=\frac{kP_{H_2}}{1+aP_{HCl}}$. The present author has derived the above expression by considering this reaction from the theory of absolute reaction rate, and arrived at the conclusion that the rate detmg. step in the reactions is the formation of activated complexes between a gas molecule and the dual site of surface active points. By this mech. the reaction rate has been calcd. to be $2.8 \cdot 10^{15}$ molecules/cm^2. sec. for hydrogen and $0.57 \cdot 10^{14}$ molecules/cm^2. sec. for deuterium, whereas the observed values are $3.2 \cdot 10^{14}$ for hydrogen and $1.5 \cdot 10^{14}$ for deuterium. The values of a in the above expression have been calcd. and compared with the observed values. The discrepancy between them is discussed.

Author.