

ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

Vol. XVI

April, 1942

No. 1

1—GENERAL

(STRUCTURE—PROPERTIES—REACTIONS)

A study of nickel amalgam by X-ray. N. Kato. *J. Chem. Soc. Japan*, **62**, 29—30 (1941).—When nickel amalgam was prepared by electrolysing nickel sulphate with nickel and mercury used as anode and cathode resp., a solid crystal was formed. Examn. by X-ray showed that the crystal was of simple cubic and its lattice const. 3.0097 \AA .

J. C. L.

A study of the compounds, Fe_2O_3 , $\text{CaO}\cdot\text{Fe}_2\text{O}_3$, and $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ by X-rays. K. Akiyama. *Waseda Applied Chem. Soc. Bull.*, **18**, 10—14 (1941).—The crystal structure of Fe_2O_3 is not changed by heating at $1,100^\circ$ in oxydation atmosphere. The compds. corresponding to $\text{CaO}\cdot\text{Fe}_2\text{O}_3$, $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and $3\text{CaO}\cdot\text{Fe}_2\text{O}_3$ were prepared by burning and exmd. by X-rays. The former two were found to be the desired compds., while the last was considered to consist of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and fused free lime.

J. C. L.

An electron diffraction study of chemical reaction products of metals. The reaction between hydrochloric acid and Na, Ca, Be, Zn, and Al. S. Yamaguchi. *Sc. P.*, **38**, 298—303 (1941).—All diffraction patterns obtained here with $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$, ZnCl_2 , AlCl_3 , and KHCO_3 crystals are specimens of the N-Pattern revealing the existence of a large crystal. These metal salts are known to be very easily soluble in water.

Therefore, in the electron camera kept in vacuum these salts crystallize out of their solns. very slowly, and consequently the crystals obtained are very large. It has already been proved by the present author, from the crystallization of ZnCl_2 and ZnBr_2 from their aq. solns. which takes place so slowly that the halo patterns are observed before the ring patterns appear, that the process of crystallization from solns. of such salts is very slow. It is also here observed that the desiccation of hygroscopic compd. as beryllium halides is often impossible. It is thus realized that the density of atoms constituting the crystals produced is a function of the reaction velocity and the affinity of the salt for water.

Author.

On the molecular structure of thiophosphoryl bromide. K. Suenaga. *J. Chem. Soc. Japan*, **62**, 107—111, 227—233 (1941).— PSBr_3 was prepared by the method of Baudrimont. Using regular octahedral and hexahedral crystals, the structure was detd. by the Laue-photographic oscillation and rotation methods. The unit cell is of the dimensions $a=11.03 \text{ \AA}$ and contains 8 PSBr_3 mols.; hence the density is calcd. to be 2.98, which is in good agreement with the value 2.97 directly detd. The corresponding space group is $T_h^h-Pa_3$, and the minimum mol. symmetry C_3-3 . The atoms of S and P are arranged in the position (c) of the "Internationale Tabellen", and Br in (d) with $x \approx$

α , $\gamma \approx 0$, $z \approx 1/4$. This structure is of the so-called SnI_4 type, but this substance, which possesses the formula AX_3Y and crystallizes in this type, is for the first time found. The dipole moment of this substance was measured using its dilute solns. in benzene and carbon tetrachloride. The observed moment did not show any temp. dependence, and the values obtained are 1.58 D (C_6H_6 : 10°C , 25°C , 28°C) and 1.43 D (CCl_4 : 0°C , 25°C). Beside these measurements, the dielectric consts. at 40°C of the system $\text{PSBr}_3\text{—CCl}_4$ for various concns. were measured, and the P_{12} and P_2 curves were prepared. The dielectric consts. of pure thiophosphoryl bromide in liquid and solid states were also measured in the temp. range from 18°C to 48.8°C . As the result, the apparent value is found: $\epsilon = 3.7$ ca for solid, and $\epsilon = 6.2$ ca for liquid, the latter decreasing with increasing temp. This behaviour is quite reasonable from the view-point of crystal and molecular structures. Further discussion on the structure of PSBr_3 molecule is made from the obtained data of the X-ray crystallographic and dielectric measurements and also from the theory of valence bond structures. Author.

On the relative expansion of solids from the absolute zero to the melting temperatures. A. Harasima. *Proc. Phys.-Math. Soc. Japan*, III, 22, 636—639 (1940).—Relative expansion of monatomic solids from the absolute zero to the melting temps. is calcd. by the theory of fusion which was previously presented by the writer (*Proc. Phys.-Math. Soc. Japan*, 21, 156—165 (1939)). It is shown that the relative expansion from 0°K . to the melting temp. is given by $\frac{10.6}{\Theta_D} \sqrt{\frac{T_m}{Mv^{2/3}}}$, where T_m is the melting temp. in $^\circ\text{K}$., M the atomic weight, v the molar volume and Θ_D Debye's characteristic temp. The agreement between the calcd. values and the observed ones is good. Author.

On the ΔE -effect of iron, nickel and

cobalt. M. Yamamoto. *Nippon Kinzoku (Gakkai-Si)*, 5, 167—174 (1941).—The ΔE -effect, i.e. the change of Young's modulus of elasticity with magnetization, in the annealed state of electrolytic iron, decarburized 0.1 percent carbon steel, electrolytic nickel and electrolytic cobalt, is measured in detail, in the magnetic field up to 900 Oersteds by the method of magnetostrictive oscillation. In every metal the course of change of Young's modulus by magnetization is found to be not so simple as was hitherto known; the moduli of iron and nickel display both a secondary increase in the field range preceding the satn., and that of cobalt shows a max. and a min. in the weak field or the low magnetization range. The satn. value of ΔE -effect in decarburized mild steel coincides perfectly with the value expected from the exptl. results on the ΔE -effect in steels of various carbon contents, described in the previous report. The comparison of the exptl. results of the ΔE -effect of both iron and nickel with the theories proposed by Akulov and Kondorsky, Brown, Tagaki, and Becker and Döring indicates that, every theory agrees well with the expt. for the ΔE -effect of iron, while for that of nickel only two theories by Takagi and Becker-Döring give the calcd. values coinciding with those measured. Author.

The vapour pressures of some molecular crystals. I. S. Seki and I. Nitta. *J. Chem. Soc. Japan*, 62, 581—586 (1941).—Using a glass manometer of the Bourdon type, the vapour press. of mol. crystals of PSBr_3 , C_2Cl_6 and $\text{C}(\text{CH}_2\text{Br})_4$ were measured at various temps. extending to liquid state. From these data the changes of thermodynamic quantities, ΔH , ΔF , $\Delta F_{298.1}$, $\Delta S_{298.1}$ for the phase change equilibria were also measured. The heat of sublimation of PSBr_3 crystals was found to be 14.62 kcal/mole and some aspects of physico-chem. importance were discussed from the point of view of the crystal structure. The transition temp. detd. from the vapour press.-temp. curve of C_2Cl_6 crystals was in

good agreement with the values from other methods. Below this transition point, the values of vapour press. obtained by Nelson was certainly too low, while, above this the data of the present expt. agrees very well with those measured by van der Lee. The heat of fusion of $C(CH_2Br)_4$ was obtained to be 5.49 kcal/mole. From this the mol. depression of the melting point was calcd. to be 26200, which suggests the possibility of utilization in certain cases of this substance as the solvent for the mol. weight detn.

Authors.

Molecular structure and dielectric strength of liquid dielectrics. M. Suzuki and R. Fujioka. *J. Inst. Elec. Eng. Japan*, 61, 266—268 (1941).—With the object of studying the relation between the dielectric strength and mol. structure of liquid dielectrics, the electrical breakdown voltages of 24 liquids were tested with the impulse voltage. The electrodes were 11.8 mm ϕ spheres and the gap was 0.1 mm. The results are summarized as follows. (1) The greater the mol. volume and the smaller the dipole moment, the higher the breakdown potential gradient of liquid dielectrics. (2) Ionization potential and electron affinity, etc. of mols. do not seem to affect dielectric strength essentially. (3) In short, the dielectric strength of a liquid has an intimate relation to chem. structure of its constituent mols., and if its structure is known, its dielectric strength is surmisable to some extent.

Authors.

The solubility of solid benzene in several non-polar liquids. R. Negishi. *This Journal*, 15, 99—117 (1941).

Solubility of soaps. (supplementary note) J. Mikumo. *J. Soc. Chem. Ind. Japan*, 44, 389 (1941).—The solubilities of K salts of palmitic acid, stearic acid and arachidic acid for water at 20°C are measured and compared with those of Na salts of the said fatty acids. Behenic acid K soap is more

crystalline than the corresponding Na salt. The solubilities at 20°C of K and Na salts of satd. fatty acids above C_{18} are about 1×10^{-4} mol/L.

J. C. L.

On the solubility of cellulose derivatives. IV. Dissolution of nitrocellulose in mixed solvent containing alcohol. Y. Inoue. *J. Soc. Chem. Ind. Japan*, 44, 5, 377—380 (1941).—In alcohol, ether, or benzene, the nitrate cong. ca. 11.0% nitrogen is most easily solved and its solubility is least affected by temp., while the dissoln. becomes harder and the influence of temp. becomes more remarkable with the nitrogen content greater or less than 11.0%. The solubility of higher nitrate decreases with the rise of temp. and that of lower nitrate increases. In general, the influence of the amt. of "Bodenkörper" is comparatively less prominent, but it becomes accentuated if the amt. of alcohol in the mixed solvent decreases below a certain limit. The decrease of percentage of alcohol also causes the tendency similar to those recognized in acetone-alcohol-water [cf. *J. Soc. Chem. Ind. Japan*, 44, 4, 283—288 (1941)], namely, it decreases the solubility and affects the temp. so much that the nitrocellulose becomes more easily soluble at a higher temp. rather than at a lower temp.

Author.

Studies on the nitro-acetyl cellulose. V—VI. Determination of expansion and contraction of films of nitrocellulose, acetylcellulose, nitro-acetyl cellulose and cellulose hydrate. S. Oguri, M. Takei and N. Kosaka. *J. Soc. Chem. Ind. Japan*, 44, 158—161 B (1941).—The present paper deals with an investigation of the effect of temp. on the length of the films of cellulose nitrate (11.60—12.69% nitrogen), cellulose acetate (55.4—58.5% CH_3COO), nitro-acetyl cellulose (1.08% nitrogen, 23.63% CH_3COO) and cellulose hydrate. The samples dried for two hrs. at 50—60°C and cut off as large as 1 × 15 cm were suspended vertically in an apparatus filled with dry air, satd. water vapour

and water resp. Then, after 1 hr., the vertical length of the sample was observed by means of a cathetometer with rising temp. It was found that the temp. has no influence on the length of the films of all samples so long as no water is present. In liquid water and in satd. water vapour, however, expansion and contraction take place to some extent on the films of all the samples with rising temp., but it must be noted that expansion and contraction of the films of acetyl-cellulose and cellulose hydrate are more remarkable than that of nitro-cellulose and nitro-acetyl cellulose, and also that the change in the length of the film of nitro-acetyl cellulose is very small as compared with the other samples.

Authors.

Physical properties of synthetic resins. I. Structures of phenolic resins and the method of studying physical properties. S. Tsuruta and R. Kawai. *J. Electrochem. Assoc. Japan*, 8, 5, 131—134 (1941).—Reviewing the recent advances of the chemistry of phenolic resins the authors discuss the following two fundamental problems: (1) Has the formation of phenol alcohols ever been recognised in the reaction process of Novolak resins? (2) Is the constitution of Novolak resins perfectly linear, having no side branches? As the chemical methods are very hopeless for these problems the authors intend to study the physical properties systematically.

Authors.

Physical properties of synthetic resins. II. Some physical properties of hardening phenolic resins. R. Kawai and S. Tsuruta. *J. Electrochem. Assoc. Japan*, 9, 5, 135—138 (1941).—Some physical properties as weight decrease, specific gravity (a), coeff. of thermal expansion (b), thermal conductivity (c), specific heat (d) and Young's modulus of elasticity (e) were observed on the hardening resins prepared from reaction mixts. in various ratios of phenol/formaldehyde (ammonia as catalyst). When the ratio is less than 1 the resins have nearly const. physical properties

after curing for some hrs. at 100°C. i.e. (a) 1.266 ± 0.003 (15°C), (b) $5-7 \times 10^{-6}$ (30—60°C) (c) 0.16—0.17 Kcal/mhr °C (40°C), (d) 0.421 cal/g °C (52°C) and (e) 660—700 kg/mm² (15°C), while when the ratio is greater than 1 the resins have a kind of softening temp. below 100°C and near it physical properties show a remarkable change.

Authors.

Diffusion of CH₄ or CO₂ into the air. Y. Yamada. *Bull. Mining Eng. Soc. Kyushu*, 12, 185—189 (1941).—Two glass tubes, each 3 cm in inner diameter and 50 cm in length, are joined end to end, with a partition inserted between the two. One is filled with the air, while the other is with CH₄ or CO₂. By removing the partition the change of the gas compn. is observed. The difference of diffusion of the gases is examd. when the air tube is placed vertically above or below the other tube or when the two are laid horizontally. The relation is thus studied between the distribution of gases in coal pits and the places of exhausted CH₄ or CO₂.

J. C. L.

Studies on the thermal diffusion of solution. I. On the measurement of the thermal diffusion coefficient. K. Hirota. *J. Chem. Soc. Japan*, 62, 480—484 (1941).—It is shown that the thermal diffusion app. of Clusius and Dickel having a comparatively large distance is suited for the detn. of the thermal diffusion coeff. of liquid solns. Using an app. with an annular distance of 1.5 mm and with a length of 94 cm, the separations of 1N HCl, 1N H₂SO₄ and 1N NaCl solns. were carried out. The observed results were shown to be in concordance with the theory of Debye (*Ann. d. Physik*, 36, 284 (1939)), and gave reasonable thermal diffusion coeffs. (2.6×10^{-7} , 2.0×10^{-7} and 4.2×10^{-8} for HCl, H₂SO₄ and NaCl, resp.).

Author.

The atomization of liquid by means of an air stream. S. Nukiyama and Y.

Tanasawa. *Nippon Gakujutu Kyōkai Hōkokū*, **14**, 248—249 (1939).—A new method of atomization of liquid was investigated in the authors' laboratory. A jet of liquid was atomized by a stream of compressed air issuing from a nozzle around the jet, and the atomizing phenomenon observed in detail by means of instantaneous stereo-photography to study in what way the droplets were formed. Capturing the droplets upon an oil-filmed glass plate placed in front of the jet, the size of the droplets was measured with a microscope. Water was taken first to study the influence of the relative quantity and velocity between it and the air stream upon the size of the droplets, and then the effect of physical properties of liquids, as density, coeff. of viscosity, surface tension and etc., upon the atomizing process was investigated. As one of the results, the following expression giving the mean size of the droplets was obtained, which is satisfied by all liquids under certain conditions:

$$d_0 = 585 \frac{\sqrt{\sigma}}{\sqrt{V\rho}} + 597 \left(\frac{\mu}{\sigma\rho} \right)^{0.35} \times \left(1000 \frac{Q_l}{Q_a} \right)^{1.5}$$

where, d_0 = mean diameter of the droplets (μ),
 σ = surface tension (dyne/cm), ρ = density (μ/cm^3),
 μ = coeff. of viscosity (dyne-S/cm²),
 V = relative velocity between air and liquid (m/s),
 Q_l = volume of liquid, Q_a = volume of air.
 Authors.

On valency. S. Kaneko. *Bull. Electro-techn. Lab.*, **5**, 408—409 (1941).—The following three eqs. can be given for the definition of valency:

Valency = Electrovalency + Covalency (1)

Valency = Electrovalency - Covalency (2)

Valency = | Electrovalency | + Covalency (3)

But none of them is quite satisfactory. The following eq. is equiv. to the first eq.:

Valency = Number of Valency Electrons - (Number of lone pairs \times 2). (4)

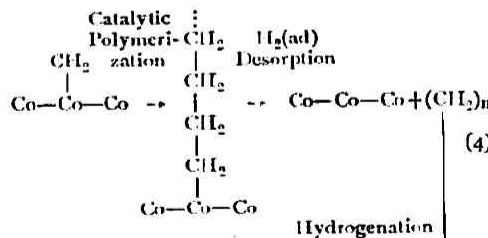
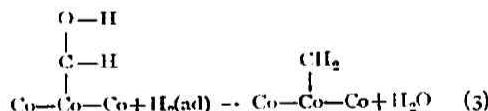
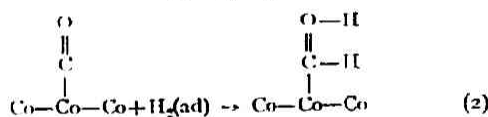
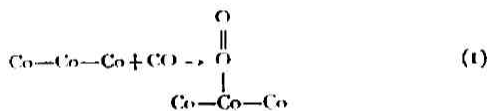
Author.

On explosive reactions of gases. I. Explosion limits of oxyhydrogen gas.

S. Kimata, N. Aomi, and R. Goto. *This Journal*, **15**, 42—53 (1941).

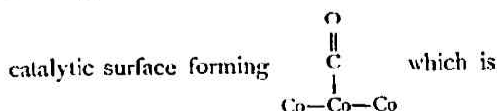
On explosive reactions of gases. II. Spark ignition of oxyhydrogen gas at low temperatures. A. Hayakawa and R. Goto. *This Journal*, **15**, 118—126 (1941).

Physico-chemical investigations on catalytic mechanism. I. Note on the Fischer-Tropsch synthesis of hydrocarbons with special reference to its reaction mechanisms. S. Hamai. *J. Chem. Soc. Japan*, **62**, 516—518 (1941).—The author points out that the mech. for the Fischer-Tropsch synthesis has not so far been well discussed and settled although there are numerous publications. A probable mech. concerning this synthesis is presented which can be summarized as follows:



Higher Hydrocarbons ← (liquid hydrocarbons).

Namely, carbon monoxide is adsorbed on the



transformed by the catalytic reduction in the

presence of $H_2(ad)$ to $\begin{array}{c} O-H \\ | \\ C-H \\ | \\ Co-Co-Co \end{array}$; the latter

reacts with $H_2(ad)$ to form $\begin{array}{c} CH_2 \\ | \\ Co-Co-Co \end{array} + H_2O$,

it being consistent with the observed fact of the initial appearance of H_2O . By the catalytic polymerization, $CH_2(ad)$ is then trans-

formed to $\begin{array}{c} \vdots \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ Co-Co-Co \end{array}$, and proceeds to $(CH_2)_n$

by desorption; and by hydrogenation, the final products of higher hydrocarbons (liquid hydrocarbons) are formed. The author also discusses, in connection with his new mech., the following facts: 1) The formation of methane at the initial stage. 2) The non-formation of methane when H_2 alone is passed at $200^\circ C$. after evacuating the reaction system immediately after the regular synthesis (and the methane formation at $300^\circ C$.) 3) Secondary nature of CO_2 formation in the case of the Fe type catalyst. 4) Applicability of the same mech. to the Fe type catalyst.

Author.

Spectroscopic study of the combustion of hydrocarbons. M. Miyani. *Nippon Gakujutu Kyokai Hokoku*, **16**, 38—42 (1941).—According to the results given by Withrow, his coworkers and Boyd, the spectra of combustion flames of gasoline produced in the detonating zones of gas engines were similar to that of inner corn of coal gas flames, and the spectra of after glow to that of outer corn. They also found the formation of aldehyde in the fuel-air mix. prior to inflammation in knocking conditions. In the present expt. a similar study was carried out concerning the oxydation of iso-octane and normal-heptane in a state of low press. The ignition spectra of the mixt. of these hydrocarbons and oxygen

kept in glass tubes were also similar to those of inner corn of coal gas flames, and in the case of iso-octane the intensity of the band spectra of C_2 was especially strong as compared with that of normal-heptane. From this fact it seemed that the probability of production of C_2 molecules was greater than that of CH molecules in the former as compared with that in the latter. The absorption spectra of the mixts. in various temps. were examined. In the case of normal-heptane the absorption spectra of aldehyde began to appear from a temp. of about $250^\circ C$. and they became remarkable at a temp. of about $300^\circ C$. but not in the case of iso-octane. The light absorption of molecules $(C_2H_5)_4Pb$ disappeared at the temp. of about $280^\circ C$. and when a trace of the molecules was added to the mixt. of normal-heptane and oxygen, no light absorption of aldehyde was observed though it was heated to $410^\circ C$. Thus the formation of aldehyde began to take place at about $250^\circ C$. and the dissocn. of tetra-ethyl lead at about $280^\circ C$. This dissocn. therefore seemed to have a certain relation to the anti-knocking effect for the combustion of normal-heptane.

Author.

The decomposition velocity of the organic peroxide. T. Yamada. *Researches Electrotech. Lab.*, **443**, 1—70 (1940).—The mech. of oxidation of the substance showing auto-oxidation is assumed from the decompn. velocity of peroxide. That the decompn. velocities of tetraline peroxide and oxidation product of turpentine oil are taken to be a monomolecular reaction and a bimolecular one resp. is ascribed to the difference of the affinity or stability between the peroxide and the substance showing auto-oxidation.

J. C. L.

The homogeneous exchange reaction between water and hydrogen. S. Abe. *Bull. Inst. Phys. Chem. Research*, **20**, 264—276 (1941).—The mechanism, $DO' + HH + DOD \rightarrow DOH + HD + OD'$, proposed by Bonhoeffer for the exchange reaction taking

place when heavy water solution of KOH and H_2 gas are shaken at $100^\circ C$ is examd. The velocity of the said reaction is dependent on KOH and it is more or less reduced by the addition of As_2O_3 and H_2S . The KOH heated with iron wire reacts actively, but in the lapse of time it loses its activity, depositing a thin plate-like crystal of $FeO \cdot H_2O$. That is, this exchange reaction is brought forth not by acid or base as catalyst, but by the impurities present in KOH. J. C. L.

The homogeneous interchange reaction between hydrogen and water. S. Abe. *Se. P.*, 38, 264—276 (1941).—Wirtz and Bonhoeffer [*Z. Physik. Chem.*, I, 177 (1936)] have found that hydrogen, when shaken at $100^\circ C$ with 1N KOH soln. of ca 100% heavy water, was appreciably shifted in deuterium content, suggesting the mech. of acid-base catalysis for the reaction. This mech. being, however, incompatible with the theory of acid-base catalysis proposed by Horiuti, further exptl. investigation was carried out to afford a sound basis for deducing a proper mech. Allowing normal hydrogen to react with 1N KOH, 1N HCl soln. in 90% heavy water or with the pure solvent at $100^\circ C$ in vacuum for several hrs., the following results were obtained. The observed transfer of deuterium from the soln. to hydrogen is the isotopic interchange reaction taking place in the liquid phase. The reaction in the liquid phase can not be an acid-base catalysis, but it may be due to some catalyst contained originally in the alkali preparation. The possible catalyst is colloidal iron contaminated in alkali in the course of the concn. by evaporation in an iron pot, decaying away as a catalyst in the form of ferrous hydroxide which is pptd. when the soln. is treated at $100^\circ C$.

Author.

Catalytic study of the reaction between hydrogen peroxide and iodine ion. I. The velocity constant of the fundamental reaction. K. Okabe. *J. Chem. Soc. Japan*, 61, 1235—1238 (1940).—

The reaction, $H_2O_2 + 2HI \rightarrow 2H_2O + J_2$ (1), in an acidic soln. in a reaction $2HI + JO' + J' \rightarrow J_2 + H_2O$ following a reaction $2H' + JO' + J' \rightarrow J_2 + H_2O$ (2). If the reaction velocity of reaction 1 is measured from the product J_2 , the velocity formula will be very complex and it is difficult to know the mech. of the catalytic action of the salt of heavy metal on the reaction concerned. When a small quantity of starch paste and a given amt. of sodium thiosulphate are added to the reacting soln. of reaction 1, JO' of reaction 2 reacts on thiosulphate ion and turns into J' . Accordingly, so long as sodium thiosulphate is present, the concn. of J' is const., and when the whole of thiosulphuric acid becomes tetrathionic acid, J_2 acting on starch shows blue. Measuring the lapse of time, the velocity const. k_2 of reaction 2 is obtained: $k_2 = 0.66 \text{ mol/L. /minute}$, with varying initial concns. of hydrogen peroxide, the concns. of sodium thiosulphate and potassium iodide being 0.023×10^{-2} and $0.023 \text{ mol/L. resp.}$ J. C. L.

The self-exchange reaction of aniline hydrochloride and its derivatives.

I. Aniline hydrochloride. N. Okazaki. *J. Chem. Soc. Japan*, 62, 52—56 (1941).—The exchange reaction of hydrogen atom between the phenyl radical and amino radical of aniline hydrochloride is studied with deuterium at about the temp. of the melting point. The migration of deuterium from amino radical to phenyl radical proceeds considerably fast above $180^\circ C$ and much more so above the melting point ($198^\circ C$). Of the hydrogen atoms of phenyl radical, three in ortho and para position with respect to the amino radical take part in the reaction. *O*- and *p*-trideutero aniline hydrochlorides make reverse reactions. The drying of sample, exerts no influence on the reaction and so there is little possibility that the reaction is caused partially by a trace of water. The mech. of the reaction is also discussed. J. C. L.

The reaction of high polymers in solution. The alkaline saponification

of polyvinyl acetate. Preliminary report. A. Horiuchi. *This Journal*, 15, 71—77 (1941).

The reaction of high polymers in solution. The alkaline saponification of polyvinyl acetate. I. On the method of measurement of reaction velocity. A. Horiuchi. *This Journal*, 15, 78—85 (1941).

Studies on the resinification. I and II. K. Kaneko. *J. Soc. Chem. Ind. Japan*, 44, 471—478 (1941).—Several formulas, which show the relation between viscosity and concn. of the resin solns., are found in literature. But the range of the concn., in which they are applicable, is limited. Therefore the author proposed in the first report a new formula: $\eta_r = 1 + a \cdot c\varphi / (100 - c\varphi) + b\{c\varphi / (100 - c\varphi)\}^2$, and proved the conformity between it and the results in literatures. It was applicable for the range of 0—40% concn. in the case of acetone soln. The specific volume φ was generally smaller than 2 and varied slightly with the time of reaction, the quantity of catalyser, the temp. of measurements and the ratio of phenol to formaline. In the second report the author proposed a method of inferring the shape of particles in soln. from the viscosity data. First, he drew the $c - c/\eta_{sp}$ -curve, and then calcd. the value of $dc/\eta_{sp}/dc$ at the point of $c=0$ on the curve. It is $-(a+b)/a^2$ from the author's formula and amts. to -1.1 when the particles are spherical. This value coincides with that of phenol resin in acetone soln., but not in alcohol or acetic acid soln. The influences of low molecular compds. and catalysers are also considered. Author.

Chemical reaction between calcium carbide and carbon dioxide and monoxide at high temperatures. T. Aono. *J. Electrochem. Assoc. Japan*, 9, 81—82 (1941).—(1) At a temp. below 600°C crude calcium carbide reacts upon CO_2 . The reaction $CO_2 + C \rightarrow 2CO$ begins somewhat below 600°C,

and at 650°C and above the CO thus formed reacts with CaC_2 according to the equation: $CO + CaC_2 = CaO + 3C$. At higher temps. the reaction $CO_2 + 2CaC_2 = 2CaO + 5C$ also takes place, and its velocity is very large at about 1100°C. Excess of CO_2 combines with the free carbon forming CO and leaving CaO in the carbide. The final change is $CaC_2 + 3CO_2 = CaO + 5CO$. (2) In the presence of calcium carbide CO changes at 400°C, thus: $2CO + CO_2 + C$. The reverse reaction $CO_2 + C = 2CO$ takes place somewhat below 600°C. At 650°C CO combines very rapidly with CaC_2 according to $CO + CaC_2 = CaO + 3C$. (3) The above two reactions proceed almost perfectly at 1000—1100°C. Author.

On the chemical action of steam on calcium carbide at a high temperature. T. Aono. *J. Electrochem. Assoc. Japan*, 9, 143—146 (1941).—The chemical action of steam on calcium carbide at 400—900°C was studied exptl. The main reactions are $CaC_2 + H_2O = CaO + C_2H_2$ and $C_2H_2 = 2C + H_2$, while the latter predominates above 600°C, the concn. of H_2 in the gas produced amtg. to more than 80%. At 400—600°C CH_4 is formed in a considerable quantity. The formation of acetylene-black and CO, CO_2 and H_2 due to this carbon, and their action upon CaC_2 at these high temps. are also discussed. To show the relation between temp. and velocities of the total gas formation, a fixed curve is drawn. The apparent heats of activation for the reaction were calcd. from which the main reactions were inferred. At 400—600°C, some liquid products, such as $CH_3 \cdot CHO$, $CH_3 \cdot CO \cdot CH_3$, C_6H_6 , etc., were also obtained in small quantities. Author.

Process of calcium carbide formation in an electric furnace. T. Aono. *J. Chem. Soc. Japan*, 62, 349—359 (1941).—An electric furnace of 100 kW capacity, with which calcium carbide was prepared continuously for 287 hrs., was stopped suddenly and the contents were dissected after rapid

cooling. From the microscopic observation and chemical analysis it was found that mutual diffusion of lime and carbon is taking place before chemical reaction. The reduction of lime (in solid or sintering state) to Ca (vapor or liquid), and the combination of the Ca produced with carbon to become CaC_2 can take place slowly at moderate temp. But when the temp. was elevated rapidly, the melting of lime (with impurities) or dissoln. of CaO in the molten CaO— CaC_2 , and the combination of solid carbon with this molten or dissolved CaO to become CaC_2 take place. Actually the latter process will predominate in the carbide furnace. Author.

Studies on the reactions in solid

state at higher temperatures. VII. **The reaction between magnesium oxide and aluminium oxide in solid state.** Y. Tanaka. *J. Chem. Soc. Japan*, 62, 477—479 (1941).—It is found that pure $\text{MgO} \cdot \text{Al}_2\text{O}_3$ is formed at first in this reaction, and the solid soln. rich in Al_2O_3 is gradually formed when an excess of Al_2O_3 is present. Although there exists a rapid initial reaction, the later reaction is controlled by the diffusion of the two components through the reaction product. The energy of activation of the process between 800° and 1200° is calcd. to be 41.1 Kcal. per mole. The reaction proceeds more easily with the mixts. contg. an excess of MgO than with other mixts. Author.

2—SUB-ATOMICS, RADIOCHEMISTRY AND PHOTOCHEMISTRY

Pair production by gamma rays from fluorine bombarded with protons. K. Shinohara and M. Hatoyama. *Se. P.*, 38, 253—262 : 326—327 (1941).—Pair production by gamma rays from fluorine bombarded with protons was investigated in a cloud chamber. A value of $6.2 \sim 0.1$ MeV for the energy of the gamma rays was obtained, which agreed with the results of other workers. The probability of division of energy between positive and negative electrons was studied and compared with the theoretical results of Bethe and Heitler. The exptl. curve showed more marked decrease of probability for unequal division of energy than the theoretical. Authors.

Photo-fission of uranium and thorium produced by the γ -rays of lithium and fluorine bombarded with high speed protons. B. Arakatsu, Y. Uemura, M. Sonoda, S. Shimizu, K. Kimura and K. Muraoka. *Proc. Phys.-Math. Soc. Japan*, III, 23, 440—450 (1941).—By using

the γ -rays of the resonance excitation due to $\text{Li} + p$ and $\text{F} + p$ reactions, whose quantum energies are 17 MeV and 6.3 MeV resp., the photo-fission phenomena were easily observed when uranium and thorium nuclei were exposed to them. The cross sections of these nuclei were detd. by directly counting the number of fission fragments ejected from the known quantity of U_3O_8 or ThO_2 for the measured number of the irradiating γ -ray quanta resp. They are summarised to be $\sigma_U(17) = 16.7 \times 10^{-27} \text{ cm}^2$, $\sigma_{\text{th}}(17) = 7.2 \times 10^{-27} \text{ cm}^2$, and $\sigma_U(6.3) = 2.2 \times 10^{-27} \text{ cm}^2$, while the effect of the γ -rays from Ra was observed to be so slight that the cross section of uranium had to be estimated as $\sigma_{\text{th}}(2.2) \ll \sigma_U(2.2) \ll 0.005 \times 10^{-27} \text{ cm}^2$. These results suggest that the fission cross-section of an element is approximately proportional to the square of the quantum energy $(h\nu)^2$ of the irradiating γ -ray, though it seems probable that, in the case of uranium, a certain threshold value $(h\nu_0)$ exists between 6 MeV and 2.2 MeV. It is, therefore, finally noted that the cross section of uranium

would be presumably formulated into $\sigma = \sigma_0 \left(\frac{h\nu}{me^2}\right)^2 \left[1 - \left(\frac{h\nu_0}{h\nu}\right)^n\right]$, in which, assuming $n = 4$, σ_0 and $h\nu_0$ may be taken as $\sigma_0 \doteq 1.45 \times 10^{-29} \text{ cm}^2$ and $h\nu_0 \doteq 3 \text{ MeV}$. Authors.

Liberation of neutrons in the nuclear explosion of uranium irradiated by thermal neutron. T. Hagiwara. *This Journal*, **13**, 146—150 (1941).

Variation of the atomic structure factor with wave-length in the region of anomalous dispersion. S. Yoshida. *Sci. P.*, **38**, 263—271 (1941).—The intensity distribution with wave-length of continuous X-rays reflected by various kinds of single crystals was investigated qualitatively for the immediate neighbourhood of an absorption limit of the constituent atom of the crystal. It was found that in the cases of molybdenite, quartz and sodium chlorate the observed intensity distribution curve presents a remarkable increase of reflection on the short wave-length side of the absorption limit, contrary to the usual case. In these cases also the effect of the surface treatment such as grinding was examd. The observed curves were compared with the variation curve of the atomic structure factor with wave-length in the region of anomalous dispersion computed by the dispersion theory. It is concluded that in the cases of mosaic crystals the observed curve deviates from the theoretical one on account of the large true absorption on the short wave-length side on the limit, while in the cases of perfect crystals such as molybdenite, quartz and sodium chlorate the observed curve closely, though not satisfactorily, resembles the calcd. one. Author.

On the Paschen-Back effect of the lines H_α and D_α . T. Sakurai. *Sci. Repts. Tohoku Imp. Univ.*, **29**, 504—541 (1941).—This paper describes the results of the observation of the magnetic splitting of the spectra lines H_α and D_α in the magnetic fields

up to the intensity 27450 Oersted. The Paschen-Back effect was observed for both lines in the fields stronger than 9440 Oersted. The third component σ_{111} which Paschen and Back have found in their observation on the line H_α and one of the corresponding π components π_{111} were also observed in both lines in strong fields. The splitting and the intensities of the components in the fields were measured, and it was shown that the intensity anomaly of the doublet of the lines in the absence of the magnetic field was found. By Darwin's method, the calcs. of the intensities of the components in the fields were made under three different assumptions. The observed intensities of the components in the fields seem to be in very good accordance with those calcd. under the assumption that the above anomaly is due to the enhancement of the transition ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$. Author.

Stark effect on hydrogen molecule. (Part 1) G. Hayakawa. *Proc. Phys.-Math. Soc. Japan*, **III**, **23**, 318—335 (1941).—The Stark effect on H_2 -spectrum in the red and yellow region (H_α -5690 Å) was measured using dispersion about 8.1 Å/mm. With a field strength 208,000 V/cm better resolution of components was obtained than in the former investigations. The results were compared with the theoretical displacements roughly calcd. as due to the mutual influences among the neighbouring terms, specially for anti-symmetrical lines of $\alpha(0, 0)$ band.

Author.

Spectra of mercury at high vapour pressure in condenser discharge. T. Harada and R. Miyasaka. *Proc. Phys.-Math. Soc. Japan*, **III**, **23**, 370—376 (1941).—The condenser discharge spectra of mercury at high vapour press. are studied up to about 15 atm. and 3000 amps. The lines of the series ${}^3P-{}^3D$ become very broad and continuous as compared with the other lines due to the high sensitivity of the 3D terms to the Stark effect. At 15 atm. all the lines become absorption lines or disappear at all in the continuous

background except probably the line 3984 ($5d^96S^2D_{21/2} - 5d^96P^2P^{\circ}_{11/2}$) which remains relatively sharp up to the highest press. The energy distribution in the visible range, however, displays the existence of the very broad emission bands near the atomic lines and has not the smooth form of the black body radiation type of definite temp., showing that the quant. states are not completely destroyed in the above mentioned discharge condition.

Authors.

Rotational analysis of γ system of ZrO bands. T. Tanaka and T. Horie. *Proc. Phys.-Math. Soc. Japan*, **III**, **23**, 464—484 (1941).—(1) The rotational analysis of the γ system bands was made by using, the third order emission spectra due to 21-foot concave grating. (2) These bands can be attributed to the transition of $^3\Sigma \rightarrow ^3\Pi$, of which the final state coincides with that of the α system. (3) The trebling of the level with each value of K in the $^3\Sigma$ state cannot be found, and the levels for small values of K of the branches of $v' = 0$ undergo peculiar perturbations. (4) The $^3\Pi$ state gives an example similar to Case a. (5) The following values of the rotational consts. are obtained: $B_e' = 0.5658 \text{ cm}^{-1}$, $a' = 0.0077$, $r_e' = 1.477 \times 10^{-8} \text{ cm}$, $B_e'' = 0.6189 \text{ cm}^{-1}$, $a'' = 0.0038$, $r_e'' = 1.412 \times 10^{-8} \text{ cm}$. The consts. of the final state are close to those obtained by Lowater for α system. (6) The Λ -type separations in the $^3\Pi$ state are detd. (7) The isotope effect is discussed. Authors.

Studies on the near ultraviolet absorption spectra of benzene and its derivatives. III. Phenol. K. Asagoe, Y. Shimokawa and S. Kageyama. *J. J. Phys.*, **14**, 11—16 (1940—1941).—In continuation of the researches in *Cl*- and *Br*-benzene (*Proc. Phys.-Math. Soc. Japan*, **22**, 677—690 (1940)), a weak absorption spectrum of phenol in the near ultraviolet region from 2500 Å to 2800 Å was studied. The absorption tube was about 1 m in length. It was filled with the phenol vapour at the satn. vapour press. at

20°C. The estimated absorbing power of phenol is more than 230 times stronger than that of benzene. Comparing the value with Sklar's theoretical one (20 times of benzene), the latter seems to be too small. The vibrational structure of the phenol spectrum is quite similar to those of *Cl*- and *Br*-benzene. $O \rightarrow O$ transition is observed at 36356 cm^{-1} . Several const. frequencies, namely 779(*c*), 932(*d*), 982(*b*), 473(*a*) and 1272(*e*) cm^{-1} are found. Although the phenol mol. is different in structure from those of *Cl*- and *Br*-benzene, because the substituted radical consists of two atoms, and the *O—H* bond is not parallel to the *C—O* bond, the result of the analysis of the bands shows that the differences may be disregarded at least in the vibrational phenomena, owing probably to the small mass of *H*-atom. Thus the above frequencies may be regarded as the totally symmetrical vibrations in the upper stage and probably correspond to 813, 1002 (or 1024), 1024 (or 1002), 614 and 1253 cm^{-1} in the lower state resp. Two or three (or more) overtones and combinations of these frequencies with one another are also found. Upon each of these main bands, several 220 and 60 cm^{-1} progressions are also found on the red side. These may be interpreted as due to the series of $n \rightarrow n$ transitions. The 60 cm^{-1} progressions may tentatively be represented as concerned with the Raman frequency 235 cm^{-1} , and the 220 cm^{-1} ones with 523 cm^{-1} . Nearly all the bands are thus interpreted well. Some assignments given by R. Witte and J. Savard about the regularity of the spectrum are completely included in the present analysis. The wave numbers of the bands thus analyzed are given in tables, and energy levels for the phenol mol. and the transition between them are shown schematically. Authors.

On the triboluminescence of rubber. K. Koshiyama. *J. Chem. Soc. Japan*, **62**, 597—598 (1941).—The author found that cohesive substances such as sticking plaster and rubber tape which are chiefly composed

of elastic rubber, emit faint light when they are pulled apart vigorously and violently in a dark room, and so he tried to find out if the light was emitted only by the substances made of pure rubber. The rubber cement obtained by dissolving pure rubber in benzene was applied to two pieces of cloth and left until they had become rather dry and sticky. They were pressed together under a weight for two or three days. When they were completely glued together, they were taken into a dark room and pulled apart and they emitted bluish green light. It is proved thus that the luminescence is caused by pure rubber. When we pull apart a rubber-cemented cloth glued on a rubber or celluloid or glass plate, we see the same kind of luminescence. If we let a pure rubber sheet run at high speed over the pulley of a small motor and let a metal rod or a glass rod touch it, then we see here again luminescence, but if we use a highly vulcanized rubber we can not see it. A rubber-cemented cloth which is wet does not emit light, but a dry one does. If we stick a rubber-cemented cloth on a dry camera plate and then pull it off and develop the plate, we shall see that the plate has been exposed to light. But if we stick a rubber-cemented cloth on a glass plate and pull it apart after placing a dry plate beneath it, we

shall see that the dry plate has not been effected by light. This shows that the light is very faint and is absorbed by a single plate of glass. If we experiment with buna, the polymerised butadiene, in the same manner, we shall see it radiate light and affect a dry camera plate. Guttapercha, however, does not radiate light and does not affect a camera plate. Neoprene, the polymerised chloroprene, does not radiate, but the plate shows signs of having been affected by faint light. When rubber is vigorously pulled apart, rubber molecules are partly stretched and some electrons from the atoms belonging to the molecules which are stretched are thrown momentarily into a high quantum state by the energy of stretching, and the next moment the electrons return to their normal state. Therefore the triboluminescence of elastic rubber can be considered to be a phenomenon arising when the electrons return to the normal state. The fact that buna as well as natural rubber emit light shows that the two substances are quite akin to each other in their molecular structures. On the contrary, the fact that guttapercha does not emit light is noteworthy. Neoprene does not emit visible rays, but judging from the fact that it affects a dry camera plate, it is apparent that it emits some ultraviolet luminescence.

Author.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY (THERMODYNAMICS)

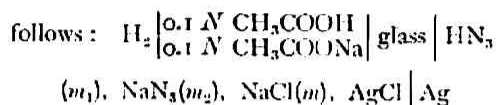
On the dissociation constant of hydrogen selenide. H. Hagiwara. *Bull. Inst. Phys. Chem. Research*, 20, 384—389 (1941).—The disso. const. of hydrogen selenide were detd. by means of a glass electrode at 25°C, measuring the pH value at each stage of titration of hydrogen selenide soln. with sodium hydroxide. From the results the first disso. const. was found to be $K_1 = 1.30 \times 10^{-4}$, 1.32×10^{-4} , and 1.28×10^{-4} . The mean value $K_1 = 1.30 \times 10^{-4}$

was adopted. The $p[H]$ value of sodium biselenide was graphically found to be 7.30 from the titration curve. From this value $K_2 = 1 \times 10^{-11}$ may be taken as the second disso. const. of hydrogen selenide.

Author.

On the dissociation constant of hydrazoic acid. N. Yui. *Bull. Inst. Phys. Chem. Research*, 20, 390—398 (1941).—The disso. const. of hydrazoic acid was detd. by

means of a glass electrode at 25°C. measuring the pH value at each stage of titrations of hydrazoic acid solns. with sodium hydroxide and of sodium azide solns. with hydrochloric acid. From the result of these titrations the dissocn. const. $2 \cdot 16 \times 10^{-5}$ was computed as a mean value. On the other hand the const. was also detd. using the cell without liquid junction. The cell combination was as follows:

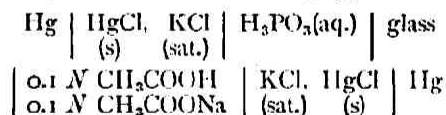


where m_1 , m_2 , and m_3 represent the molalities of HN_3 , NaN_3 , and NaCl resp. The apparent consts. were calcd. on the basis of e. m. f. measurements at various ionic strength of solns., and the true const. was detd. by extrapolating to zero ionic strength. The const. thus obtained was 1.91×10^{-6} . Consequently

$$\text{HN}_3(a=1) = \text{H}^+(a=1) + \text{N}_3^-(a=1) \\ \Delta F_{298}^\circ = 6.442 \text{ cal.}$$

Author.

On the dissociation constants of phosphorous acid. K. Takahashi and N. Yui. *Bull. Inst. Phys. Chem. Research*, 20, 521-528 (1941).—The dissocn. consts. of phosphorous acid were detd. at 25° by means of a glass electrode, measuring the pH value at each stage of titration of phosphorous acid solns. with sodium hydroxide. The cell employed was of the following type:



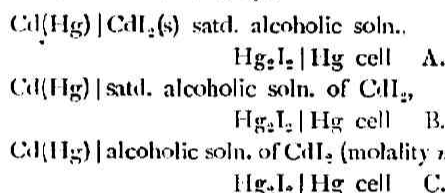
From the result the first dissocn. const. was computed as 0.031 ~ 0.021 and the second, const. about 1.5×10^{-7} in the concn. range of about 0.04 ~ 0.01 mol/l. The first dissocn. const. was not const. and increased considerably in proportion to the acid concn. This irregularity may be explained qualitatively by assuming the formation of a polymer of this acid such as $\text{H}_6\text{P}_2\text{O}_6$ which may be considered stronger than the monomolecular acid. The strength of many oxy-acids increases with the

number of oxygen atoms, e. g. HClO , HClO_2 , HClO_3 , $\text{H}_2\text{N}_2\text{O}_2$, HNO_2 , HNO_3 etc., but in the case of oxy-acids of phosphorus, H_3PO_2 , H_3PO_3 , H_3PO_4 the strength seems to be nearly the same or rather shows a decreasing tendency with increasing oxygen atoms. This fact also may be elucidated by assuming the polymerization of lower oxy-acids of phosphorus.

Authors.

A thermodynamic study of dissolution of cadmium iodide in alcoholic solutions.

M. Miyoshi and H. Hagiwara. *Bull. Inst. Phys. Chem. Research*, 20, 514-520 (1941).—The theoretical heats of soln. of CdI_2 in satd. alcoholic solns. were detd. at 25° and 30° by measuring the solubilities and the electromotive forces of the following reversible cells at various temps.



The theoretical heat of soln. may be calcd. by the eqs.:

$$Q = 2FT\{(dE/dT)_A - (dE/dT)_B\} \quad (1)$$

$$Q = 2FT(dE/dC)_T(dC/dT) \quad (2)$$

The following values were obtained exptl.

$$Q_{200} = 478 \text{ cal.} \quad Q_{250} = 445 \text{ cal.}$$

By comparing these values with the corresponding values for aqs. solns., i.e. $Q_{100} = -1.350$ cal and $Q_{180} = -1.237$ cal, we can easily elucidate the fact that in the case of alcohol the solubility of CdI_2 decreases slightly with rise of temp., whereas in the case of water it increases in a greater extent. The differential free energies of soln. $(d\Delta F/dm_2)n_1$ of CdI_2 in alcoholic solns. of various concns. were detd. at 25° and 30°, and compared with those for aq. solns. The former values were found to be more negative than the latter values; the difference may be attributed to a greater tendency to complex ion formation in alcoholic than in aq. solns.

Authors.

Electrolysis of the solution of heavy metal salt. S. Kaneko. *Bull. Electrotech. Lab.*, 5, 279—280 (1941).—The voltage-current curve is detd. in electrolysis of copper sulphate soln. The current increases at first, shows a saturation phenomenon and then increases again. At this last point the metal deposits as a power. Author.

On the thermal conductivity of binary system: air-SO₂, air-ethyl ether, and air-benzene. F. Ishikawa and T. Abe. *Bull. Inst. Phys. Chem. Research*, 20, 5, 292—300 (1941).—The thermal conductivity of the above-mentioned binary systems was measured at 25° under various total pressures. The max. ether content of the air was 47.1% and the max. benzene content 7.78%. The conductivity curves were generally convex to the compn. axis except that of the system air-benzene at 300 mm where a strictly linear relation was observed. The relation: $100 \times V_m = V_{SO_2} \times x + V_{air} \times (100 - x)$ may approximately hold for the system air-SO₂ at 760 mm. In the above expression V_m is the conductivity of the mixt. expressed in volts, V_{SO_2} and V_{air} are the conductivities of SO₂ and air at their resp. partial press., and x is the percentage of SO₂ in the mixt. The value of ϑ for SO₂ in $K = \vartheta \eta C_v$ (K is the true conductivity, ϑ the const., η the viscosity, and C_v the specific heat at const. volume) was detd. by $V = C_1 / \sqrt{K}$ (C is the const.) using the values of V_{SO_2} , V_{air} for the pure components and $\vartheta_{air} = 1.91$. ϑ_{SO_2} was found to be 1.62, which was in good agreement with the value 1.65 calcd. by the relation $\vartheta = \frac{1}{3} (9\tau - 5)$, where $\tau = C_p / C_v = 1.29$ for SO₂. By the thermal conductivity method, SO₂ and the organic vapours contd. in the air may be estimated with the accuracy of about 0.15%. Authors.

Contribution of conduction electrons in a metal to the thermal expansion. Z. Mikura. *Proc. Phys.-Math. Soc. Japan*, III, 23, 309—318 (1941).—The approximate proportionality between the thermal-expansion

coeff. and the atomic heat of a metal in the moderate temp. region is well known. However, it seems that this relation should be changed at those extremely low temps., where the contribution of the conduction electrons to the atomic heat is relatively large. It is the purpose of this paper to construct a formula for thermal expansion to cover this temp. region. The result is that in this region the thermal-expansion coeff. is no longer proportional to the atomic heat, and that it consists of two parts, corresponding to the Debye and the electronic terms of the latter resp. The electronic term of the thermal-expansion coeff. is generally not proportional to that of the atomic heat. However, the former as well as the latter is proportional to the absolute temp. at low temps. From the new formula a possible explanation of the small expansibility of "Invar" is suggested. Author.

On the specific heats of iron oxides at high temperatures. S. Umino. *Rep. Nippon Seitetsu, Yawata Research Lab.*, 22, (1) 1—25 (1941).—(1) Heat contents of some iron scales ranging from 27.53 to 55.37% ferrous oxide, 68.32 to 39.88% ferrous ferrite, 0.19 to 0.55% metallic iron, and 3.22 to 4.36% impurities are measured by the method of mixt. at different high temp., and the heat content-temp. relations of ferrous oxide FeO and ferrous ferrite Fe₃O₄ are obtained by the calcn. The apparent and true specific gravities of these scales were 5.275 and 5.303 resp. as the mean values. As the softening temp. of one scale, 1356° was obtained. (2) The mean specific heat of iron scale at high temps, increases with the heating time and temp. (3) The heat conductivity of iron scale is small in the range of low temp., but increases gradually with the rise of temp. (4) As the Curie point of ferrous ferrite Fe₃O₄, 590° was obtained from the heat content temp. curve of iron scale. (5) The magnetic transformation in ferrous ferrite takes place in a range 190—200° or so, and the heat of transformation is about 15.34 calories per unit mass.

This heat is about 4.33 times greater than that of A_2 transformation in pure iron. (6) By the method of calcn., the heat contents and specific heats of ferrous oxide, FeO , and ferrous ferrite, Fe_3O_4 , in the temp. range $100-1100^\circ$ were obtained from the heat content-temp. relation of iron scale. (7) The mean specific heat of ferrous oxide is always greater than that of ferrous ferrite in the temp. range $100-1100^\circ$, but the order of the true specific heats in the range of magnetic transformation is reversed. Both of these true specific heats, except that in the range of magnetic transformation of ferrous ferrite, are represented approximately by the following equations: $FeO \dots C_p = 0.218 + 3 \times 10^{-5}t$ and $Fe_3O_4 \dots C_p = 0.128 + 1.1 \times 10^{-4}t$. (8) From the change of weight of the scales before and after the expts., it is seen that the rate of

transformation from ferrous oxide FeO to ferrous ferrite Fe_3O_4 is proportional to the heating time and its temp., and the effect of heating time is less than that of the rise of temp.
Author.

Freezing point of H_2O-D_2O mixture.

S. Kaneko. *Bull. Electrotechn. Lab.*, **5**, 319—322 (1941).—Freezing point of H_2O-D_2O mixt. is calcd. under the assumption that the equil. const. between DHO , H_2O and D_2O is 4. The freezing point and the heat of fusion of DHO are also theoretically calcd., their values being $276.96^\circ K$ and $1,522$ cal. resp.
Author.

Hydrocarbons from carbide. Thermodynamics. R. Negishi, O. Kimura and O. Kamiike. *This Journal*, **15**, 31—41 (1941).

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY (CONTACT CATALYSIS)

On the effect of amino-acids and peptides upon some surface active substances. Y. Mutô. *J. Biochem.* **33**, 1—15 (1941).—The surface tension of solns. contg. surface active organic acids and amino-acids was measured by the max. bubble press. method. Surface tension of solns. contg. β -naphthalene-sulphonic acid or octylsulphuric acid is greatly lowered by adding a small amt. of amino-acids or peptides which are only slightly surface active. Leucine, lysine, phenylalanine, isoleucine, leucyl-glycine, glycyl-leucine and leucyl-glycyl-glycine were tested. But the addn. of glycocoll, glycyl-glycine, etc. produced no, or almost no, such effect. When strong organic acid was replaced by weak carbonic acid, such as caproic acid, such effect became quite small. Author.

Studies on the dielectric properties of a substance in the sorbed state. I.

I. Higuchi. *Bull. Inst. Phys. Chem. Research*, **20**, 489—513 (1941).—The apparent dielectric const. of *n*-propyl alcohol sorbed by titania gel was measured by a beat method at frequencies 3, 1.5, 0.869, and 0.374 megacycle and in the temp. range from $70^\circ C$ to $-70^\circ C$. When at each temp. the capacity increase (ΔS) of the measuring condenser, which holds activated gel, is plotted against the sorbed quantity (A), a straight line is obtained with a break corresponding to the change in the sorbed state, i.e. from the adsorption to the capillary condensation. The relative press. corresponding to this break at each temp. is, as expected, in a good agreement with the value calcd. by the theoretical formula $a\sigma = -k' \ln\left(\frac{P}{P_0}\right)$, which was previously derived by the present author for the critical limit of capillary condensation (a is the effective surface area occupied by a mol. and σ is the surface tension). By dint of some idealised

model a relation $\Delta S = (\epsilon - 1) \frac{C_0 \beta_A}{\omega a}$ was derived, from which the dielectric const. (ϵ) of the alcohol in each sorbed state was calcd. As a consequence of this expt. the following conclusions were derived. The first part of sorption is the so-called adsorption in the ordinary sense, and the dielectric const. of the sorptive in this state is mainly due to the electronic and atomic polarization, especially at low temps. With the rise of temp. the dielectric const. grows larger on account of the mobility of the sorbed mol. In the second part the sorptive condenses as a liquid in capillary pores. This was confirmed by the following facts: the values of ϵ become larger than those in the adsorption state; the temp. coeff. of ϵ was the same as the pure liquid; and, as is expected from Debye's theory and Mizusima's expt., an abnormal dispersion was found at low temps. and at high frequencies, the dispersion showing a decreasing tendency with the lowering of frequency. Author.

Influence of alcohol on the precipitation of the hydroxides of aluminium and iron. T. Katsurai and M. Fuda. *Se. P.*, 38, 328—300 (1941).—The sedimentation volume of the hydroxides of aluminium and iron increases when they are pptd. in the presence of alcohol. Hydrus ferrous-ferric oxide becomes non-magnetic when it is pptd. in the presence of alcohol. Author.

A study of konnyaku paste. S. Amano. *J. Soc. Textile Industry Japan*, 4, 7, 130—137 (1941).—This is an attempt to determine the variation of viscosity and permeability of konnyaku paste with reference to the time of heating and freshness of the material. The material for the expt., the fresh konnyaku powder, was furnished by Sanyo Ltd., Gumma prefecture, five year ago. The konnyaku powder was said to have been prepared in the following manner:—konnyaku harvested in October was washed and cut into slices of about 2—3 mm. thickness and dried

in the sun. The dried slices were then ground in a stone grinder. Starting from the year of its preparation, the author carried out, in November of each year, the expts. with the same material of konnyaku powder stored in an air-tight and light-tight bottle. 1% solns. of konnyaku powder were boiled for various durations of time. After filtering through a fine wire gauze, the viscosity of the paste was detd. at 20°C with the steel ball falling method, using a 100 cm. cylinder. The permeability was detd. at the same temp., using filter paper No. 1. The results obtained are as follows:—(1) The less the time of heating the higher the viscosity. (2) The viscosity of the paste prepared from preserved konnyaku powder decreases with the lapse of time of preservation. After 4 years of preservation the viscosity was found to have decreased by 75% in comparison with the fresh powder. (3) Regarding the permeability of the above soln. the following relation was found to exist between h (the height of capillary rise) and t (time interval).

$$\log h = \log K + m \log t.$$

(where K and m are consts.)

$$h = Kt^m.$$

(4) The following relation holds between the permeability and the time of heating (θ): $h_0^2 - h^2 = \infty \log \theta$, where h is the height of capillary rise for any time, h_0^2 , the height of capillary rise of prepared konnyaku paste (94—95°C) and ∞ a const. Author.

Reflection factors of evaporated metal films on glass in the near ultra-violet and visible region. Y. Moriya. *Electrotech. J.*, 61, 264—265 (1941).—The reflection factors of evaporated metal films on glass, for an angle of increase of 20°, from 2500 Å to 8000 Å are detd. by a direct method for the following metals: Ag, Au, Cu, Mg, Al, Be, C, Cr, Mn, Fe, Ni, Pd, and Bi. Author.

The catalytic activity of magnesium oxide. T. Waida. *Repts. Osaka Ind. Re-*

search Lab., 21, (9), 1—61 (1941).— $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is prepared from magnesite, which has been calcined and dissolved in sulphuric acid, Na_2CO_3 being allowed to act on it; and the thermal decompn. of it is observed. Dehydration and decarbonisation start at 120° and 300° , and are completed at 450° and 550° resp. $\text{Mg}(\text{OH})_2$ prepared from MgSO_4 , MgCl_2 and NaOH , and the hydration product of MgO obtained from $\text{Mg}(\text{OH})_2$ are dehydrated by about 90% of the theoretical value at 400° , 360° and 375° . The velocities of the hydration are different, that of $\text{Mg}(\text{OH})_2$ prepared from the salt being greatest. This may be ascribed to small difference between the properties of the hydration water. The rate of hydration of MgO obtained by calcining $\text{Mg}(\text{OH})_2$ is smaller than that of MgO obtained by calcining MgCO_3 . The specific gravity of MgO is affected by the temp. and time of calcining of MgCO_3 or $\text{Mg}(\text{OH})_2$ and that of MgO obtained from MgCO_3 is always small. The rate of increase of the specific gravity with rising temp. of calcination is markedly large in the case of MgO from MgCO_3 . The decompn. rate of hydrated Mg -oxide is always large as compared with that of anhydrous Mg -oxide and the former is more active in promoting the formation of butadiene. It is concluded that this is due to hydration water, judging from the quantity of combined water contained in the catalyst after the reaction. J. C. I.

The reaction between nitric oxide and oxygen at low temperatures. V. The reaction on the surface of glass. Y. Hiraki. *J. Chem. Soc. Japan*, 61, 1155—1165 (1940).—It is exptl. demonstrated that the surface of glass has a catalytic activity. On the surface of glass the reaction product retards the reaction in question as on a thin film of mercury, and the reaction velocity is expressed thus: $-d[\text{O}_2]/dt = k[\text{NO}][\text{O}_2]/[\text{N}_2\text{O}_4]$. When the reaction vessel is preliminarily treated with heat, the reaction activity and the adsorptive activity for NO are in-

creased, though both fall in the lapse of time. This is ascribed to the removal of the substances covering the surface, as gases are emitted from the glass wall other than that of the reaction tube under heat treatment. The reaction product markedly reduces the adsorptive activity as well as the activity of the glass surface. Both the activities are affected by NO (O_2 has no influence). The adsorption of NO reaches equil. instantaneously. From the adsorption isotherm of Langmuir and the relation between the adsorbed amt. and press., the adsorbed mol. proves to be N_2O_2 . Accordingly, the oxidation consists of $2\text{NO} = \text{N}_2\text{O}_2$ and $\text{N}_2\text{O}_2 + \text{O}_2 = \text{N}_2\text{O}_4$, the rate-detg. step. J. C. I.

On the catalytic decomposition of neutral salts by Japanese acid clays and other minerals. II. On the actions of kaolinite, Japanese colloid earth, bauxite and diatomaceous earth. K. Kobayashi and H. Ishikawa. *J. Soc. Chem. Ind. Japan*, 44, 449—451 (1941).—The authors carried out the expt. on the reaction between NaCl and kaolinite, Japanese colloid earth, bauxite or diatomaceous earth under the same condition as the previous expt. for the purpose of comparing with the result with Japanese acid clay. The samples: (1) kaolins, Potter's Clay (Bulus Alba), Ph. Jap., Naeki clay Gifu Prefecture and Gairome clay of Aichi Prefecture; (2) Japanese Colloid Earth (the main constituents of which are considered to be an intimate mixt. of colloidal $\text{Al}(\text{OH})_3$ and $\text{SiO}_2 \cdot x\text{H}_2\text{O}$); from Koganei and Kanuma in Tochigi Prefecture; (3) bauxite, from India; (4) diatomaceous earth, (Super-Cell) from the United States of America; (5) Naeki Clay heated at 600°C in the presence of steam for 10 hrs.; (6) bauxite heated at 800°C in the presence of steam for 10 hrs. The results: Generally, the decompn. degree of NaCl by kaolin, bauxite or diatomaceous earth at temps. lower than 500°C is inferior to Japanese acid clay, while that of Japanese colloid earth is superior to it. From these

expts., it is also concluded that the decompn. degree of NaCl at temps. lower than 500°C corresponds to the degree of certain adsorptive power, and in the case of Japanese colloid earth it depends upon the presence of $\text{Al}(\text{OH})_3$ in active state, which adsorbs chem. Na-ion of NaCl. When potter's clay and bauxite are treated resp. at 600° and 800°C in the presence of steam, the decompn. degree of NaCl is remarkably promoted. Authors.

On the catalytic decomposition of neutral salts with Japanese acid clay and other minerals. III. The action of activated clays, silica gel, hydrous aluminium hydroxide and ferric hydroxide gels. K. Kobayashi and H. Ishikawa. *J. Soc. Chem. Ind. Japan*, 44, 540—542 (1941).—The authors carried out the expt. on the catalytic decompn. of NaCl with the

artificial activated clays, silica gels, hydrous $\text{Al}(\text{OH})_3$ gel and $\text{Fe}(\text{OH})_3$ gel under the same condition as described in the previous report. Activated clay and $\text{Al}(\text{OH})_3$ gel show in general the superior decompn. powers, particularly at temps. lower than 500°C, and with $\text{Al}(\text{OH})_3$ gel, the theoretical decompn. degree of NaCl is attained at these temps. Silica gel and hydrous $\text{Fe}(\text{OH})_3$ gel show the inferior decompn. power at temps. below 500°C, while at temps. over 600°C, the tendency to promote the decompn. degree of NaCl appear gradually. The exptl. results lead to the conclusion that the difference of decompn. powers for NaCl of activated clay and silica gel must be ascribed to their permeability to a NaCl soln., and the high decompn. degree of NaCl with $\text{Al}(\text{OH})_3$ gel or Japanese colloid earth is probably due to a firm chem. affinity.

Author.