

General and Physical Chemistry.

The Refractive Index of Mixtures of Gases. S. VALENTINER (*Ber. Deut. physikal. Ges.*, 1914, **16**, 363—366).—By application of the method proposed by Richarz and Neumann (Marburg Universitätsprogramm, 1909) for the detection of systematic errors in experimental observations, it is found that the conclusions drawn in a previous paper (Valentiner and Zimmer, this vol., ii, 81) are completely justified.

H. M. D.

Indices of Refraction of Binary Mixtures of Isofluidic Compounds. (MILLE.) O. M. MORGULEVA (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 235—246).—The author has measured the indices of refraction at 20° for the *C*, *D*, *F*, and *G* lines of the following binary mixtures of non-associated, non-dissociated, isofluidic liquids, with which there is no tendency to chemical interaction: chloro- and bromo-benzenes; ethyl *isovalerate* and *isobutyl acetate*; propyl acetate and ethyl propionate; ethyl butyrate and *isobutyrate*; *m*- and *o*-xylenes; *p*- and *m*-xylenes; *o*- and *p*-xylenes; ethylbenzene and *o*-xylene; ethylbenzene and *m*-xylene; ethylbenzene and *p*-xylene. Comparison of the experimental values with those calculated on the assumption that the index of refraction is an additive property shows that only with the various mixtures of *m*- and *p*-xylenes do the differences exceed the limits of accuracy of the measurement. The conclusion is drawn that the index of refraction is additive in character, independently of the nature of the light.

A table is given which shows for the various mixtures the values of the above difference for the *C* line, the differences between the critical pressures of the two components, and the contraction constants *K* (compare Biron and Morguleva, A., 1913, ii, 174; Biron, Nikitin and Jakobson, A., 1913, ii, 175).

T. H. P.

Spectroscopy of the Electric Brush Discharge in Weak Acids and Solutions. HAROLD SMITH (*Phil. Mag.*, 1914, [vi], 27, 801—823. Compare A., 1913, ii, 360).—The earlier experiments have been extended in order to include the ultra-violet spectrum of the discharge, and also to investigate the differences between the positive and the negative brush.

The series and secondary spectrum of hydrogen, which are characteristic of the brush discharge, are obtained in much greater intensity when the discharge takes place in distilled water in place of aqueous solutions. These spectra depend on the potential to a much greater extent than do any of the other spectra. Since the spectra are not affected by the nature of the ions contained in the solution or by the sign of the brush, it follows that their appearance is not determined by electrolytic action.

In all salt solutions, the spectrum of the metal appears at the
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negative pole only when the solution is dilute; in stronger solutions it begins to show at the positive pole, but the intensity is relatively small. For a constant current, the intensity increases with increasing concentration, and reaches a maximum for salts of the alkali metals between 0·005 and 0·01%. For solutions of magnesium sulphate, the maximum is reached at 0·02%, and for zinc sulphate at 0·1%. These solution spectra can be accounted for on the basis of the electrolysis which accompanies the discharge.

The elementary line spectrum of oxygen is found in both the positive and negative brush with distilled water. It is much more intense in the positive for solutions of acids and salts. The "water vapour" bands are equally developed in the positive and negative brushes.

H. M. D.

The Atomic Weights of the Elements of Nebulæ. J. W. NICHOLSON (*Compt. rend.*, 1914, **158**, 1322—1323).—The author claims that the work of Bourget, Fabry and Buisson (compare this vol., ii, 313) supports his view as to the existence of a number of "simple elements" in nebulae and Wolf-Rayet stars (compare Monthly Notices Roy. Astron. Soc., November, 1911, *et seq.*). The element they call nebulium he has called archonium. W. G.

Certain Doublets of Lithium and their Resolution in a Magnetic Field. NORTON A. KENT (*Physikal. Zeitsch.*, 1914, **15**, 383—385).—The four lithium lines λ 6708·2, 6103·77, 4972·11, and 4602·37 have been found to be true series doublets corresponding with the doublets shown by the other alkali metals. A detailed examination of the behaviour of the lines in magnetic fields of varying intensity has shown that all four pairs are resolved into normal triplets in strong magnetic fields. H. M. D.

Ratio of the Intensities of the D-Lines of Sodium. R. W. WOOD (*Physikal. Zeitsch.*, 1914, **15**, 382—383).—From photographs of the sodium D-lines, which were obtained by exposure to a very weak sodium flame, it has been found that the intensity of the D_2 line is from three to four times as great as that of the D_1 line. The values of the intensity ratio recorded by previous observers vary from 1·3 to 1·6. The difference is probably due to variations in the intensity of the sodium flame, for with a very strong sodium flame the author finds that the two lines are of nearly equal intensity. It is probable that the higher value represents the true ratio, for in the case of a weak sodium flame the disturbing effects of absorption are reduced to a minimum. H. M. D.

Flame Reactions. II. WILDER D. BANCROFT and HARRY B. WEISER (*J. Physical Chem.*, 1914, **18**, 281—336).—The cause of the luminosity of flames is discussed in reference to the literature of the subject, and the authors draw the conclusion that a transparent gas will not emit light at any temperature unless some reaction takes place.

Some experiments have been made to determine the nature of the reactions which occur in flames containing tin and copper or

the salts of these metals. These would seem to show that the reaction $\text{Sn} \rightarrow \text{Sn}$ produces a carmine-red luminescence, whilst the reaction $\text{Sn} \rightarrow \text{Sn}^+$ is the cause of the green colour of flames containing tin. The differences between the spectra of tin chloride, bromide, and iodide are due to the absorption of light by the halogens and the salts, and also to the emission of light by the reactions of the halogens.

The colours shown by flames containing copper are said to be due to the following changes: $\text{Cu} \rightarrow \text{Cu}^+$, giving a green colour; $\text{Cu}^+ \rightarrow$ cuprous salt, a red colour; and $\text{Cu}^+ \rightarrow$ cupric salt, a blue colour. The intensity of the green colour is so great that the blue colour cannot be directly observed even when the third reaction is the principal reaction taking place in the copper flame. No characteristic luminescence has yet been detected for the reverse reactions.

H. M. D.

A New Absorption Spectrum of Oxygen in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1914, **158**, 1161—1164).—The spark spectra from various metals such as bismuth, aluminium, cadmium, tin, thallium, after long-continued sparking, exhibit a certain number of bands, which, while differing in intensity from metal to metal, are identical as regards structure and situation. In the interior of the band, the dark rays, which are relatively sharp at the beginning of the band, gradually broaden and extend to several Ångström units, whilst the clear spaces separating them become narrower. Five bands were discovered, three of which, namely, 1864·0—1881·3, 1882·0—1899·4, 1900—1919·2, are identical with those obtained by Steubing using a mercury arc (compare A., 1910, ii, 913). The other two, 1923·4—1936·5 and 1946·5—1957·4, are new. All the bands possess the same structure, and are capable of representation by Deslandres' formula. The results point to the probability that the absorption by the air in the extreme ultra-violet commences at $\lambda 1957$, and is manifested by a spectrum of regular bands, very probably belonging to oxygen.

W. G.

Calculation of the Absorption Spectrum of a Substance from its Chemical Constitution. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1914, **158**, 1114—1117. Compare this vol., ii, 318, 319).—The authors show that it is possible to calculate the absorption spectrum of a substance containing two chromophores by means of the general formula

$$\epsilon = p\alpha_1 v e^{-\beta_1(v - v_1 - \Delta v)^2} + p\alpha_2 v e^{-\beta_2(v - v_2 - \Delta v)^2},$$

where ϵ is the molecular constant of absorption, α_1 , β_1 , and v_1 ; α_2 , β_2 , and v_2 the constants characteristic of each chromophore; p is the hyperchrome effect; and Δv the hypsochrome effect exerted by the two groups on each other. If the two chromophores are adjacent, p is small and Δv large, while if the groups are far apart in the molecule, p is large and Δv is small. The curves measured and calculated, as given for phorone, show close agreement.

W. G.

Absorption Spectra of Several Aromatic Nitro-compounds in Mixtures of Alcohol and Water. FR. BORTINI (*Zeitsch. physikal. Chem.*, 1914, **87**, 104—115).—The absorption spectra of picric acid, 2:4-dinitrophenol, and *p*-nitrophenol have been determined in aqueous, alcoholic, and aqueous alcoholic solutions. It is shown that the absorption spectrum of the three substances in absolute alcohol changes rapidly on the addition of small quantities of water, and that the addition of only a small percentage of water changes it entirely into the same spectrum as that obtained for an aqueous solution of the same concentration. The amount of water to be added to bring this about is largest in the case of *p*-nitrophenol and least in the case of picric acid. Thus the amount of water to be added increases with the strength of the acids. The quantity of water is not proportional to the quantity of nitro-compound in the solution. It is shown that Beer's law holds approximately for picric acid in water and in 90% alcohol solution, and for dinitrophenol in absolute alcohol solution, but it does not hold for an absolute alcohol solution of picric acid. J. F. S.

Ultraviolet Absorption Spectrum of Buchu-camphor. MARIO MAYER (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 439—442).—The ultraviolet absorption spectrum of synthetic buchu-camphor shows a band (maximum at 3750) as well as the usual absorption of the extreme ultraviolet rays shown by many substances. This is consistent with the existence of an equilibrium in the solution between two isomerides, but as the band corresponds with one of those of benzene, it may be due to the presence of the benzene nucleus.

R. V. S.

Absorption Spectrum of Alcoholic Solutions of Santonin and its Derivatives in Presence of Alkali. M. MAYER (*Atti R. Accad. Lincei*, 1914, [v], **23**, i, 442—446).—The paper deals with the absorption spectra of the reddish-violet solutions of santonin and dihydrosantonin in alcoholic potassium hydroxide, and of the hydroxysantonins in alcoholic sodium ethoxide. The examination of the visible spectra shows that the reaction, lactone \rightarrow hydroxy-acid, proceeds very similarly in all three cases, the principal band lying at 540—440 $\mu\mu$. The small differences noticed are, however, accentuated in the ultra-violet, where the curves of dihydrosantonin and hydroxysantonin resemble one another, whilst that of santonin differs from them.

R. V. S.

The Spectral Structure of Substances of the Hæmoglobin Group. FRED VLÈS (*Compt. rend.*, 1914, **158**, 1206—1208).—A comparative examination of the spectra of substances of the hæmoglobin group shows a certain number of coincidences in these spectra. It seems probable that these spectra can be represented by a law similar to one of the laws of Deslandres for the band spectra of nitrogen. In the law for the spectra of these colouring matters, the superposition of at least three principal series probably intervenes. The most important series is apparently more specially

dependent on the pyrrolic nuclei of the molecule, whilst the others are dependent rather on certain of the side-chains. W. G.

Absorption Phenomena of Hæmatoporphyrin and of Mesoporphyrin in the Grating Spectrum. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1914, **90**, 1–31).—The absorption spectra of hæmatoporphyrin and mesoporphyrin in aqueous hydrochloric acid (D 1·124) differ in that the bands lie 2·5 $\mu\mu$ nearer the red in the hæmatoporphyrin solution. In both cases, all the bands are displaced towards the violet when the amount of hydrochloric acid present is decreased. For instance, the position of the sixth hæmatoporphyrin band is at 407·5 $\mu\mu$ in 25% acid, at 401 $\mu\mu$ in 0·1% acid. The spectrographic observation of this band permits of the detection of very small quantities of the porphyrins, as apparently almost colourless solutions show it very plainly.

Willstätter's phylloporphyrin in hydrochloric acid (D 1·124) gives a spectrum which differs only very slightly from that of mesoporphyrin.

The spectra of alcoholic solutions of hæmatoporphyrin hydrochloride and mesoporphyrin hydrochloride are very similar to one another, and are markedly altered by the merest trace of hydrochloric acid. The spectra of solutions of the same substances in alcohol containing ammonia are also very similar, the bands of the hæmatoporphyrin solution lying about 1–1·5 $\mu\mu$ nearer the red.

Fresh alkaline solutions of hæmatoporphyrin hydrochloride containing a considerable excess of alkali have four absorption bands. The fifth band, described by Lewin, Miethe and Stenger (*Pflüger's Archiv*, 1907, **118**, 80), appears only when the solution has been exposed to the light of the lamp for some time. Fresh alkaline solutions show no violet band, and thereby differ distinctly from hydrochloric acid solutions.

The spectrum of alkaline solutions of mesoporphyrin hydrochloride changes with the quantity of alkali present, and with their treatment (action of the air). They show the blue band of Lewin, Miethe and Stenger only when decomposition has begun. Solutions in N/10-potassium hydroxide have no band in the violet, differing, thereby, from the solutions in hydrochloric acid.

R. V. S.

Fluorescence of Gases Excited by Ultra-Schumann Waves. R. W. WOOD and G. A. HEMSALECH (*Phil. Mag.*, 1914, [vi], **27**, 899–908 *).—The ultra-violet luminosity observed in the neighbourhood of the condensed spark discharge (A., 1910, ii, 915) has been further investigated with an improved form of apparatus. The fluorescence excited by the radiation from the spark was resolved by a quartz prism placed in front of a quartz-fluorite achromatic lens, behind which was situated the plate on which photographs were taken. In this way, the spectra obtained in an atmosphere of oxygen, nitrogen, air, carbon dioxide, hydrogen, and coal gas have been examined. The most interesting results are those

* and *Physikal. Zeitsch.*, 1914, **15**, 572–578.

obtained by comparing the fluorescence of gases in a stationary and in a moving condition. Some gases show a much more brilliant fluorescence when moving across the jet of rays from the spark, whilst others show no luminosity in these circumstances, although they respond vigorously to the excitation when quite stagnant.

H. M. D.

The Biochemistry of the Action of Rays. I. The Relationship between the Action of Mineral Catalysts and Fluorescent Dyes. C. NEUBERG and A. GALAMBOS (*Biochem. Zeitsch.*, 1914, **61**, 315—331).—The action of dyes from the following groups on glycerol, alanine, and tartaric acid was investigated: fluorescein, rhodamine, anthracene, acridine, triphenylmethane dyes, ethyl-red, nigrosine, and æsculine. Of the dyes investigated, sodium dichloroanthracenedisulphonate, and sodium anthracene-2:7-disulphonate, were the only substances which were found capable of inducing decomposition of chemical substances in light, and they produced in this way degradation of a large number of organic substances. The theory of the action is discussed by the authors, who reject von Tappeiner's idea that dyes act catalytically in light by virtue of their fluorescing properties. They suggest that the active substances can function as oxygen acceptors in light.

S. B. S.

Deductions from the Valency Theory. III. Natural Rotation of the Plane of Vibration of Light. J. STARK (*Jahrb. Radioaktiv. Electronik*, 1914, **11**, 194—211. Compare A., 1912, ii, 403, 621; this vol., ii, 86).—The author's valency hypothesis (A., 1908, ii, 138) is applied to the rotation of the plane of polarised light. It is shown that the field of the valency electron and the electrostatic field of the light wave act on one another with a slight rotation of the plane of vibration of the light. This is developed for numbers of valency electrons up to four, and it is shown that only in the case of four unsymmetrically arranged valency electrons is there a definite resultant twist given to the plane of vibration. This conception is then applied to various cases, and the influence of changing the position of two of the substituting groups, namely, two of the valency fields, is shown to reverse the direction in which the plane is rotated. Similarly, when two of the valency fields are made equal, it is shown that no resultant twist is given to the vibration plane. The Walden inversion is discussed on this hypothesis, and an explanation of the mechanism of the change given.

J. F. S.

Theory of the Rotatory Power of Liquids. ARRIGO MAZZUCHELLI (*Gazzetta*, 1914, **44**, i, 410—417).—According to van't Hoff's theory and to Guye's results, the rotatory power of a substance depends on the degree of asymmetry of the molecule, but since this varies with the orientation of the molecule, it would seem that the observed rotatory power represents the mean of a number of values differing more or less among themselves. If, therefore, the molecules can be constrained, wholly or partly, to assume a

definite orientation, the optical activity should be changed. With the liquid crystals examined by Vorländer (A., 1908, i, 641), the great superiority of the rotations over those exhibited by the same compounds in solution renders it probable that the liquid crystal consists of an asymmetric aggregate of many simple molecules. That liquid crystals are highly polymerised is, indeed, indicated by their relatively slight solubility.

In the case of an electrolyte, the charges of the ions are regarded as localised at certain points occupying invariable positions in the molecule. If the electrolyte is optically active, the action of a current passing in the direction of the ray of polarised light constitutes a force applied only at one portion of the molecule, and should hence tend to orientate the latter in a definite direction. Any variation in the rotation would depend solely on the direction, and not on the sense, of the electric field, since, according to Helmholtz's principle of reciprocity, all modifications produced in a ray of light in its passage through any medium are independent of the direction of that passage.

Experiments made with solutions of potassium uranylmalate showed, however, that the passage of a current is accompanied by no appreciable alteration in the rotation. The author draws the conclusion, which is confirmed by calculation, that the directive force of the current is very small in comparison with the active forces exerted between the molecules.

T. H. P.

Influence of Solvents on the Optical Activity of Camphoric Esters. J. MINGUIN and R. BLOC (*Compt. rend.*, 1914, **158**, 1273—1276).—The authors have determined the optical activity of the methyl, ethyl, propyl, and butyl hydrogen esters of ortho- and *allo*-camphoric acids, and also of the normal esters in alcohol, benzene, and toluene. In the ortho-series, leaving out the methyl ester, the molecular rotation is practically constant for all the esters in each solvent, but the value is much higher in solution in benzene and toluene than in alcohol. This increase with the solvent is not noticeable in the *allo*-series, whilst the normal esters, on the other hand, resemble the ortho-esters in this respect. Molecular-weight determinations in benzene solution show that the normal esters are not molecularly associated, whilst the ortho- and *allo*-esters are partly associated.

W. G.

Kinetics of Photochemical Reactions. FRITZ WEIGERT (*Zeitsch. physikal. Chem.*, 1914, **87**, 87—92).—A criticism of Bodenstein's hypothesis of the mechanism of photochemical reactions (A., 1913, ii, 1039). It is shown that the reactions, anthracene → dianthracene (A., 1904, ii, 463; 1905, ii, 785; 1909, ii, 632), the polymerisation of β -methylanthracene (this vol., ii, 11, 159), *o*-nitrobenzaldehyde → *o*-nitrosobenzoic acid (A., 1913, i, 872; ii, 370), and other reactions, all of which Bodenstein classifies as primary photochemical reactions, fail to fulfil the essential condition of primary photochemical reactions. This condition is that the quantity of absorbed light energy is strictly proportional to

the velocity of the reaction. The decomposition of ozone by chlorine in the presence of light is classified by Bodenstein as a primary reaction, but the author gives reasons which show that it must be regarded as a secondary reaction.

J. F. S.

[**Kinetics of Photochemical Reactions.**] MAX BODENSTEIN (*Zeitsch. physikal. Chem.*, 1914, **87**, 93—103. Compare preceding abstract; also Bodenstein, A., 1913, ii, 1039).—An answer to Weigert; it is shown that the non-agreement of the reaction anthracene → dianthracene, and the polymerisation of β -dimethyl-anthracene, with the condition for primary reactions, is to be explained by the assumption that in the process, after the initial separation of an electron from the reacting molecule, the positive residue does not combine quickly enough with a similar residue, and consequently must recombine with an electron, with the reformation of the original molecule. This brings about a decrease in the reaction velocity, which ought to have resulted from the absorbed energy.

J. F. S.

Photochemistry of Ammonia. ALFRED COEHN and GEORGES PRINGENT (*Zeitsch. Elektrochem.*, 1914, **20**, 275—278).—It has been shown by Regener (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1228), Berthelot and Gaudeckon (A., 1913, ii, 458), and others that ammonia is practically completely decomposed by ultra-violet light. The object of the present work was to see whether this decomposition was complete or whether a determinable amount of ammonia still remained undecomposed. Ammonia was sealed up in quartz tubes and exposed to the light of a quartz mercury lamp, and the gas examined after various periods of exposure. It was found that after one hour ammonia was still present, but after six hours ammonia could not be detected by means of Nessler's reagent, thus showing that the decomposition was complete. Weigert (A., 1908, ii, 5) has shown that when a mixture of nitrogen and hydrogen is sensitised by the addition of chlorine, ammonia is formed by ordinary visible light. The authors have passed similar mixtures, dry and damp, through a quartz tube which passed down the centre of a quartz mercury lamp, and have been unable to show the formation of ammonia even in such small amounts as would give the reaction with Nessler's reagent.

J. F. S.

Photochemistry of the Hydrates of Chromic Chloride. B. KURILOV (*Kolloid. Zeitsch.*, 1914, **14**, 171—172. Compare A., 1913, ii, 31).—The behaviour of the green and violet solutions of chromic chloride on exposure to light has been examined by measurements of the extinction coefficient for light of wave-length $\lambda = 485 \mu\mu$. Comparative observations were made on solutions which were kept in the dark. The author considers that the results afford evidence of a photo-effect in the transformation of the green into the violet salt.

H. M. D.

Supposed Chemical Changes in Light. E. SERNAGIOTTO and A. BARON HOSCHEK (*Zeitsch. physiol. Chem.*, 1914, **90**, 437—440).—A

repetition of Inghilleri's work on this subject (A., 1911, i, 354, 709; 1912, i, 831) does not give the results obtained by that author. When formaldehyde and water are exposed to light, no methyl alcohol is formed. When formaldehyde, water, and methyl alcohol are exposed to light, methylal is produced, but not methyl formate. The exposure to light of a mixture of formaldehyde, water, and ammonia yields hexamethylenetetramine, which is presumably Inghilleri's "new alkaloid." When a mixture of glycerol and oxalic acid is kept either in the light or in the dark, formic acid is produced; a relatively small quantity of butyric acid can also be found, but this can be obtained in control experiments with glycerol alone.

R. V. S.

The Photochemical Decomposition of Lactic Acid in Presence of Uranyl Sulphate. IWAN BOLIN (*Zeitsch. physikal. Chem.*, 1914, **87**, 490—506).—The decomposition of lactic acid by light in the presence of uranyl sulphate has been examined with the object of determining whether the uranyl salt acts catalytically or whether the action is purely one of oxidation by the uranium salt. The experiments were carried out in flat, thin glass flasks, in which the reaction mixture, in the absence of air, was subjected to the light from a carbon arc. The reaction consists in the decomposition of lactic acid into acetaldehyde and carbon dioxide. Experiments were also carried out with sodium lactate under the same conditions. It is shown that the amount of acetaldehyde and carbon dioxide produced is proportional to the amount of uranyl sulphate reduced to the uranous condition, and the reaction is to be represented by the equation :

$$\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{COO}' + \text{UO}_2^{\bullet\bullet} + 3\text{H}^{\bullet} = \text{CH}_3\cdot\text{CHO} + \text{CO}_2 + \text{U}^{\bullet\bullet\bullet\bullet} + 2\text{H}_2\text{O}.$$

Consequently, in the absence of oxygen, the reaction is not catalytic. Experiments were then carried out in which the original conditions were maintained, with the exception that oxygen was slowly passed through the solution, and in this case the reaction is strictly catalytic, since the uranous salt is oxidised by the oxygen to the uranic condition, and can consequently convert an indefinite amount of lactic acid into acetaldehyde. The reaction is strictly photochemical, for there is no change at all in the dark, and the effect of sunlight is the same as that of the arc light. Experiments were then carried out with ferric sulphate as the oxidising agent, and the conditions here found to be the same as in the preceding case, namely, that in the absence of oxygen the reaction is not catalytic, and is to be represented by

$$\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{COO}' + 2\text{Fe}^{\bullet\bullet\bullet} + \text{H}^{\bullet} = \text{CH}_3\cdot\text{CHO} + \text{CO}_2 + 2\text{Fe}^{\bullet\bullet} + 2\text{H}^{\bullet}.$$

In the presence of air or oxygen, this reaction is catalytic.

J. F. S.

Influence of Occluded Gases on the Selective Photoelectric Effect. R. POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1914, **16**, 336—344).—According to Wiedmann and Hallwachs (this vol., ii, 162), the photo-electric activity of potassium is dependent on the presence of gases in the surface layers of the metal. In

view of the importance of this result for the explanation of the nature of the selective photo-electric effect, the authors have made a further examination of the photo-electric behaviour of potassium on similar lines to those adopted by Wiedmann and Hallwachs. The observations show that potassium which has been boiled for 180 to 430 hours at 350° to 400° in the highest vacuum attainable by the continuous action of a Gaede pump, exhibits the same photo-electric activity as the original metal from which the gases have not been removed when light of frequency corresponding with the selective effect is allowed to act in the metal. Under the above treatment, the gas evolution per c.c. of potassium was reduced to 4×10^{-4} c.c. of hydrogen per hour, whereas the original metal was found to give off 2 c.c. of hydrogen per hour under similar conditions.

The authors draw the conclusion that the presence of hydrogen in the metal is not essential for the development of the selective photo-electric effect.

H. M. D.

The Tyndall Phenomenon in Liquids. WALTHER KANGRO (*Zeitsch. physikal. Chem.*, 1914, **87**, 257—292).—Attempts have been made to prepare an optically clear liquid by the settling of precipitates in liquids; the liquids were examined by means of a photographic photometric method, and it is shown that by this method optically clear liquids cannot be obtained. It is shown also that the use of the light deflection as a differential method is not possible. The Rayleigh theory of the dependence of the intensity of the deflected light on the wave-length is confirmed qualitatively, and the conclusion is drawn that deflected light of different coloured solutions cannot be directly compared. The great difference in the nature of the deflected light from crystalloid and colloid solutions is confirmed. A method of producing optically clear solutions by means of distillation was tried, and in this way it is shown to be possible to effect a purification of the solutions, but not to obtain absolute optical homogeneity.

J. F. S.

The Variations in the α -Rays Emitted from a Radioactive Solution. THE SVEDBERG (*Physikal. Zeitsch.*, 1914, **15**, 512—516).—In place of an earlier view that the probability variation in the emission of α -particles from a radioactive solution involves the spontaneous concentration variations according to the kinetic theory, the author accepts Schweidler's result that there should be no difference between a radioactive solution and solid, and gives a simple proof of it. The experiments show, however, a very large departure from the theoretical formulæ in case of solutions. The part of the radioactive solution near the bounding surfaces gives out radiation of special character, the intensity of which depends on the nature and treatment of these surfaces. The variations for this "surface radiation" obey the simple law for solids. Working with liquid solutions of polonium or gaseous solution of radium emanation, the surface effect can be eliminated, and the frequency numbers experimentally found agree with another formula, which

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departs so largely from the simple formula that the difference cannot be due to error of experiment. A solution of radium-barium chloride was laid on a fluorescing diamond and covered with a cover-glass, kept at a distance of 0·1 mm. from the diamond by a ring of platinum wire. The radium was carefully freed from disintegration products before use. The results showed clearly that the α -particles from the inner part of a radioactive solution do not obey the simple law, but another, which cannot be theoretically explained. The law experimentally obeyed was derived from a theory which implied a connexion between the concentration and the variations of disintegration, which shows that there is some connexion between these. The cause of this connexion, however, remains unknown. It is possible that along the paths of the α -rays there may be a short-lived accumulation of radioactive atoms, in the neighbourhood of each disintegrating atom, which may account for the effect, but there is no experimental or theoretical foundation for such an accumulation.

F. S.

The Passage of α -Particles through Hydrogen. E. MARSDEN (*Phil. Mag.*, 1914, [vi], 27, 824–830).—In the collision of an α -particle with an atom of hydrogen, on the nucleus theory of the atom, if the direction of projection of the hydrogen atom makes the angle θ with the direction of the α -particle, and the latter is moving with velocity V , the velocity of the hydrogen atom will be $1.6V \cos \theta$. In an “end-on” collision, where $\theta=0$, it can be deduced that the “H-particle” so resulting will have a range about four times that of the α -particle. In the first experiments, a movable source of 25 millicuries of radium emanation contained in an α -ray tube was placed in a wide tube filled with hydrogen at variable pressure, and the scintillations counted on a zinc screen cemented to the end of the wide tube. Whereas the α -rays did not traverse a distance beyond 24 cm. in hydrogen at atmospheric pressure, scintillations, similar to, but less intense than, those produced by α -particles, at the rate of ten per minute, were observed at 38 cm., and these continued in diminishing number up to a distance of 82 cm. In air at 17 cm. pressure, in which the range of the α -particle was the same as that in hydrogen at atmospheric pressure, only 0·5 scintillation per minute were observed at a distance of 26 cm. By inserting a screen of aluminium leaves, sufficient to stop the α -particles, near the source the H-particles were suppressed; but with the same screen near the zinc-sulphide screen, the scintillations were again observed. This shows that these scintillations have their origin in the hydrogen by the impact of the α -particles.

In the next series of experiments, the hydrogen was contained in a metal vessel at 4·5 atmospheres' pressure, and the distances between source and screen reduced to one-fourth. A magnetic field was used to deflect the β -rays. An arrangement of metal foils mounted on a disk was employed, so that any one of four different foils could be introduced directly in front of the zinc-sulphide screen without opening the apparatus. The pressure was

one-sixth greater than that which would stop the α -particles. In experiments on the absorption of the H-particles in aluminium, copper, tin, and platinum, a similar law of absorption to that for the α -particles was found, the weights per unit area of different metals necessary to produce the same absorption being proportional approximately to the square roots of the atomic weights. Experiments are in progress to measure the number of H-particles produced by a known number of α -particles of definite velocity, and their distribution in direction, by passing the α -particles through films of substances rich in hydrogen, such as indiarubber or paraffin wax.

F. S.

Intensity Distribution in the Magnetic Spectrum of the β -Rays of Radium *B+C*. J. CHADWICK (*Ber. Deut. physikal. Ges.*, 1914, **16**, 383—391).—The magnetic spectrum of the β -rays emitted by radium *B+C* has been investigated by Geiger's counting method (A., 1913, ii, 745), and also by a method depending on the ionisation produced by the rays.

The results obtained by both methods indicate that the β -radiation yields a continuous spectrum, on which is superposed a line spectrum of relatively small intensity. Both methods indicate the existence of four lines (or groups of lines) in the region of the slowly moving β -rays. The observations are accordingly at variance with the results obtained by photographic methods, for these are supposed to indicate that the β -radiation of radium *B+C* consists of a large number of groups of homogeneous rays. The discrepancy is attributed to the very large variation in the sensitiveness of photographic plates for small changes in the intensity of the rays.

H. M. D.

The Wave-lengths of the Soft γ -Rays from Radium-*B*. SIR ERNEST RUTHERFORD and E. N. DA C. ANDRADE (*Phil. Mag.*, 1914, [vi], **27**, 854—868).—It was anticipated that each of the various homogeneous types of γ -rays given by the radio-elements should give definite line-spectra when reflected from crystal surfaces. The determination of the wave-lengths of γ -rays by this method was found to be more difficult than for the *X*-rays, long exposures, of twenty-four hours or more, being necessary, with special precautions to protect the plate from the penetrating γ -rays and from the swiftest primary and the secondary β -rays. The source was a tube of emanation 1 cm. long, behind a massive block of lead, in a strong magnetic field, provided with a slit 3 mm. wide. The crystal of rock-salt or heavy spar was mounted on a turn-table, and the plate and source were equidistant from the crystal. The lines due to the penetrating γ -rays of radium-*B* and -*C* are faint compared with those due to the soft γ -rays of radium-*B*, and have not yet been fully investigated. The stronger lines of radium-*B* appear with great distinctness. The main features of the spectrum with a rock-salt crystal are two strong lines at almost exactly 10° and 12° ($10^\circ 3'$ and $12^\circ 3'$), and a number of fainter ones between 8° and 14° . There is also a large group of lines, too faint to measure

accurately, between 18° and 22° , some of which are probably second-order repetitions of the first order. With a heavy-spar crystal the lines for the soft rays were less intense. The angles of the two strong lines of radium-*B* were $7^\circ 52'$ and $9^\circ 28'$, which, multiplied by the factor 1.278, as determined experimentally with the *X*-rays for the two crystals, agree closely with those found with rock-salt, and shows that the lines are true diffraction-lines. The wave-lengths of the two strong lines of radium-*B* are 0.982 and 1.175×10^{-8} cm. The detailed structure of the images of these lines shows the sharp and well-marked edges and less intense centre characteristic of α -rays when the image of a cylindrical α -ray tube produced through a narrow parallel slit is photographed by its own rays.

The spectrum of radium-*B* was examined to see whether it was identical with that of the *X*-ray spectrum of lead, as is to be expected on the general theory of Soddy and Fajans, since radium-*B* has been shown by Fleck to be isotopic with lead. Moseley has found for the nucleus charge, or atomic number, of gold, 79, so that of lead should be 82, and the strongest line of lead, as calculated from this number, should be reflected from rock-salt at 12.07° , which is in very close agreement with the angle, 12.05° , actually found.

To test the point directly, the γ -ray spectra of radium-*B* was compared with the strong, characteristic "L" type of radiation excited by the β -rays of radium-*B* and -*C* in lead, as discovered by Richardson. A piece of lead was put in place of the emanation tube and exposed to the β -rays from the emanation tube, which was placed at one side out of the line through the slit. Only a few faint lines of lead could be measured under these conditions. Two of these gave reflexion angles of $10^\circ 2'$ and $12^\circ 0'$, in good agreement with the strong lines of the radium-*B* spectrum. On substituting the piece of lead for a piece of platinum, the position of the lines was quite distinct, in fair agreement with those given by Moseley and Darwin for platinum. The reflexion angles of the γ -rays of radium-*B* are believed to be correct to 0.3%, whereas a mistake of one unit in the atomic number would make a difference of 2% in the angle. According to radioactive calculation, the atomic weight of radium-*B* is 214, whilst that of lead is 207. These results, therefore, confirm the deduction of Soddy and Fajans in an unexpected way, and verify the hypothesis that two elements of different atomic weights may have identical spectra and identical chemical properties.

F. S.

The Absorption of γ -Rays. S. OBA (*Phil. Mag.*, 1914, [vi], 27, 601—607).—The effect of passing γ -rays through various metals before determining their absorption coefficient in a given metal has been examined in detail. The first metal acts always to "harden" the rays, but with increasing thickness the effect appears to approach a limiting value. Rays so hardened gradually become softer as they pass through increased thicknesses of the second metal, and may even regain their initial penetrating power. The

effects are complicated by the heterogeneity of the rays used, which were a mixture of the γ -rays of radium-*B* and -*C* derived from a tube of radium emanation.

F. S.

Method for the Production of Preparations of Radium Emanation. ERICH ESSLER (D.R.P. 270705).—The method consists in the adsorption of radium emanation by colloidal silicic acid, which, after removal from the emanation, shows the same period of decay as the emanation itself.

F. S.

The Activity of Freshly-formed Radium Emanation. HORACE H. POOLE (*Phil. Mag.*, 1914, [vi], 27, 714—718).—A test of the activity of the radium emanation at different periods from the moment of its formation showed no variation with age. A steady blast of air was swept over a film of radium salt, deposited on a platinum ribbon maintained at a white heat, through a series of vessels. The radiation in two vessels, one at the beginning and one at the end of the series, was compared, the direction of the air current through the vessels reversed, and the measurements repeated. A difference of 5% in the activity would have been observed, but none was found.

F. S.

Determination of the Periods of Transformation of Thorium and Actinium Emanation. P. B. PERKINS (*Phil. Mag.*, 1914, [vi], 27, 720—731).—In order to determine these constants more accurately, the ratio of the initial to the final activity, and the time of decay, were made greater by initially introducing capacities in parallel with the leaf-system, and cutting them out as the emanation decayed. Thus, for the actinium emanation, the decay was followed for forty-three seconds, in which time the activity fell to less than 1/2000th of the initial value. The half-value periods for thorium and actinium emanations were found by this method to be 54.53 ± 0.041 and 3.92 ± 0.004 seconds respectively, the corresponding values for the λ 's being 0.01271 and $0.1768/(\text{sec.})^{-1}$.

F. S.

The Transformations in the Active Deposit of Actinium. E. MARSDEN and P. B. PERKINS (*Phil. Mag.*, 1914, [vi], 27, 690—703).—A search was made for a small proportion of α -rays of longer range than 5.4 cm. in the α -radiation of actinium-*C*, which was covered with a standard thickness of mica of known stopping power and mounted at a fixed distance from a zinc sulphide screen in a vessel in which the pressure of air could be varied. The results indicated that about 0.15% of the particles penetrate much further than 5.4 cm. The effects observed were small, and difficult to measure accurately. The range of these long-range α -rays is 6.4 cm. The effect was shown not to be due to radium-*C* or radio-thorium by special experiments, and the conclusion is drawn that they were not due to recoiled actinium-*X*, although the range differs little from that of the α -particles of actinium-*A*, on account of the nearly constant ratio obtained in the experiments and the rate of decay of the long-range α -particles.

No evidence of this small proportion of long-range α -particles can be obtained from a study of the range-ionisation curve, contrary to the earlier observations of Mlle. Blanquies (A., 1909, ii, 634). It was found that the curves for polonium, actinium-C, and thorium-C are not exactly superimposable, as might have been anticipated, although not previously observed, owing to the straggling of the longer range α -rays and their becoming less homogeneous in their passage, some of the α -particles suffering more severe atomic encounters than others. A scheme of transformation, analogous to that accepted for radium-C and thorium-C, is put forward, in which actinium-C suffers a dual transformation, 99·85% of the atoms expelling first an α - and then a β -ray, the remainder expelling the rays in the inverse order. F. S.

The Ionometer and its Application to the Measurement of Radium and Röntgen Rays. H. GREINACHER (*Physikal. Zeitsch.*, 1914, **15**, 410—415).—A simple and transportable form of direct-reading instrument is described, by means of which the ionisation in gases can be determined very conveniently. The construction is based on the same principle as that which has been adopted in the Bronson instrument. One of the most important differences between the two forms lies in the fact that no quadrant electrometer is required in connexion with the new type of ionometer.

It is shown that the apparatus may be employed for the measurement of radium and radium emanation, and also for the determination of the intensity and the hardness of Röntgen rays.

H. M. D.

Origin of Thermal Ionisation from Carbon. O. W. RICHARDSON (*Proc. Roy. Soc.*, 1914, **A**, **90**, 174—179).—The conditions obtaining in the experiments made by Pring (A., 1913, ii, 1005) are discussed, and the author draws the conclusion that the experiments in question cannot be held to prove that the emission of electrons from heated carbon is a consequence of chemical action between the carbon and the surrounding gases, or to invalidate the theory which regards this effect as a fundamental property of the heated substance.

It is probable that in the experiments at the highest temperatures, none of the electrons emitted by the carbon would reach the collecting electrode, and in regard to the experiments at lower temperatures it cannot be said, with certainty, that the observed thermionic currents are smaller than those which would be expected on the basis of the thermionic theory.

The fact that the observed currents increase with increasing pressure of the surrounding gas is to be expected, on account of (a) the interference of the gas molecules with the motion of the electrons; (b) the combination of electrons with atoms and molecules of the gas. The large specific effects observed in certain cases would suggest that the combination factor is of special importance.

H. M. D.

Thermionic Currents in High Vacuum. II. The Electron Emission from Tungsten and the Effect of Residual Gases. IRVING LANGMUIR (*Physikal. Zeitsch.*, 1914, **15**, 516—526).—In absence of gas, the current carried by the electrons from a hot cathode reaches a limiting value, but in the presence of gas, and with potentials above 40 volts, there is commonly a strong positive ionisation, which diminishes the electronic emission and permits the flow of a larger current through the gas. Contrary to the view generally held, the presence of gas diminishes the electronic emission at low temperatures, and the effect vanishes at high temperatures. The constant b of the equation $i=a\sqrt{Te^{-b/T}}$, expressing the relation between electronic emission and temperature for tungsten, is diminished by oxygen, nitrogen water vapour, carbon monoxide, or carbon dioxide, but argon, mercury vapour, and hydrogen have no effect. In a perfect vacuum, $a=23.6 \times 10^6$ and $b=52,500$, corresponding with a current of 0.0042 ampere per cm.² at 2000°. The action of nitrogen, but not of oxygen, depends on the anode potential, and in many cases a feeble current passes with 240 than with 120 volts.

The theory is proposed that the action of gases in altering the saturation current is due to the formation of compounds on the surface of the cathode, either by direct reaction (oxygen), or by reaction with positive ions (nitrogen), or by volatilisation in consequence of the bombardment of positive ions. The conclusion is reached that the electronic emission from a solid body at high temperature in a very high vacuum under proper conditions is an important specific property of the substance, and is not due to secondary causes.

F. S.

Ionisation Produced by Certain Substances when Heated on a Nernst Filament. FRANK HORTON (*Proc. Camb. Phil. Soc.*, 1914, **17**, 414—424. Compare A., 1913, ii, 272).—Experiments have been made to determine whether the emission of negative electricity by calcium oxide, heated on a Nernst filament, is comparable with that obtained when the oxide is heated as a superficial layer on platinum, and, further, to ascertain whether the emission of positive electricity from a Nernst filament is increased by covering the filament with a layer of sodium phosphate.

The observations show that the negative emission from the glowing filament is enormously increased by a covering of calcium oxide, and is of the same order of magnitude as the negative emission from platinum covered with a thin layer of oxide. This result indicates that the emissive effect is in no way connected with the metal in contact with the calcium oxide.

The positive emission from the glowing filament is increased by a coating of sodium phosphate, the increase depending on the pressure of the surrounding gas. Curves showing the variation of the thermionic current with the pressure at 1422° are recorded, and from these it is apparent that the sodium phosphate exerts a considerable influence on the nature of the current-pressure curve. This influence is supposed to be due to the increased forma-

tion of positive ions, and to the change in the nature of the gaseous atmosphere in contact with the filament. H. M. D.

The Ionisation of Water Vapour by the α -Rays of Polonium.
 B. BIANU (*Le Radium*, 1914, 11, 65—69).—A special apparatus for the determination of the Bragg ionisation-distance curve in water vapour at temperatures up to 100° was constructed, which was air-tight and insulated by amber, which was not affected by the high temperature and the water vapour so long as it did not condense. The range of the α -particle of polonium was determined in water vapour at temperatures between 75° and 100° . At the last temperature it was 6·2 cm., whereas in air at 100° , calculated from its density, it should be 5·08. The ratio 0·819 is only 3·5% different from that calculated from the square root of the atomic-weight law. The Bragg curve in water vapour at 83° , using a tension of 580 volts per cm., was compared with that in dry air at 26·3 cm. pressure, the range of the α -particle in the two cases being the same. The water-vapour curve departed from the air curve in the same sense as Taylor found for hydrogen; but the areas of the surfaces of the two curves were the same, showing that the total ionisation in water vapour is sensibly the same as that in air.

The ionisation curve as a function of the potential (saturation curve) in water vapour at 83° showed that the third part of the curve, due to ionisation by collision, began at 750 to 800 volts per cm. A comparison of the curve with the theory of Townsend showed great divergences at higher pressures. F. S.

Method for the Preparation of Therapeutically Useful Compounds of Radium. E. MERCK and WILH. EICHHOLZ (Austrian Patent 63166).—The method is characterised by the feature that the solution of the radium salt is precipitated by solutions of selenites, selenates, tellurites, or tellurates of the alkalis or alkaline earths, and the precipitation completed with alcohol. The selenium or tellurium is employed, not as the healing agent, as in Wassermann's method, but as transporting agent to carry the radium into the diseased tissue when the compound is administered intravenously or subcutaneously. F. S.

Method for the Separation of Mesothorium and Radium in the Manufacture of Thorium from Thorium-containing Minerals. KARL SCHWAB (D.R.P. 269541).—In this method the water used for diluting the product obtained by heating the monazite with sulphuric acid is saturated with barium sulphate before use by the addition of from one-third to two-thirds of the quantity of barium, mixed with the monazite initially. The product, diluted with two or three times its volume of water, is separated from the heavy, unattacked constituents of the sand, and the muddy liquid poured into thirty to sixty times as much water, containing barium, as the quantity of the sulphuric acid product used, when the mesothorium—radium—sulphate is completely precipitated with the crude thorium phosphate. F. S.

The Distinguishing Between Radium Preparations and Between Mesothorium Preparations of Unequal Age by means of their Radiation. OTTO HAHN (*Le Radium*, 1914, 11, 71—74).—Five different preparations were used, consisting of: (1) pure radium bromide; (2) freshly prepared commercial mesothorium bromide; (3) ditto, two years old; (4) new bromide of mesothorium free from radium; (5) radiothorium, separated from mesothorium a long time ago, and purified by precipitation. The absorption curves of the γ -radiations in lead were determined in the same electroscope, of lead 3·3 mm. thick, and showed that it was possible to distinguish certainly between all the preparations. The activity of mesothorium is measured commercially through 5 mm. of lead. Calling the radiation at this thickness 100, the following table shows the radiations unabsorbed by further thicknesses of lead for the five preparations above. In the first column the thickness of the lead electroscope is included:

Mm. of lead.	(1)	(2)	(3)	(4)	(5)
5	100	100	100	100	100
10	68·1	70·0	70·3	69·7	74·7
15	49·7	60·07	32·15	49·4	54·2
20	37·3	37·0	38·8	36·1	42·3
25	28·65	27·3	29·5	26·1	33·5
30	22·0	20·4	22·7	19·14	26·8
35	16·92	15·45	17·65	13·97	21·65
40	13·38	11·42	13·8	10·54	17·6
45	10·63	8·65	10·65	7·75	14·27

The old mesothorium and the radium have initially and finally the same ratio, but may be distinguished at the intermediate thicknesses 10 and 20 mm. In the last line, if the value for radium is made 100, the values for the other preparations are: (2) 81·4; (3) 100·2; (4) 73·3; (5) 134·3 (compare Russell and Soddy, A., 1911, ii, 88).

F. S.

Range of α -Particles in Air at Different Temperatures. A. F. KOVARIK (*Le Radium*, 1914, 11, 69—71).—The range of α -particles from polonium has been determined in an apparatus, similar to that of Geiger and Nuttall, at temperatures between 90° and 362° A. (-183° and 89°). It was found that the range divided by the absolute temperature was constant, except for liquid-air temperature, but the difference is probably not greater than the experimental error at this temperature. From 90° to 362° A. the range increases from 1·13 to 4·73 cm.

F. S.

The Influence of the Presence of Other Substances on the Adsorption of Uranium- X_1 . (On the Question of "Identical" Radio-elements.) H. FREUNDLICH, W. NEUMANN, and H. KAEMPFER (*Physikal. Zeitsch.*, 1914, 15, 537—542).—The observation of Ritzel on the prevention of the adsorption of uranium- X_1 by blood-charcoal by traces of thorium has been repeated and extended, and the explanation of Soddy that the effect is connected with the isotopism of the two elements has been found not to hold good. In absence of thorium, the β -activity of the uranium- X_1 in 11 c.c. of 0·55*N*-uranyl nitrate, shaken 230 hours

with 20 mg. of charcoal, was reduced from 154 to 26·8. In presence of 4 millimols per litre of thorium nitrate, the adsorption is completely prevented, and 0·0004 millimol. (1 mg. in 5 litres) has a clearly perceptible effect. But that this is not a specific action of isotropic thorium atoms is shown by other substances, zirconium salts, and even benzoic acid, producing a similar effect, the latter clearly perceptible at 0·006 millimol. per litre. The effect is explained as due to the substance in greater concentration driving out the first from the surface (verdrängende Adsorption). Any other substance, not a radio-element, adsorbed by charcoal is driven out by thorium nitrate. The adsorption of the copper ion was measured in very small concentration by its catalytic action on persulphate and iodine ions in presence of ferro-salts. A solution of a little copper nitrate and much sodium nitrate was mixed with water or equal volumes of thorium nitrate solution and 100 mg. of charcoal, and shaken sixty hours. The concentration of the copper ion in the solution fell from 0·0472 millimol. per litre in presence of 0·39 (millimol. per litre) of thorium nitrate to 0·0106 in absence of thorium, 0·004 of thorium nitrate producing a detectable effect. Further, it was shown that uranium- X_1 adsorbed in charcoal was driven out by subsequent addition of thorium nitrate to the solution.

No grounds are held to exist for the view that isotopic elements are more nearly related than the members of the rare earths. "Chemical mimicry" is often favoured by small concentration, and may be expected to be strongly shown by isotopic elements, and it is not wonderful that their behaviour is what it is. An observation of Ritzel that thorium emanation prevents the adsorption of uranium- X by charcoal was shown to be due to traces of thorium nitrate carried over in the stream of emanation.

F. S.

The Action of Colloids on Radioactive Products in Solution.

T. GODLEWSKI (*Phil. Mag.*, 1914, [vi], 27, 618–632).—To account for the fact that radium- C in pure water is deposited equally well at the cathode as at the anode, whereas radium- A is deposited only on the anode and radium- B only on the cathode, the hypothesis is advanced that in the α -ray change of radium- A , the radium- B atom produced is expelled from the colloidal aggregate, whereas in the β -ray change of radium- B , the radium- C atom produced is not expelled. Hence the aggregate moves to the cathode when it contains an excess of radium- B atoms, and to the anode when most of these have disintegrated and produced radium- C .

The effect of various colloids, both negative and positive, on the products of the radium emanation in solution were tried. Arsenious sulphide, colloidal platinum, and other negative colloids make the products depositing at the cathode diminish in amount, and ultimately disappear. With increasing concentrations they are then deposited on the anode. Positive colloids, such as ferric oxide, act exactly oppositely. The radioactive colloids are first precipitated by addition of a colloid of opposite sign, which at higher concentrations adsorbs them and inverts their sign. The

compound hydrosols containing both radium-*B* and -*C*, which have a smaller positive charge than the initial ones containing radium-*B* only, are first precipitated, so that at a certain concentration pure radium-*B* is deposited at the cathode. If the colloid added is precipitated by addition of a suitable precipitant, such as aluminium sulphate solution, all the radioactive products are found in the precipitate. It is thus easy to concentrate a powerfully radioactive substance on a few milligrams of precipitated hydrosol, such as gold or platinum.

The precipitation on the filter-paper of radioactive products during filtration is shown to be connected with the known fact that negative colloids rise with the water when filter-paper is immersed in the solution, but positive hydrosols are precipitated in the immersed part of the paper. Aluminium sulphate and dilute hydrochloric acid added to a solution of emanation in water increase the amount of active deposit left on the paper on filtration. With stronger acid, the filter is inactive. If all the radioactive colloids are transformed into negative colloids by addition of a citrate, the activity of the filter may be greatly reduced.

A sheet of filter-paper was partly immersed in water containing emanation. In the immersed part, radium-*B* and -*C* are in the same relative amount as in the solution, but in the higher levels only pure radium-*C* is noticeable. Only the negative hydrosols and radium-*A* and -*C* can ascend the paper, and the former can travel only for a short distance, for on transformation into the *B*-member it is stopped. These results afford new and simple methods of concentrating radioactive products by filtration and burning the paper, which are applicable to all products forming positive hydrosols. It has been employed to remove uranium-*X* from uranium at a strength of 10 grams of uranyl nitrate to the litre, and is no doubt widely applicable.

F. S.

The Radioactivity of Some Type Soils of the United States.

RICHARD B. MOORE (*J. Ind. Eng. Chem.*, 1914, 6, 370—374).—The samples of soil used in this investigation were obtained by sieving through a sieve of six meshes to the linear inch, and grinding to an impalpable powder. Strutt's method (A., 1906, ii, 411, 716) of getting the material into solution was used. The radium content was determined by introducing the emanation from the solution into an electroscope of the C. T. R. Wilson type, as modified by Boltwood (A., 1904, ii, 666), the standard used being that also suggested by Boltwood (*loc. cit.*).

The average activity of the fourteen soils investigated is 1.97×10^{-12} grams of radium per gram of soil, that of the subsoils being 1.52×10^{-12} . In the majority of cases, the soil or subsoil which has the highest activity also has the largest amount of barium plus strontium. The amount of rare earths present in the soils was so small that no conclusion can be drawn as to the relation between the rare-earth content and the activity.

The thorium content of five soils was determined, using the method employed by Joly in determining the thorium content of

rocks and minerals. The average content, namely, about 4×10^{-5} gram per gram of soil, is much higher than Joly's average, 1.58×10^{-5} , for rocks, and much higher than the results obtained by Blanc for Roman soils (A., 1909, ii, 366, 459). T. S. P.

The Measurement of the Radioactivity of Springs. C. ENGLER, H. SIEVEKING, and A. KOENIG (*Chem. Zeit.*, 1914, **38**, 425—427 and 446—450).—This paper contains details of the measurement of the radioactivity of natural waters by means of the "fontaktoscope," tables in connexion with it, the drawing and transport of the water, the sources of error, and improved forms of the measuring instruments employed. F. S.

Determination of the Electric Elementary Quantum by Thermo-mechanical Methods. FRIEDRICH WÄCHTER (*Ann. Physik*, 1914, [iv], **44**, 127—144).—The author criticises the modern theory of electricity, and maintains that the elementary quantum cannot be regarded as an ultimate and fundamental constant of nature. The electrons are supposed to represent the smallest units of matter which owe their electrical charge to their kinetic energy. If the mechanical view is admitted as a working hypothesis, the so-called elementary quantum may be deduced from: (1) the kinetic energy of gas molecules; (2) the specific heat of solid substances; (3) the specific heat of liquid substances; (4) the specific heat of gases at constant volume. The agreement between the values obtained by these different methods is practically as good as that shown by the values obtained by methods which are based on the generally accepted modern views. H. M. D.

[**Electrical] Resistance of some Iron Nickel Alloys.** A. P. SCHLEICHER and W. GUERTLER (*Zeitsch. Elektrochem.*, 1914, **20**, 237—252).—Measurements of the electrical resistance have been made with wires of iron-nickel alloys containing respectively 35.25% Ni, 30.6% Ni, and 25.2% Ni. The measurements were made at temperatures from 0° to about 1000° in a vacuum. The object of the experiments was to determine the position of the equilibrium curve for the reversible and irreversible iron-nickel alloys. A number of curves are given, and from those obtained from the most trustworthy experiments, it is seen that a perfect parallelism exists, from which the conclusion is drawn that all three lie in a homogeneous field of the condition diagram, which extends for 25% nickel alloy upwards to 900° , for 30% nickel alloy up to 700° , and for 35% nickel alloy upwards to 420° . It is held that a second homogeneous field lies above this, and the transition curve probably lies between them. J. F. S.

Electrical Conductivity and Pressure of Flow of Alloys of Potassium and Rubidium. N. S. KURNAKOV and A. I. NIKITINSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 360—371).—The composition-electrical conductivity curve for mixtures of metals forming isomorphous mixtures in all proportions is a continuous curve exhibiting a minimum, the corresponding curve connecting the

composition with the temperature-coefficient of resistance being symbatic in form. Consequently, at low temperatures the minimal conductivity for such mixtures should become more pronounced, and at high temperatures less so. The measurement of conductivity at high temperatures is, however, accompanied by considerable difficulty, and few results have been obtained in this direction. This difficulty is avoided in the authors' measurements on alloys of potassium and rubidium, which fuse at low temperatures. The conductivity was measured at various temperatures from 0° to 100° with both liquid and solid alloys of different compositions. The alloys were prepared, and the measurements made in an atmosphere of nitrogen in special forms of apparatus.

At 0° and at 25° the conductivity curves show very flat minima at 73.11 and 80.57 atom % rubidium respectively, rise of temperature thus displacing the minimum towards the conductivity of the component with the lesser conductivity. The curves at 50 — 100° for the liquid alloys possess no minima, the conductivity increasing continuously from that of rubidium to that of potassium. The curves for the solid alloys resemble those usually obtained for liquid solutions, owing to the slight lowering in the conductivity produced by adding potassium to rubidium, 19.43 atom % of the former metal changing $k_0 \times 10^4$ only from 8.86 to 8.6. The temperature-coefficient of resistance curves are similar to those of conductivity.

Addition of rubidium to potassium is accompanied by a sharp rise in the pressure of flow at 22° from 0.09 to a maximum of 0.28 kilos. per sq. mm. with 14.29 atom % rubidium, after which a continuous fall takes place to the value 0.08 for the latter metal. The curve is thus antibatic to those of conductivity and temperature-coefficient of resistance. It is evident that the pressure of flow is more sensitive than the electrical conductivity as an indicator of those changes which accompany the formation of isomorphous mixtures of plastic substances.

T. H. P.

Relation between Ionic Mobility and Ionic Volume. G. R. MINES (*Kolloid-Zeitsch.*, 1914, **14**, 168—170).—The electrical conductivity of solutions of CeCl_3 and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ has been measured at concentrations varying from 1/20 to 1/2560 molar. The conductivity of the simple salt is somewhat smaller in the more concentrated solutions, and a little greater in the more dilute solutions, but the differences are always small. The two salts have also been compared in respect of the rate at which they diffuse into gelatin which was placed in contact with 0.1 molar solutions of the salts. The observations show that the complex salt diffuses appreciably faster than the simple salt. It seems necessary to assume, therefore, that the simple metallic cation carries a much larger water envelope than the complex cation, and the author considers that the extent to which hydration of the ions occurs is determined by the size of the ion. In the case of a small ion, which is characterised by a large surface density of the electrical charge, the forces brought into play will be such as to bring a

relatively large number of water molecules into close association with the ions. The larger the volume of the free ion and the smaller the electrical density, the smaller will be the number of water molecules which are affected. These views are applied to the consideration of the relations subsisting between the mobilities and volumes of the alkali metal ions.

H. M. D.

The Action of Electrolytes on the Dissociating Power of Solvents. I. A. SACHANOV (*Zeitsch. physikal. Chem.*, 1914, **87**, 441—448).—A series of electro-conductivity measurements have been made with mixtures of electrolytes in solvents of low dielectric constant; these include mixtures of potassium formate and pyridine, pyridine acetate and aniline acetate in acetic acid (DC 6·5); mixtures of tetraethylammonium iodide and aniline hydrobromide, tetraethylammonium iodide and ammonium iodide in aniline (DC 6·8); mixtures of pyridine hydrobromide and diethylamine hydrobromide, pyridine hydrobromide and pyridine hydrochloride in chloroform (DC 4·7). Comparative measurements were made in aqueous solutions of binary mixtures of potassium chloride with succinic acid and tartaric acid, and of sodium chloride with the same acids. The specific conductivity measured in the case of the aqueous solutions is always smaller than that calculated from the single conductivity values, whereas the specific conductivity in the other cases is always larger than the calculated values, in some cases being six times as large. The increase in the conductivity is greater the smaller the dielectric constant of the solvent, and the presence of two salts with a common ion in these solvents also shows an increased conductivity. The conclusion is therefore drawn that in solvents of small dielectric constants, electrolytes exert a dissociating action on one another.

J. F. S.

Distribution of Solvent between Solutes. II. Electrical Conductivity of Mixtures of Salts of the Alkaline-earth and Alkali Metals. A. G. DOROSCHEVSKI and S. V. DVORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 371—379).—The measurements now described were made at $18^\circ \pm 0.02^\circ$ under the same conditions as those made previously (A., 1913, ii, 1014). For the separate salts of the alkaline-earth metals, the conductivities, within the limits of dilution, $v=10-100$, are found to be in good agreement with the formula $\lambda = A - a/v^{1/4}$, the constants A and a , calculated from Kohlrausch's results, being respectively 122·77 and 61·852 for $\frac{1}{2}\text{CaCl}_2$, 121·32 and 69·269 for $\frac{1}{2}\text{Ca}(\text{NO}_3)_2$, 126·98 and 64·774 for $\frac{1}{2}\text{BaCl}_2$, 124·45 and 89·74 for $\frac{1}{2}\text{Ba}(\text{NO}_3)_2$, and 116·93 and 59·809 for $\frac{1}{2}\text{MgCl}_2$. For potassium iodide, the formula $\lambda = 131\cdot50 - 38\cdot082/v^{3/8}$ holds, and for $\frac{1}{2}\text{K}_2\text{SO}_4$ and $\frac{1}{2}\text{Na}_2\text{SO}_4$ the formula $\lambda = A - a/v^8$. A and a being 178·37 and 111·625 in the former and 151·90 and 98·10 in the latter case.

The results obtained with mixtures, each containing the chlorides of one alkaline-earth and one alkali metal, show that solutions

of salts of these two types of metals are isohydric at equivalent concentrations. This conclusion embraces salts the conductivities of which are expressed by the formulae containing either $\sqrt[3]{v}$ or $\sqrt[4]{v}$ or $\sqrt[8]{v}$, and is hence of wider application than Barmwater's formula for the conductivity of mixtures (A., 1899, ii, 274, 396), as this is valid only when the conductivity of the salts is given by $\lambda = A - a/\sqrt[3]{v}$.

With mixtures of salts containing different negative ions, the calculated values of the conductivities are arrived at by assuming that the above condition of isohydry persists with the four salts formed from a binary mixture. Comparison of these calculated values with the experimental data shows, however, that the latter are in some cases lower, and in others higher, than the former. "Depression" of the conductivity occurs with $\text{KNO}_3 + \frac{1}{2}\text{BaCl}_2$, $\frac{1}{2}\text{K}_2\text{SO}_4 + \frac{1}{2}\text{MgCl}_2$, $\text{KNO}_3 + \frac{1}{2}\text{Na}_2\text{SO}_4$, $\text{NaNO}_3 + \frac{1}{2}\text{BaCl}_2$, $\text{NaNO}_3 + \frac{1}{2}\text{CaCl}_2$, and $\frac{1}{2}\text{Na}_2\text{SO}_4 + \frac{1}{2}\text{MgCl}_2$, whilst "exaltation" takes place with mixtures in which the negative ions are interchanged. The conditions governing the magnitude of the "depression" or "exaltation" are being investigated.

T. H. P.

New Electric Crucible Furnace for Laboratory Use. PAUL ASKENASY (*Zeitsch. Elektrochem.*, 1914, **20**, 253).—An electrical crucible furnace is described in which the usual platinum resistance is replaced by a common metal. This is prevented from oxidising by a packing of powdered charcoal, which is placed in the space between the actual furnace and the outer casing. The furnace is 50 mm. diameter and 80 mm. deep, and can be connected directly with the lighting circuit without any resistance in series. The efficiency of the furnace is high, and a temperature of 800° can be obtained in ten minutes, and one of 1100° in thirty minutes. The highest temperature obtainable in this furnace is 1100° .

J. F. S.

Allotropy and Electromotive Equilibrium. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam.*, 1914, **16**, 1002—1005).—A reply to Cohen's claim for priority (this vol., ii, 332) in respect of the accelerating influence of salt solutions on the attainment of equilibrium in metals. It is pointed out that the author's theory has reference to the equilibrium between different kinds of molecules in a metal, whilst Cohen's observations refer to the transformation of one polymorphic modification into another.

H. M. D.

Further Investigations on the Electrode-like Behaviour of Organic Substances which are Insoluble in Water. R. BEUTNER (*Zeitsch. physikal. Chem.*, 1914, **87**, 385—408. Compare A., 1913, ii, 468, 469, 662).—A continuation of the work previously published; the present paper deals with the measurement of the E.M.F. of galvanic elements composed of two conducting electrodes (Hg , Hg_2Cl_2 , $n\text{KCl}$), solution of a salt, and an organic substance insoluble in water. The element can be represented by

$NE \cdot n/10\text{KCl}$ salicylaldehyde NE .

$N/10$ -solutions of NH_4Cl , BaCl_2 , MgCl_2 , and CaCl_2 were substi-

tuted for the potassium chloride in the element given above. By this arrangement, the *E.M.F.* at the surface of the solution and the salicylaldehyde is measured. Measurements are also given of elements in which salicylaldehyde has been replaced by guaiacol, acetophenone, benzyl alcohol, benzaldehyde, anisaldehyde, cinnamaldehyde, and ethyl acetoacetate, and in which the hydrochlorides of aniline, benzylamine, methylaniline, and dimethylaniline have been substituted for the metallic chlorides. It is shown that in elements where the hydrochloride of an organic base is measured against a solution of sodium chloride through an organic liquid, namely, aniline hydrochloride | salicylaldehyde | *N*/10-sodium chloride, the organic hydrochloride solution is always negative. This is in agreement with the theory previously put forward (*loc. cit.*), since it can be assumed that the partition-coefficient of the organic hydrochloride between water and the organic liquid is greater than that of sodium chloride between the same solvents. In elements where the sodium salt of an organic acid is measured against sodium chloride, the first-named solution is always positive. Substances with a relatively high partition-coefficient show an irreversibility of the potential difference. In binary salt solutions, the *E.M.F.* does not change in a linear manner with the composition. Addition of salts of large partition-coefficient influences the potential difference more than that of salts of low partition-coefficient. From the above-mentioned results, the author draws the conclusion that an *E.M.F.* is set up by two equally concentrated electrolytes, separated by a conducting organic liquid, insoluble in water, which is dependent on the partition-coefficients of the two salts between water and the organic liquid. It is shown that the idea of an adsorption potential (Baur, *Zeitsch. Elektrochem.*, 1913, **19**, 590) is unnecessary for the explanation of these potential differences on the basis of thermodynamic laws.

J. F. S.

Influence of the Superposition of Alternating Current on Direct Current in Electrolysis. O. REITLINGER (*Zeitsch. Elektrochem.*, 1914, **20**, 261—269).—In the electrolysis of many substances the overvoltage is responsible for the nature of the product, and as in many cases the same overvoltage, which is advantageous for the product of the reaction, also works disadvantageously toward certain intermediate products. The superposition of an alternating current on a direct current has the effect of reducing the overvoltage, and with the object of seeing whether such a current would give a yield of the intermediate product instead of the usual product, electrolyses were carried out. Thus, in the electrolysis of sulphuric acid, instead of persulphuric acid, ozone was obtained. In the electrolysis of ethyl and propyl alcohols, acetaldehyde and propaldehyde were obtained instead of the corresponding acids, as is usual. This result confirms the experiments of Dony-Hénault (A., 1900, ii, 644), which show that when the potential of the anode is kept low enough, aldehydes are formed from alcohols, but at higher potentials acids are produced. A pulsating negative direct current opposed to the ordinary current reduces

the anode potential, and an increased yield of ozone is obtained. If the alternating current has a high frequency, its depolarising action is weaker, and this is shown to be due to the strong phase displacement brought about by the high capacity of the electrode. Experiments were also made on the oxidation of ammonia in sodium hydroxide solution in the presence of copper as catalyst. In this case a yield of 40·2% of the theoretical amount of nitrous acid was produced without any nitric acid. Benzoic acid and benzaldehyde were obtained from toluene suspended in sulphuric acid ($D\ 1\cdot22$), using lead peroxide anodes, and *p*-benzaldehyde-sulphonic acid was obtained from the sodium salt of *p*-toluenesulphonic acid dissolved in dilute sulphuric acid, using lead peroxide anodes.

J. F. S.

Electrolysis of Mixtures of Molten Potassium and Sodium Salts. BERNHARD NEUMANN and EINAR BERGVE (*Zeitsch. Elektrochem.*, 1914, **20**, 271—275).—Castner has shown in the preparation of sodium from fused sodium hydroxide that the yield of metal is better the lower the temperature of electrolysis. The present paper deals with attempts to lower the melting point of molten sodium hydroxide by the addition of salts of sodium and potassium, and from the mixtures of low melting point to obtain pure sodium by electrolysis. The first part of the paper deals with determinations of the melting point of sodium hydroxide to which various quantities of potassium hydroxide, sodium carbonate, a mixture of 48·5% sodium carbonate and 51·5% potassium carbonate, and a mixture of potassium hydroxide and sodium carbonate have been added. Complete melting-point curves are given for the above-mentioned mixtures, and minima are indicated as follows: 41·6% NaOH + 58·4% KOH, m. p. 167°; 17% Na_2CO_3 + 83% NaOH, 280°; 79·3% NaOH + 20·7% ($Na_2CO_3 + K_2CO_3$ as above), 265°. The lowerings of the melting point of sodium hydroxide have been controlled by calculations based on the Raoult law of proportionality of the lowering of the freezing point, and the calculated figures agree well with those determined experimentally. These various more fusible mixtures have been electrolysed, and in every case an alloy of sodium and potassium was obtained. The electrolysis was effected in a nickel crucible, using an annular nickel anode, and a nickel rod as cathode, with an *E.M.F.* of 3·9 volts and 1 ampere per sq. cm. of anode as the current density. Using a constant current for electrolysis, the content of the metal deposited on potassium increased with increasing concentration of potassium in the melt. With the mixture 60% NaOH 40% KOH, the metal deposited had the composition 60% Na 40% K. On increasing the current density, the alloy increased its percentage of potassium; these same effects were also observed in the melts containing carbonate.

J. F. S.

The Electrolytic Deposition of Alloys and their Metallographical and Mechanical Investigation. II. Deposition of Copper-Tin Bronzes. R. KREIMANN, C. TH. SUCHY, J. LORBER, and R. MAAS (*Monatsh.*, 1914, **35**, 219—288).—The experiments were

conducted on the same lines as those described in the previous investigation (this vol., ii, 96), potential measurements being first carried out in order to determine with what concentrations and under what conditions the deposition potentials of the two metals were close together. Baths made up from copper sulphate, stannous chloride, and ammonia solutions, with or without the addition of sodium hydroxide and ammonium chloride, did not give satisfactory results, but bronze could be deposited either from tartrate or cyanide baths, a necessary condition for a good deposit in sheet form being a high content of free alkali hydroxide. As the content of alkali increases, the deposits become more elastic, and contain less hydrogen and cuprous oxide. With high concentrations of alkali hydroxide, however, the copper anode becomes passive, and accompanying this passivification, especially in tartrate baths, decomposition of the electrolyte takes place, thus limiting the length of time the bath may be used to a few days. There is an optimum alkali concentration which gives the best results. The decomposition in the tartrate baths is due to oxidation of the tartaric acid and subsequent reduction of the copper salt.

Investigation of the microscopic structure, of the *E.M.F.*, and of the sclerometric hardness of the deposits, showed that the bronzes obtained from the cyanide baths were more uniform in structure than those from the tartrate baths.

Technically, owing to the decomposition of the tartrate baths and the less uniform structure of the deposits, the cyanide baths are to be preferred.

T. S. P.

Electro deposition of Nickel. C. W. BENNETT, H. C. KENNY, and R. P. DUGLISS (*J. Physical Chem.* 1914, **18**, 373—384).—Experiments have been made to ascertain the conditions which affect the electro-deposition of nickel from a solution of nickel ammonium sulphate. This solution contained 80 grams of the double sulphate and 10 grams of nickel chloride per litre, and nickel anodes, containing 7·6% of iron, were used.

A good deposit of nickel may be obtained if the solution at the surface of the cathode is kept alkaline. The efficiency of the process depends on the alkalinity of the cathode solution, and diminishes if the alkalinity is reduced by vigorous stirring of the solution.

The iron content of the deposit formed on a rotating cathode is found to be greater than that of the deposit on a stationary cathode. The efficiency is not materially affected by the iron content of the anode.

H. M. D.

The Interpretation of the Magnetic Properties of Mixtures of Oxygen and Nitrogen. ALBERT PERRIER and H. KAMERLINGH ONNES (*Compt. rend.*, 1914, **158**, 1074—1076).—A theoretical discussion of results already obtained on the effect of diluting oxygen with nitrogen, the coefficient of magnetisation of the first element increasing towards the value which satisfies Curie's law.

The variation in density of oxygen only modifies its specific magnetisation, without varying its Curie constant. The molecular field varies practically with the density, although for large dilutions the variation is apparently slightly more rapid. W. G.

The Magneton Theory. R. GANS (*Ber. Deut. physikal. Ges.*, 1914, **16**, 367—368).—A reply to Heydweiller's criticism (this vol., ii, 24). H. M. D.

The Magneto-chemistry of Nickel Compounds and the Theory of the Magneton. B. CABRERA, E. MOLES, and J. GUZMAN (*Arch. Sci. phys. nat.*, 1914, [iv], **37**, 324—334; *Anal. Fis. Quim.*, 1914, **12**, 131—142).—Using the method previously described (this vol., ii, 24), the authors have determined the magnetic susceptibility of solutions of varying concentrations of nickel sulphate, nickel chloride, and nickel nitrate. The number of magnetons for nickel is found to be 16; it is independent of the concentration, and of the temperature between 14° and 25°. In the case of an almost saturated solution of potassium nickelocyanide at 15°, the magnetic susceptibility is found to be -1.77×10^{-4} , the salt being diamagnetic. T. S. P.

Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. A. E. OXLEY (*Phil. Trans.*, 1914, *A*, **214**, 109—146).—Measurements have been made of the magnetic susceptibility of a number of organic compounds, with special reference to the change in this property which accompanies the transition from the liquid to the solid state. The substances investigated were toluene, *o*-xylene, cymene, nitrobenzene, chlorobenzene, bromobenzene, aniline, benzyl chloride, benzoyl chloride, benzaldehyde, benzene, pyridine, phenylhydrazine, acetophenone, benzophenone, naphthalene, α -bromonaphthalene, and α -naphthylamine.

In most cases it has been found that the substance is more diamagnetic in the liquid than in the crystalline form. The behaviour of benzoyl chloride and phenylhydrazine is exceptional, and this abnormal change in the susceptibility was also found in the liquid crystalline compounds cholesteryl chloride and *p*-azoxyanisole. Nearly all the benzene derivatives show a change in the susceptibility of the order of 5% on solidification.

The observations are discussed in terms of the view which has been referred to in a previous paper (*A.*, 1912, ii, 325).

H. M. D.

The Differential Scale of Temperatures. THADÉE PECZALSKI (*Compt. rend.*, 1914, **158**, 1164—1166).—The author has developed an exponential scale of temperatures expressed by $T = T_0 e^{\int_{T_0}^{T_1} adt}$ where a is a constant, which possesses the essential properties of differential temperatures, and he quotes several properties of this scale bearing upon the physical properties of substances. W. G.

Expansion of Liquid Mixtures and Solutions on Heating.
 W. HERZ (*Zeitsch. physikal. Chem.*, 1914, **87**, 63—68). Compare this vol., ii, 25).—The author has applied the Mendeléev equation on the thermal expansion of liquids to mixtures of liquids and solutions. Binary mixtures of benzene, toluene, aniline, and nitrobenzene have been prepared, and their densities have been measured by means of an Ostwald-Sprengel pycnometer at temperatures from 25—90°. The value for k has been determined and used for calculating the density in each case. There is a remarkably good agreement between the experimentally determined value and the calculated value. A number of solutions—diphenylamine in aniline, iodine in benzene, benzoic acid in benzene, and iodine in toluene—have been treated in the same way, with results which are equally good. It has been previously shown (*loc. cit.*) that water does not obey the Mendeléev law, but a series of aqueous solutions treated in the same way as the substances mentioned above give good agreement at temperatures above that of the maximum density of water and in the case of concentrated solutions. Experiments were made with aqueous solutions of sodium chloride, sodium hydroxide, sulphuric acid, acetic acid, and sucrose. In the case of sodium hydroxide, a 5% solution gave a k value which differed from the mean by 20·5%, whereas a 50% solution only differed 1·8%.

J. F. S.

Theoretical Treatment of the Phenomena in Dilute Gases.
 B. BAULE (*Ann. Physik*, 1914, [iv], **44**, 145—176).—A mathematical paper in which the thermal conductivity and viscosity of gases at very low pressures are discussed.

H. M. D.

Ratio of the Specific Heats of Air, Hydrogen, Carbon Dioxide, and Nitrous Oxide. H. N. MERCER (*Proc. Physical Soc. London*, 1914, **26**, 155—163).—The cooling effect of adiabatic expansion has been made use of to determine the specific heat ratio. The change in the temperature was measured by the alteration in the resistance of a very fine platinum wire. The resistance thermometer was compensated for conduction along the leads, and by the employment of an automatic contact which closes the galvanometer circuit at the right moment, it has been found possible to obtain measurements of considerable accuracy with a vessel of only 300 c.c. capacity. The values obtained for the specific heat ratio are: air, 1·400; hydrogen, 1·398; carbon dioxide, 1·292; nitrous oxide, 1·261. The values of c_p , calculated from these ratios, are: air, 0·2403; hydrogen, 3·4704; carbon dioxide, 0·2000; nitrous oxide, 0·2185. These numbers are in good agreement with the directly determined values of c_p .

H. M. D.

Specific Heat of Liquids at Constant Volume and the Difference between the Specific Heats at Constant Volume and at Constant Pressure. DANIEL TYRER (*Zeitsch. physikal. Chem.*, 1914, **87**, 169—181).—The author has calculated the values of the

specific heat at constant volume (c_v), the difference between the two specific heats ($c_p - c_v$), and the ratio of the two specific heats, c_p/c_v , for a series of liquids from a series of previously published (T., 1913, **103**, 1675) compressibility determinations. A comparison of the c_v values for the liquid and vapour shows that the liquid value is considerably higher than that of the vapour. The hypothesis of de Heen on the change of $(c_p - c_v)$ with temperature is discussed, and it is shown that when the molecular attraction is expressed by the function a/v^2 of the van der Waals equation, the de Heen hypothesis does not hold. The expression $(c_p - c_v)v^2/(dv/dt) = \text{const.}$ is deduced on the assumption that the pressure of attraction is given by a/v^2 ; this expression holds for normal liquids within the experimental error. The product of the molecular weight and the factor $(c_p - c_v)$ is approximately constant for normal liquids at the same temperature. The equation $l.(dv/dt)/v(c_p - c_v) = 1$, in which l is the latent heat, is deduced and found to be approximately correct. A table is given of the values c_p , c_v , and the ratio c_p/c_v at a series of temperatures for the liquids benzene, toluene, chloroform, carbon tetrachloride, ether, chlorobenzene, carbon disulphide, ethyl alcohol, and water.

J. F. S.

The Pyrophoric Phenomenon in Metals. A. SMITS, A. KETTNER, and A. L. W. DE GEE (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 999—1001).—Dilatometric experiments have shown that the conversion of pyrophoric into non-pyrophoric iron is accompanied by an appreciable increase in volume. The transformation is completed in about forty-eight hours at 310—320°. The observed change in volume affords support for the theory that the pyrophoric modification consists of a mixture of different kinds of molecules which are not in a state of equilibrium (compare this vol., ii, 165).

H. M. D.

Reheating and Annealing after Tempering of Copper-Tin and Copper-Zinc Alloys. A. PORTEVIN (*Compt. rend.*, 1914, **158**, 1174—1177. Compare Grenet, A., 1911, ii, 42).—Alloys of copper-tin and copper-zinc behave in the same way as alloys of copper-aluminium (compare Portevin and Arnou, A., 1912, ii, 352) on reheating and annealing after tempering. The pro-eutectoid constituent, which had dissolved entirely or in part during tempering, separates out in such a way as to give the alloy the Widmanstaetten structure, visible under a microscope. Further, the commencement of reheating is accompanied by an increase in the hardness of the alloy.

W. G.

Thermolysis The Ludwig-Soret Phenomenon in Solids. HERMANN WESSELS (*Zeitsch. physikal. Chem.*, 1914, **87**, 215—252).—The author has investigated the manner in which the composition of solid mixtures changes when subjected to a gradation of temperature. The mixtures examined were: hydrated silica, borax glasses containing metal oxides (namely, CoO), silicate glasses coloured by

metal oxides, a solution of benzene in caoutchouc, and a 2% mixture of azobenzene in dibenzyl. It is shown that in the case of solids containing water, the water diffuses to the colder regions of the substance; the same observation is made in the benzene-caoutchouc mixture, namely, that the volatile constituent passes to the colder regions. In the cases of coloured glass, it is shown that the dissolved metal oxides pass to the colder regions of the mixture, but in the mixed crystals of azobenzene and dibenzyl the azobenzene diffuses to the warmer side.

J. F. S.

Heats of Cooling of Aluminium, Iron, Antimony, and Nickel. P. N. LASCHTSCHENKO (*J Russ. Phys. Chem. Soc.*, 1914, **46**, 311—333).—The amounts of heat developed by these metals during cooling were measured in the manner previously described (A., 1913, ii, 671).

The aluminium used contained 0·31% Si and 0·63% Fe, but was free from copper and lead. The curve connecting the amount of heat developed by 1 gram of aluminium in cooling from any given temperature to 23—24° with this temperature is continuous to 580°, and is somewhat convex towards the temperature axis. Between 580° and 590° a marked change in direction of the curve occurs, and at 670—650° a sudden increase in the amount of heat, owing to fusion of the metal. The heat of fusion is found to be 71. cal. per gram. Even when the metal is melted and heated at 700—720° it exerts no action on the quartz tube, and only at 750° does the formation of silicon occur.

In the experiments with iron, the metal used was free from pearlite, and contained only minimal inclusions of slag. The heat of cooling curve shows two marked changes in direction, at 730° (α -Fe \rightleftharpoons β -Fe) and 895° (β -Fe \rightleftharpoons γ -Fe) respectively, and beyond 900°, when the iron is in the γ -form, the specific heat increases rapidly with rise of temperature. Measurement of the heat of cooling of electrolytic iron confirms the temperature 730° for the change of α - into β -iron. The conversion of the β - into the α -modification is accompanied by the development of 5 cal. per gram or 0·28 Cal. per gram-atom, and that of γ - into β -iron by about 6·1 cal. per gram or 0·38 Cal. per gram-atom.

The nickel employed was of 99·89% purity. The heat of cooling curve shows a break at 355—365°, in complete agreement with previous observations, and indicates, further, the existence of a third modification of nickel stable above 700°. This indication is confirmed by the change of the metal at high temperatures into a brittle form with a coarsely crystalline structure (compare Cohen, *Zeitsch. Elektrochem.*, 1909, **15**, 686). The first transformation, at 363°, is accompanied by the development of about 3·11 Cal. per gram-atom.

Antimony was investigated at temperatures ranging from 200° to 680°, and within these limits the heat of cooling curve is quite continuous. This metal melts at 630°, and the latent heat is 4·85 Cal. per gram-atom.

T. H. P.

Application of Cryoscopy to the Determination of Double Salts in Aqueous Solution. E. CORNEC and G. URBAIN (*Compt. rend.*, 1914, **158**, 1118—1121).—A determination of the lowering of the freezing point of solutions of one compound in aqueous solutions of another gives an indication of the formation of a double salt. If a difference is found between the values observed and calculated, it is an indication of the existence of a double salt in solution, this difference being at its maximum when the two substances are in the molecular proportions corresponding with that of the double salt. The cases studied were cadmium iodide and alkali iodides, cadmium bromide and alkali bromides, and cadmium chloride and alkali chlorides. The results obtained were in agreement with the known constitution of the solid double salts in these cases.

W. G.

Differentiation of Racemic and Pseudo-racemic Substances. G. TAMMANN (*Zeitsch. physikal. Chem.*, 1914, **87**, 357—365).—A method of molecular-weight determination is developed for deciding whether an inactive substance is made up of mixed crystals of the *d* and *l* kinds, or whether it is a true racemic compound. The method is based on the entropy change in melting. It is shown that for the melting of a gram-molecule of a substance the entropy change is given by the equation

$$\dot{M}r_p/T_s \pm \Delta\alpha W/T_s = 10 \text{ to } 16 \text{ cal.},$$

in which $r_p M$ is the molecular heat of fusion, T_s the melting point in degrees absolute, $\Delta\alpha$ is the change in molecular concentration in fractions of a gram-molecule, and W the heat change due to the change of concentration in melting. The factor $\Delta\alpha=0$ for normal liquids, consequently $\dot{M}r_p/T_s=10—16$ cal. in these cases. This rule can also hold for abnormal liquids when $W=0$. Four cases are worked out for racemic substances and applied to the cases of carboxime and methyl tartrate. The latent heat of fusion for 1 gram of the *d*-, *l*-, and *i*-forms of these substances was determined, and in the case of the three carboximes the value of $\dot{M}r_p/T_s$ is 11·2, which indicates that there is no change of molecular weight, and that the inactive carboxime is not a true racemic compound, but presents a case of a pseudo-racemic substance. The inactive tartaric ester has a value of 17·4, whilst the *d*-ester has a normal value 11·9. From these figures and other considerations the conclusion is drawn that here a case of a true racemic compound is presented.

J. F. S.

Determination of the Critical Temperature of Some Mercury Haloids. LÉON ROTINJANZ and WŁADIMIR SUCHODSKI (*Zeitsch. physikal. Chem.*, 1914, **87**, 253—256).—The critical temperature of mercuric chloride, bromide, and iodide have been determined. The substances were sublimed in a vacuum into small quartz tubes 1 mm. internal diameter and 15 mm. long. The tubes were sealed off and bound to the junction of a platinum-rhodium platinum couple, and heated in a small electric furnace. The critical temperatures were obtained from both sides, and did not differ

more than 1° in the various determinations. The following values in degrees absolute were obtained: HgCl₂, 976°; HgBr₂, 1011°; HgI₂, 1072°. It is shown that the value T_s/T_k , where T_s is the boiling point at atmospheric pressure and T_k is the critical temperature, is equal to 0·59, a value much lower than that demanded by the formula $T_s/T_k = 0\cdot67$. Using the expression

$$T_k = T_s \cdot v_s - 273/2(v_s - 1)$$

(Thorpe and Rucker, T., 1884, **45**, 143), in which v_s is the volume at the boiling point in relation to that at zero, and using the density values of Prideaux (T., 1910, **97**, 2032), the critical temperatures of the three substances are calculated to HgCl₂, 1268°, HgBr₂, 1013°, and HgI₂, 1077°, from which it will be seen that the values for the bromide and iodide agree well with the experimental value, whilst that for the chloride is widely divergent.

J. F. S.

An Application of Nernst's Approximation [Vapour Pressure] Formula. P. WINTERNITZ (*Physikal. Zeitsch.*, 1914, **15**, 397—399).—Whereas, according to the Trouton and the Le Chatelier-Forcrand rules, the ratio Q/T should be constant, where Q is the molecular heat of vaporisation or dissociation, and T is the temperature at which the vapour pressure or dissociation pressure becomes equal to that of the atmosphere, Nernst's formula indicates that this relation cannot hold at very high or very low temperatures. By reference to the data for tungsten and hydrogen, it is found that the conclusion drawn from Nernst's formula is in agreement with experiment. According to experiment, $Q/T = 15\cdot0$ for hydrogen and $41\cdot0$ for tungsten, and the values obtained from Nernst's formula are respectively $17\cdot0$ and $42\cdot2$.

H. M. D.

The Chemical Constant of Hydrogen. von KOHNER and P. WINTERNITZ (*Physikal. Zeitsch.*, 1914, **15**, 393—397).—The so-called “chemical constant” which appears as an integration constant in Nernst's vapour-pressure formula has been calculated for hydrogen by making use of Brönsted's data for the affinity of the reaction H₂ + HgO = Hg + H₂O (A., 1909, ii, 10, 369). The value thus obtained is C = -1·303.

H. M. D.

The Atomic Character of Chemical Change in Gaseous Systems. E. BRINER (*J. Chim. Phys.*, 1914, **12**, 109—132).—From the values calculated for the heats of formation of the molecules of iodine, bromine, chlorine, sulphur, and hydrogen, it seems probable that all chemical compounds are exothermic if the energy content of the compound is compared with that of the component elements in the atomic condition. This view is applied to the consideration of the equilibrium in gaseous mixtures at high temperatures, and it is shown that the concentration of so-called endothermic compounds should pass through a maximum as the temperature increases, afterwards falling as the temperature continues to rise. The influence of temperature on the proportion of

nitric oxide which is present in a mixture of nitrogen and oxygen is discussed as a special case.

On the assumption that the formation of compounds in gaseous systems is due to the reactivity of the elementary atoms, it is possible to give a satisfactory explanation of the phenomena of "false equilibrium," and also of various catalytic effects. The assumption also affords a basis for the deduction of the relationship between the reaction velocity and the temperature of gaseous systems.

H. M. D.

The Gas Equation at Low Temperatures. O. SACKUR (*Ber.*, 1914, **47**, 1318—1323).—Basing his considerations on the quantum hypothesis, and on Planck's theory, which is based on the assumption that the kinetic energy of a substance at the absolute zero has a definite value, the author puts forward the following gas equation for low temperatures (compare A., 1913, ii, 128):

$$PV = RT \left[1 + \frac{1}{RT} \left(b - \frac{a}{RT} \right) P + \frac{1}{12M} \cdot \frac{P^{2/3}}{T^{5/3}} + \frac{1}{10} \left(\frac{A}{M} \right)^{3/4} \cdot \frac{P^{1/2}}{T^{5/4}} \right],$$

where a and b are the van der Waals' constants, M is the molecular weight of the gas, and A is a universal constant for all gases, the value of which can be calculated by the quantum theory.

According to this equation, the curve showing the relation between the pressure and the product PV should be concave towards the axis of pressure. Experiments show that this is the case for hydrogen and helium at the temperature of boiling hydrogen (-253°) and pressures below one atmosphere. It can also be shown that a similar result holds at -196° and -183° , although the effect is not so marked.

T. S. P.

Equation of Condition. A. WOHL (*Zeitsch. physikal. Chem.*, 1914, **87**, 1—39).—The author has deduced an equation of condition of the form $p = RT/(v-b) - a/v(v-b) + cv^3$, in which a and b are constants having the same values as in the van der Waals' equation, and c is a constant which is a function of the temperature. The equation has been tested by means of the data collected for fluorobenzene, *n*-pentane, β -methylbutane, ethyl alcohol, carbon dioxide, argon, oxygen, helium, and hydrogen. It is shown that in all cases that the isothermals and vapour-pressure curves can be reproduced with sufficient exactitude by means of this equation, and their constants can all be obtained from the three values R , T_κ , and p_κ . The dependence of the attraction factor on temperature is given by a/θ , that of the repulsion factor is given by c/θ above T_κ and c/θ^2 below T_κ . In the case of carbon dioxide between pressures of 100—1000 atmos., $b = v_\kappa / (\delta + \epsilon\pi)$, in which δ is approximately equal to 4. For pressures below p_κ , b is constant. A number of equations of condition of variously second-, third-, and fifth-order equations of v are discussed and compared with the present equation, and it is shown the author's equation represents the actual facts better than any of them; it is also shown that a cubic equation with R and $(v-b)$ in the numerator

cannot represent the actual conditions if the critical region is to be included in the range of the equation. J. F. S.

Some Relationships between the Compressibility and other Physical Properties of Liquids together with Remarks on the Values of a and b in the van der Waals' Equation for the Liquid Condition. DANIEL TYRER (*Zeitsch. physikal. Chem.*, 1914, **87**, 182—195).—Making use of compressibility data previously determined by the author (T., 1913, **103**, 1675), the expression $\beta = T(dv/dt) \cdot v/c$, where β is the isothermal compressibility, is confirmed. The relationship $\beta\gamma^{4/3} = \text{constant} = 0.00253$, deduced and applied by Richards and Matthews (A., 1908, ii, 158) to measurements at high pressures, is applied to the author's measurements at 1.5 atmospheres' pressure. It is shown that with increasing temperature the value increases, except in the case of water, whilst for the same temperature the value is approximately constant for all liquids except carbon disulphide, ethyl alcohol, and water. It is shown that the expression $\beta\gamma^{4/3}/T^{1/3} = k$, where γ is the surface tension and T the absolute temperature. A number of other relationships are also considered and tested on the same data. The value of b of the van der Waals equation is determined for a number of liquids (see this vol., ii, 425) from the compressibility data. It is shown that b is approximately equal to $V^{2/3} \cdot V_0^{1/3}$, where V_0 and V respectively represent the molecular volume at the absolute zero and at the experimental temperature. The value of a is obtained by substituting that of b in the van der Waals equation, and it is shown that for temperatures below that of the critical point the value of a is approximately constant.

J. F. S.

Surface Tension at the Surface of Separation of Two Solvents. OSKAR LÓRÁNT (*Pflüger's Archiv*, 1914, **157**, 211—250).—The surface tension at the surface separating water or an aqueous solution from various other liquids has been measured by the method of capillary rise, and also by the method which involves the determination of the weight of the drop which is formed at the end of a capillary tube immersed in the second liquid. In general, the results indicate that there is no simple relation connecting the tensions observed at an air and at a water surface in the case of the liquids which have been examined.

From experiments with aqueous solutions of different electrolytes in contact with ethyl ether, nitrobenzene, chloroform, and carbon tetrachloride, it has been found that the surface tension depends on the nature of the ions and on the concentration of the solution. The influence of the anions is of greater importance than that of the cations. From the observations with 1*N*-solutions of potassium salts, it is found that the anions arrange themselves in the order Cl, SO₄, Br, I, SCN in the case of ethyl ether and nitrobenzene. Chloroform and carbon tetrachloride give a somewhat different series.

Sodium oleate in 0.1*N*-solution reduces the surface tension at

all four surfaces to a small fraction (1/10 to 1/26) of the value for pure water. Ethyl alcohol and chloral hydrate have a similar, but smaller, influence on the surface tension. A solution of egg-albumin has a smaller surface tension than water, and the influence of the albumin is much greater for a liquid-liquid surface than for a liquid-air surface.

Blood serum has also a smaller tension than water at the surface of each of the four liquids investigated. H. M. D.

Work Done in the Formation of a Surface Transition Layer of a Liquid Mixture of Substances. R. D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1914, **17**, 409—413).—In a previous paper (A., 1913, ii, 26) a formula was deduced for the surface tension of a liquid on the assumption that no transition layer is formed at the surface. This formula is now extended to binary mixtures and values obtained for the surface tension of mixtures of benzene and carbon tetrachloride and of chloroform and carbon disulphide. The results show that the theoretical surface tension (λ_2) for mixtures of benzene and carbon tetrachloride is practically independent of the relative proportions of the constituents in the mixture. A similar relation is exhibited by the observed values of the surface tension (λ_1).

The difference $\lambda_2 - \lambda_1$ represents the external work done in the formation of the transition layer. For pure liquids, $\lambda_2 - \lambda_1$ is practically independent of the temperature, but for mixtures this difference increases with rise of temperature. H. M. D.

The Viscosity of Rubber Solutions. R. GAUNT (*J. Soc. Chem. Ind.*, 1914, **33**, 446—452).—The method of procedure adopted in the determination of the viscosity of rubber solutions was practically identical with that suggested by Fol (A., 1913, ii, 301). The majority of the experiments were made with the following different kinds of rubber: (a) a pale, thin plantation crêpe Hevea, coagulated by means of acetic acid; (b) fine, hard Para; (c) Castilloa, prepared by centrifugalisation; (d) Funtumia sheet; (e) Ceara biscuits. The solvents, which were specially purified, with the exception of commercial xylene, were benzene, ether, light petroleum distilling below 50°, toluene, chloroform, and commercial xylene. The viscosities were measured at 20° with an Ostwald viscometer.

The Castilloa and Funtumia rubbers mix with the solvents in all proportions, whereas the Para and Ceara rubbers are only partly soluble; in the latter cases the greater the proportion of rubber to a given quantity of solvent, the more rubber dissolves, the dissolved rubber causing a partial solution of the insoluble constituent; moreover, crêping the Para rubber for forty-five minutes in cold water increases the solubility.

The relation between the viscosity (η) of the rubber solutions in all the various solvents and the concentration (x) is given by the formula $\eta = \kappa^x$, where κ is a constant. The inclination of the straight lines obtained by plotting $\log \eta$ against x , towards the

axis of x , gives the best method of comparing the viscosity of rubber solutions (compare Schidrowitz and Goldsbrough, A., 1913, ii, 760).

Rubber solutions diminish in viscosity on keeping, and heat, as well as light, increases the rate of diminution in viscosity. At high temperatures the effect of light is less marked than that of heat. Such diminution takes place in the absence of air, and cannot be ascribed to oxidation; probably the dissolved rubber undergoes a physical change, the so-called "depolymerisation." The change in viscosity follows the law: $x = a + b \log t$, where x is the diminution in viscosity in the time t , a is the diminution in the first unit of time, and b the increment of diminution with time. The greater the concentration of the solution the more rapid is the diminution in viscosity.

The results of experiments are also detailed, in which the change of viscosity (1) of the same rubber in different solvents, and (2) of different rubbers in the same solvent, was investigated. The presence of xylene or higher hydrocarbons in commercial benzene affects the viscosity, and hence the necessity of using pure solvents (compare Schidrowitz, *loc. cit.*). T. S. P.

Connexion between the Adsorption Isotherm and the Laws of Proust and Henry. W. P. A. JONKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 970—974).—If a substance is in distribution equilibrium with respect to two immiscible media, then at a given temperature and pressure the three-component system is characterised by one degree of freedom. It follows that the concentration of the third substance in the one medium must be a function of its concentration in the second medium.

It is shown that the formation of a definite compound by combination of the third substance with one of the immiscible media and the distribution of the substance in a constant ratio may be regarded as special cases of the general law of adsorption.

H. M. D.

Theory of Adsorption. A. EUCKEN (*Ber. Deut. physikal. Ges.*, 1914, 16, 345—362).—The nature of adsorption is discussed in reference to the special case of the adsorption of a gas by a chemically indifferent solid substance. On the assumption that the adsorption is due to the formation of a highly compressed layer of gas under the influence of the molecular attractive forces, formulæ are deduced for the adsorption of (1) an ideal gas, (2) an actual gas above its critical temperature, (3) a vapour. In agreement with experiments, these formulæ indicate that at low pressures and high temperatures the quantity of gas adsorbed is proportional to the pressure of the gas. The dependence of the adsorption on the temperature observed by Homfray (A., 1910, ii, 771) and Titov (A., 1910, ii, 1041) is also shown to be in general agreement with the requirements of the author's formulæ. These also lead to values for the heat of adsorption which agree with the observed heat changes.

In consequence of the diminution of the compressibility which

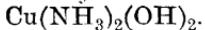
is shown by all gases as the density increases, the adsorption approximates to a maximum with increasing pressure. The surface saturation which corresponds with the attainment of this maximum can only be reached in the case of vapours if the adsorption takes place at a rough surface.

H. M. D.

Adsorption. X. Adsorption by Starch in Aqueous Ammoniacal Solutions of Cupric Hydroxide. A. V. RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 246–258. Compare *A.*, 1913, ii, 303).—The preparation of large quantities of pure cupric hydroxide is somewhat difficult. If copper sulphate solution is precipitated by sodium or potassium hydroxide, not taken in excess, the precipitate contains a considerable proportion of SO_4 , which has a marked influence on the adsorbing properties of the hydroxide. If, on the other hand, the alkali hydroxide is added in excess, and especially if it is used in dilute solution (0·5%) to wash the precipitate, the latter readily changes, even below 15° , into cupric oxide, which is but sparingly soluble in aqueous ammonia. The best method to overcome these difficulties is to precipitate and wash the hydroxide with aqueous ammonia, which dissolves only very little of the cupric hydroxide gel.

In the present experiments, potato starch alone has been used. It has been found previously (*A.*, 1913, ii, 302) that strongly dissociated alkalis are adsorbed in considerable proportions by starch, whereas the adsorption of the feebly dissociated ammonia is slight, and falls virtually to zero in presence of the strongly dissociated barium hydroxide. The base $\text{Cu}(\text{NH}_3)_n(\text{OH})_2$ is a strong alkali, and may be expected to behave similarly to barium hydroxide as regards the adsorption of ammonium hydroxide by starch. The diminution in the concentration of the ammonia accompanying adsorption of aqueous ammoniacal cupric hydroxide solution may thus be taken to correspond with that entering into the composition of the complex alkali. Consequently, if the adsorbed copper and ammonia are determined simultaneously, the value of n in the formula $\text{Cu}(\text{NH}_3)_n(\text{OH})_2$ will be obtained. A number of such determinations, made with ammonia solutions varying in concentration from 1·7 to 11·5*N*, gave values of n ranging from 1·89 to 2·07, the mean being 1·96. Under these conditions, therefore, a base of the composition $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$ is always adsorbed.

Measurements of the velocity of adsorption show that the adsorption of $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$ resembles that of barium hydroxide in so far as it is a complex process, the second stage of which proceeds very slowly, but differs from it in the diminution of the adsorption during this second stage. The cause of this complexity lies in an irreversible change of the starch resulting from the adsorption, the starch gelatinising and gradually passing into solution with formation of a product or products with adsorbing properties, which differ from those of the starch granule and are greater in the case of barium hydroxide and less with



Over their whole range the adsorption isotherms are expressed

neither by the equation $C_2 = \beta C_1^{1/p}$, nor by the equation for hydrolysis. The latter is applicable or inapplicable according as the concentration of the alkali is such that the volume of the deposited starch does not or does change considerably (by more than 100%).

T. H. P.

Physico-chemical Force of Attraction. L. GURVITSCH (*Zeitsch. physikal. Chem.*, 1914, **87**, 323—332)—Cases of irreversible adsorption have been examined, in which a chemical change or a change in the adsorbed substance is impossible. Such cases are found when the gently heated mineral floridin (a hydrated silicate of aluminium, magnesium, and calcium containing on the average 56·5% SiO_2 , 11·6% Al_2O_3 , 6·3% MgO , 3·3% CaO , and 18% H_2O) is used as the absorbent for solutions of naphthenic acids, benzoic acid, or valeric acid. It is shown that floridin adsorbs 6% of the naphthenic acids which cannot be extracted by light petroleum, but can be removed by ether. A series of adsorption experiments were made with solutions of benzoic acid in benzene, benzoic acid in light petroleum, and valeric acid in light petroleum. These solutions were all shaken with floridin. The results are calculated by means of the Freundlich formula, $y = ax^n$, and it is shown that the values found experimentally do not agree with those calculated, the difference between the calculated and experimental results increasing with increasing concentration. A formula of the type $y = A + Kx^n$, however, gives values which agree well with the experimental values. A series of partition experiments on valeric acid in the binary mixtures, benzene-sulphuric acid and light petroleum-sulphuric acid, were also carried out. It is shown that the amount of valeric acid taken up by the sulphuric acid as calculated by the Nernst partition formula does not agree with the experimental results, the divergence increasing with decreasing concentration. A good agreement between calculated and experimental quantities taken up by the sulphuric acid can be got by a formula of the type $y = A + f(x)$, in which x is the amount of dissolved acid originally present in the other solvent. As a result of these experiments, the author specifies the characteristic properties of the three forces, (a) physical attraction, (b) chemical attraction (affinity), (c) physico-chemical attraction. Physical attraction is not specific; it has an unbounded sphere of action; its action on a given mass is independent of the presence of other masses; its action is not atomic, that is, it acts as a whole from a given surface, and not along separate lines. Chemical attraction is specific; its sphere of action is limited, probably to atomic distances; its action on a given mass is conditioned by its "saturation" with other masses; its action is atomic, that is, it acts along a small number of lines and is discontinuous. Physico-chemical attraction is specific; its sphere of action limited, probably to molecular distances; its influence on a given mass is unaffected by the simultaneous presence of other masses; it is not atomic, that is, it acts as a whole, and not along separate lines. The force, therefore, which comes into action in the processes of solution and adsorption is intermediary between

the chemical and physical forces; it is more related to the chemical force, but differs quantitatively from this in its smaller intensity and wider range of action, and qualitatively in not being atomic.

J. F. S.

The Adsorption Capacity of Kaolin. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1914, **14**, 193—195).—According to Carli (A., 1913, ii, 1029), kaolin does not adsorb colloidal ferric hydroxide to any appreciable extent. The author considers that this behaviour is conditioned by the special character of the kaolin which was used in Carli's experiment. In view of the general adsorbing capacity which kaolin has been shown to exhibit, it is to be expected that colloidal ferric hydroxide would also be adsorbed, and experiments made with kaolin from Hohburg in Saxony show that this is the case. This kaolin was found to contain 95·89% kaolin, 1·06% felspar, and 3·05% quartz. On heating to redness there was a loss of 12·67%, and it is supposed that this high value of the loss on heating is connected with the presence of organic colloids (humus substances).

H. M. D.

Adsorption by Filter Paper. M. A. GORDON (*J. Physical Chem.*, 1914, **18**, 337—354).—Experiments have been made on the behaviour of the constituents of an aqueous solution when strips of filter paper are immersed in the solution (compare Bayley, T., 1878, **33**, 304). The rise of the solution in the filter paper is accompanied by changes in concentration in consequence of selective adsorption. If the solute is adsorbed relatively more quickly than the water, the outer zone will be less concentrated than the original solution, but more concentrated if the water is more rapidly adsorbed. The capillary distribution not only depends on the nature of the solute, but also on the concentration of the solution under examination. From experiments with solutions of copper and cadmium sulphate it is found that cadmium sulphate diffuses more rapidly than copper sulphate if the concentration is less than 0·1 molar. This observation is in accord with Bayley's statement (*loc. cit.*) that cadmium can be detected in presence of copper in virtue of the difference which the sulphates show in regard to capillary rise in filter paper.

The adsorption effects diminish with rise of temperature, and certain foreign substances have a similar influence. The adsorption effects observed in the case of hydrolysable salts have no quantitative connexion with the degree of hydrolysis.

H. M. D.

The Sorption Theory. A New Theory of Dyeing. G. von GEORGIEVICS (*Chem. Zeit.*, 1914, **38**, 445—446)—A restatement of the author's views on the nature of the process by which acids and dyes are removed from aqueous solution by animal fibres (compare A., 1913, ii, 561, 562).

H. M. D.

Theory of Dyeing. III. WILDER D. BANCROFT (*J. Physical Chem.*, 1914, **18**, 385—437. Compare this vol., ii, 178, 250).—Further extracts from the literature have been collected together,

more particularly with reference to the nature of mordants and mordanting. These are discussed in terms of the author's adsorption theory.

According to this theory, a mordant is a substance which is adsorbed strongly by the fibre and at the same time is capable of readily adsorbing the dye. There is no evidence that definite compounds are formed when the mordants are taken up by wool, silk, or cotton. The difference between the behaviour of wool and cotton is merely a difference in degree determined by the magnitude of the adsorption-coefficients.

The metallic mordants are in all probability hydroxides, and not basic salts, and the mordanting process is said to be influenced to a greater extent by the rate of coagulation of the hydroxide than by the degree of hydrolysis of the corresponding salt. These views are examined in some detail with reference to the mordanting action of aluminium salt solutions, the phenomena observed with aluminium hydroxide being regarded as typical of basic mordants.

H. M. D.

The Changing Over of an Adsorption Reaction into a Diffusion Reaction. M. TRAUTZ (*Verh. Ges. deut. Naturforsch. Aerzte*, 1914, **11**, 314—317).—The author shows, theoretically, how a gas reaction may be changed from an adsorption reaction into a diffusion reaction, by varying the temperature at which the reaction occurs, the volume of the gas, and the surface of the containing vessel. All the predictions of the theory have been verified by experiments on the reaction between oxygen and hydrogen iodide at temperatures between 100° and 230°.

T. S. P.

The Rate of Dissociation of Nitrogen Peroxide. W. L. ARGO (*J. Physical Chem.*, 1914, **18**, 438—450).—From measurements of the wave-length of stationary waves in nitrogen peroxide and air, it has been found that the value of $d\rho/dp$, where ρ is the density and p the pressure of the gas, is in agreement with the assumption that the dissociation equilibrium responds to the rapid changes of pressure which occur during the passage of the sound waves. This high velocity of the opposed reactions was found in the case of nitrogen peroxide which had been dried over phosphoric oxide, and of nitrogen peroxide which contained 0·32% by volume of water vapour.

The measurement of the velocity of sound in nitrogen peroxide cannot be used for determining the value of the specific heat ratio c_p/c_v .

H. M. D.

Diffusion of Some Dyes. R. O. HERZOG and A. POLOTZKY (*Zeitsch. physikal. Chem.*, 1914, **87**, 449—489).—A number of dyes in 0·25% aqueous solution have been allowed to diffuse in Öholm's apparatus (*ibid.*, 1904, **50**, 309) into pure water, and at stated intervals of time the concentration of the dye at various heights in the water layer was determined colorimetrically. Parallel with the foregoing experiments, 5% gelatin

solutions of the same dye were allowed to diffuse into 5% gelatin, and the concentration at various heights at stated intervals determined colorimetrically. A very voluminous series of tables of results is given for some twenty-six dyes, and from it the following general conclusions are drawn. The retarding influence of gelatin on the diffusion is noticeable in all cases, and in the case of rhodamine it is shown that the difference between the diffusion in 15% and 10% gelatin is much less than the difference between that in 10% and 5% gelatin. A small addition of sodium hydroxide or hydrochloric acid to solutions of Capri-blue and rhodamine is without influence on the coefficient of diffusion; traces of impurities have a marked influence on the diffusion-coefficient, as is shown by the influence of dialysis on primulin. The partition of the dye in the different layers in many cases corresponds with the Stefan formula, and in others it does not hold in the sense that the higher layers contain too much dye in relation to the lower layers. This is explained on the assumption that in those cases where the formula does not hold the dye is made up of particles of different sizes, of which the smaller diffuse more quickly. In gelatin solutions the divergence from the Stefan formula is still greater, which is to be explained by the fact that the larger particles will be relatively more retarded than the smaller, and also by the adsorption of gelatin by the particles. Biltz (*van Bemmelen-Gedenboek*, 1904, 112) has shown that in dialysis dye molecules of less than 45 atoms in the molecule dialyse quickly, those with 55—70 atoms dialyse slowly or not at all, and those with more than 70 atoms do not dialyse at all. A similar condition is found here for the diffusion into water; dyes containing up to 50 atoms in the molecule have a diffusion-coefficient which lies near, but above, 0·2, with a larger number of atoms the diffusion-coefficient is less than 0·2. If the Stefan formula does not hold, the above regularity also does not hold. In general, a parallelism exists between dialysis and diffusion. There is no regularity observed between the diffusion-coefficient in water and in gelatin, the ratio between the two values fluctuating between 2 and 10. The experiments lead the authors to the conclusion that diffusion is an additive constitutive property, in which the relationship between the solvent and the dissolved substance plays an important part. J. F. S.

Osmotic Compressibility of Emulsions Considered as Fluids with Visible Molecules. JEAN PERRIN (*Compt. rend.*, 1914, **158**, 1168—1171).—A theoretical discussion of the experimental work of Costantin (compare following abstract). By the application of van der Waals' equation to very dilute emulsions it is possible to find the molecular weight of a fluid compressed to invisible molecules, thus giving an emulsion, and also to determine Avogadro's number, the value 60×10^{22} being obtained. W. G.

Experimental Study of the Osmotic Compressibility of Emulsions. RENÉ COSTANTIN (*Compt. rend.*, 1914, **158**, 1171—1173. Compare Perrin, preceding abstract).—A study of the variations

of the osmotic pressure with concentration, by means of micro-photographs, the number of uniform grains present in horizontal strips being counted for different emulsions. The law governing the results is markedly different, at a concentration of 1%, from van't Hoff's exponential. The results indicate the existence of a term of negative internal pressure, and the curve plotted from these figures indicates that for concentrations greater than 2–4% this internal pressure diminishes in absolute value. W. G.

Changes of Volume Occurring in the Dissolution of Certain Solids. A. CAVAZZI (*Gazzetta*, 1914, **44**, i, 448–468).—The author has measured the changes in volume occurring when a number of salts and acids and sucrose are dissolved in water, and when crystalline copper sulphate is dissolved in ammonia solution, sulphur or iodine in carbon disulphide, or iodine in ether. The measurements were made at 15°, and the numerical results, which are given in full, lead to the following conclusions.

The specific gravity of substances in solution gradually diminishes as the concentration increases, and this happens also with anhydrous salts, especially when the concentrations giving diminutions in volume are surpassed, that is, when the specific gravities of the solutes assume positive values. The predominating cause of this variation of the specific gravity of solutes, particularly with substances which under ordinary conditions separate from solution in an anhydrous state, is the dissociation, but the specific gravities of sucrose in water and of sulphur in carbon disulphide are sensibly greater in dilute than in concentrated solutions.

Of all the compounds examined, ammonium chloride is the only one which has the same specific gravity in very dilute solution, as in the solid state, but here, too, diminution accompanies increasing concentration.

Substances which dissociate in water and are readily soluble and crystalline in the anhydrous form, produce, when dissolved in their concentrated solutions, increases of volume corresponding exactly or nearly so with the ordinary specific gravities; the same is the case when boric acid is added to its nearly saturated solution at 15°, but oxalic acid behaves differently.

Of all the compounds containing water of crystallisation, oxalic acid alone has a specific gravity less than the normal value in both concentrated and dilute solutions.

Selenite exhibits in solution a high specific gravity, which is otherwise found only with anhydrous salts which become hydrated in contact with water. It would appear then that, when dissolved in water at 15°, selenite forms a stable hydrate more complex than $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and less complex than that obtained by shaking an excess of powdered selenite which has been moderately heated with water at a low temperature.

That potassium fluoride, like anhydrous calcium, barium, and strontium chlorides, undergoes hydration when dissolved in water is shown by its very high specific gravity in comparison with those of potassium and sodium chlorides, and is confirmed by the deposi-

tion of anhydrous crystals at 40° and of crystals containing 2H₂O by evaporation in the cold or by addition of alcohol.

The contraction in the volume of the solvent produced by dissolution of anhydrous sodium carbonate and by magnesium, zinc and copper sulphates is undoubtedly due principally to the hydration of the salts.

T. H. P.

Influence of Neutral Salts on the Condition of Ions in Solution. I. G. POMA and A. PATRONI (*Zeitsch. physikal. Chem.*, 1914, **87**, 196—214).—The authors have determined the concentration of copper ions in solutions of copper nitrate and copper sulphate of various concentrations to which neutral salts of the same anion had been added in a series of different concentrations. In the case of copper sulphate, magnesium sulphate was added up to a concentration of 4·8*N*, and in the case of copper nitrate the nitrates of rubidium, potassium, sodium, lithium, strontium, calcium, and magnesium were added; a series of determinations was also made with a solution of copper nitrate to which alcohol in concentrations up to 72% had been added. The measurements were all made by means of *E.M.F.* determinations. From the results, the authors have calculated the factor Cu₀^{..}/Cu^{..}, in which Cu₀^{..} is the concentration of the copper ion in a solution to which no neutral salt has been added, and Cu^{..} the concentration in the same solution to which a neutral salt has been added. The results obtained with copper sulphate show that this ratio is always greater than unity, and increases with increasing concentration of the neutral salt, which points to a decreased ion concentration in the solutions to which the neutral salt has been added. In the case of copper nitrate, with the addition of rubidium and potassium nitrates, the ratio also increases in the same way, but in the cases of the addition of the other nitrates and of alcohol, the value either falls at once below unity and steadily decreases with increasing concentration of the neutral salt, or, at first (namely, with the lowest concentration of neutral salt), rises above unity and then steadily decreases until it is less than unity, this pointing to an increased ionisation, or at least an increased copper ion concentration which increases with increasing concentration of neutral salt or of alcohol. The order of the influence is seen from the values of Cu₀^{..}/Cu^{..} for a 0·008*N*-solution of copper nitrate to which 2*N*-solutions of the nitrates of other metals have been added: Rb, 1·44; K, 1·67; Na, 1·14; Li, 0·75; Sr, 0·97; Ca, 0·89; and Mg, 0·81; with 72% alcohol the value falls to 0·2. These results are explained on the hypothesis that in the solution an equilibrium Cu(H₂O)_n^{..} ⇌ Cu^{..} + nH₂O exists, and of the two ions, the non-hydrated ion alone reacts with the electrode. When a neutral salt is added, there is a competition between it and the hydrated ion for the water with which it is combined, and if the neutral salt forms hydrated salts, it will take some of this water, more the greater the avidity with which it takes up water, and consequently the equilibrium expressed above will be displaced toward the right.

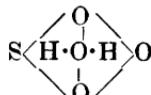
J. F. S.

Processes Operative in Solutions. XXXI. Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents. A Discussion of the Constitution of Sulphuric and other Polybasic Acids and of the Nature of Acids. HENRY E. ARMSTRONG and F. P. WORLEY (*Proc. Roy. Soc.*, 1914, [A], 90, 73—100. Compare A., 1913, i, 1116). —A comparative study has been made of a number of sulphonic acids when used as catalysts in the hydrolysis of sucrose at 25°. In most cases, the molar ratio of sucrose to acid was kept constant (0·25 : 1), whilst the ratio of acid to water was varied.

The relative values obtained for the velocity-coefficient from experiments on solutions containing the acid and water in the molar ratio 1 : 100 are as follows: sulphuric, 256; benzene-sulphonic, 220; *p*-toluenesulphonic, 217·4; mesitylenesulphonic, 203; *p*-chlorobenzenesulphonic, 216; *p*-bromobenzenesulphonic, 208; *p*-iodobenzenesulphonic, 214; α -bromocamphor- β -sulphonic, 201·3; *p*-dichlorobenzenesulphonic, 209; *p*-dibromobenzene-sulphonic, 212; *p*-di-iodobenzenesulphonic, 223; benzene-*o*-disulphonic, 452; benzene-*p*-disulphonic, 522; benzene-*m*-disulphonic, 533; benzene-1 : 3 : 5-trisulphonic, 982; toluene-2 : 4 : 6-trisulphonic, 950.

These numbers show that the substitution of hydrogen in benzene-sulphonic acid by halogens or by methyl groups has very little influence on the hydrolytic activity of the acid. The disulphonic acids show very markedly the influence of the relative position of the sulphonic groups, in that the ortho-acid is very much weaker than the other two isomerides, whilst the para-acid is somewhat less active than the meta-acid. The molecular hydrolytic activity of benzene-*m*-disulphonic acid is much more than twice, and that of benzene-1 : 3 : 5-trisulphonic acid much more than three times, as great as the activity of benzenesulphonic acid. If, however, the three acids are compared when the concentrations are equivalent instead of equimolecular, it is found that the activities are equal. In other words, the SO_3H group has the same value in each of the three acids when the amount of water present is proportional to the number of the sulphonic groups.

The properties of sulphuric acid, and in particular its activity as a hydrolyst, are considered to afford evidence that sulphuric acid is a strong monobasic acid, for which the formula



is suggested. On the assumption that the valency volume of sulphur, like that of oxygen, is twice that of hydrogen, a model has been constructed which shows the spacial relations between the atoms in the molecule.

Similar considerations are applicable to other inorganic acids, such as carbonic, silicic, phosphoric, and arsenic acids. In all cases these are to be regarded as compounds of the anhydrides with hydrone rather than as hydroxyl derivatives, and, like sulphuric, they are all essentially monobasic.

In discussing the nature of acidity, it is maintained that this property is a function of the acid molecule as a whole, and that this reacts with water, giving rise to two compounds, $\text{H}_2\text{X} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ and $\text{H}_2\text{O} < \begin{smallmatrix} \text{H} \\ \text{X} \end{smallmatrix}$. The proportions in which these are present will depend on the concentration of the solution. The lack of agreement between the results obtained by the hydrolytic and electrolytic methods of comparing acids may possibly be explained from this point of view.

H. M. D.

Processes Operative in Solutions. XXXII. The Influence of Sulphonates on the Hydrolytic Activity of Sulphonic Acids. A Contribution to the Discussion on the Influence of Neutral Salts. HENRY E. ARMSTRONG and F. P. WORLEY (*Proc. Roy. Soc.*, 1914, [4], 90, 101—111).—The influence of potassium, calcium, strontium, barium, zinc, and cadmium *p*-toluenesulphonates on the activity of *p*-toluenesulphonic acid has been examined by experiments on the rate of inversion of sucrose at 25°. The effects produced by equivalent amounts of the various salts are not very different, the velocity-coefficients varying from 235 for a solution containing the barium salt to 245 for the zinc salt, the corresponding number obtained with the acid alone being 217×10^{-5} .

From experiments in which the ratio of sucrose to water was kept constant, whilst the concentration of the acid was varied, it has been found that the relative effect of the addition of a gram molecule of the potassium salt increases as the proportion of acid in the solution decreases.

The data are applied in the calculation of “apparent hydration values.” For solutions which contain the acid, sucrose and water in the molar ratio 1:0.5:100, together with one equivalent of salt, these values vary from 7.5 for the potassium salt to 10 for the zinc and cadmium salts.

The later part of the paper is devoted to a discussion of the association hypothesis, with special reference to the recently expressed view that chemical activity is conjointly determined by the action of ions and undissociated molecules.

H. M. D.

Ideal Concentrated Solutions. J. N. BRÖNSTED (*Zeitsch. Elektrochem.*, 1914, 20, 278—279).—Polemical. An answer to Nernst's criticism (this vol., ii, 251) on the author's treatment of concentrated solutions (this vol., ii, 251).

J. F. S.

Is the Continuous Passage from the Liquid Condition to the Crystalline Possible and Can Critical Points Appear? LÉON SCHAMES (*Zeitsch. physikal. Chem.*, 1914, 87, 369—378).—A theoretical paper in which the titular questions are discussed; it is shown that, contrary to the Tammann closed curve, one with two critical points is possible. These points lie, however, at $p=0$, $T=0$, and $p=\sigma$, $T=T_k$, so that in reality a continuous change from the crystalline to the liquid condition is not possible. The

condition surface obtained on these conditions for normal and abnormal liquids is discussed, and it is shown from the measurements of Bridgman (A., 1913, ii, 39) that the second critical temperature for water is probably identical with the usual critical temperature (liquid-vapour). Since water is to be regarded as a normal liquid at such high pressures, this conclusion is to be made also in the case of other normal liquids. In the abnormal region of water, at the absolute zero of pressure and temperature, the identity of liquid water and ice I is regarded as certain, and the identity of liquid water and the other varieties of ice as very probable.

J. F. S.

Application of E. S. Fedorov's Crystallo-chemical Method in Scientific Investigations. B. ORELKIN and G. PIGULEVSKI (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 227—234).—The authors emphasise the value of crystallographic measurements in the identification of compounds, and, consequently, in following chemical changes. Several examples are given.

T. H. P.

The Mobility of the Molecules in a Solid Crystal. FRED WALLERANT (*Compt. rend.*, 1914, **158**, 1143).—As a result of experiments on fused, crystalline potassium nitrate, the author has been led to modify his views on the polymorphism of camphor, and he now considers it to be trimorphic, and not quadrimorphic (compare this vol., i, 420).

A crystal of potassium nitrate is fused and allowed to crystallise between two glass plates, and is then heated to a temperature well below its melting point. On applying pressure at one point of the top plate, one or more new crystals appear at the point of compression, and grow at the expense of the original crystal. There is, however, no relation of orientation between the new and the original crystals.

W. G.

Microscopical Metallography in Three Dimensions. A. PORTEVIN (*Intern. Zeitsch. Metallographie*, 1914, **6**, 58—71. Compare Oknov, A., 1911, ii, 495, 986).—A device is described for holding specimens in such a way that successive layers may be removed by grinding, and the same area brought repeatedly into the field of the microscope. In this way, the form of a crystal may be reconstructed from successive serial sections. The method is applied to crystals of the compounds SbSn and CuSn.

C. H. D.

Morphological Studies of Benzene Derivatives. V. The Correlation of Crystalline Form with Molecular Structure. A Verification of the Barlow-Pope Conception of "Valency-Volume." HENRY E. ARMSTRONG, R. T. COLGATE, and E. H. RODD (*Proc. Roy. Soc.*, 1914, [A], **90**, 111—173. Compare T., 1910, 1578; A., 1912, i, 756).—From an examination of the crystalline form of a large number of compounds of the type $C_6H_5R_1R_2SO_2X$, in which R_1 , R_2 , and X represent either chlorine or bromine, evidence has been obtained which is said to furnish a conclusive proof of the

validity of the postulates on which the Barlow-Pope method of correlating crystalline form with internal molecular structure is based, and also of the general accuracy of the conclusions to which the application of this method leads.

For thirty-one compounds of the above type, including fourteen examples of disubstituted sulphonyl chlorides and bromides of the para-series, six of the meta- and eight of the ortho-series, together with three monosubstituted derivatives, the mean values of the equivalence parameters are $x:y:z = 3.904: 3.360: 2.772$, the extremes being $3.806: 3.222: 2.680$ and $4.040: 3.419: 2.865$. For benzene itself, the equivalence parameters assigned by Barlow and Pope are $3.101: 3.480: 2.780$. It is to be noted that the y and z parameters are practically the same for the thirty-one compounds investigated as for benzene. The difference in the x parameter corresponds with the change brought about by the introduction of the SO_2X group. This difference ($3.904 - 3.101 = 0.803$) is practically equal to that deduced from the molecular models, constructed on the assumption that the valency volume of sulphur and oxygen is twice that of hydrogen, whilst that of the halogens is equal to the volume of hydrogen.

From a consideration of compounds in which complex radicles of equal valency volume, such as SO_2Cl , NO_2 , CH_3 , and CH_2Br , are present, it is found that these have practically the same influence on the crystalline structure. The small differences are no doubt connected with the fact that groups containing two large atoms cannot be "packed" quite in the same way as those which contain a larger number of smaller atoms.

From the same point of view, the authors have compared the crystalline forms of benzenesulphanilide and its derivatives, of acetanilide and a number of allied compounds, and find that in these cases, also, the crystalline form can be correlated with the molecular structure on the basis of the Barlow-Pope theory.

A number of benzene derivatives which have been examined cannot, however, as yet be interpreted in accordance with the authors' method. Such are compounds of the type



which crystallise in anorthic, pseudotetragonal, or pseudocubic forms.

The paper concludes with a detailed record of the crystallographic measurements made for each of the substances investigated.

H. M. D.

Atomic Theory. III. The Preparation of Colloidal Solutions by [Electric] Disintegration. D. ZAVRIEV (*Zeitsch. physikal. Chem.*, 1914, **87**, 507—510. Compare this vol., ii, 451).—The Bredig method for the preparation of colloidal solutions of metals can only be applied to the noble metals. The present paper deals with a modification of Svedberg's method for the production of colloidal solutions of metals other than the noble metals. Two electrodes made of the metal to be disintegrated are placed 1/10 mm. apart in a vessel of water, and a current is passed from

an induction coil, fed by 15—20 amperes at 120 volts, and having a spark 20 cm. long, and bound with a large condenser. In this way it is possible to obtain colloidal solutions of practically all the metals. An iron solution prepared in this way could be kept for a month, magnesium for two days, copper and aluminium for somewhat less than a month. Cobalt, zinc, and nickel could only be got to give poor solutions by this arrangement, but by replacing the coil by a large Holtz influence machine, they could readily be disintegrated when a spark-gap was connected in parallel with the metal electrodes.

J. F. S.

Fluctuations of Concentration in a Colloidal Emulsion.
RENÉ COSTANTIN (*Compt. rend.*, 1914, **158**, 1341—1343).—A mathematical paper in which the author shows that his results on the compressibility of a colloidal emulsion (compare this vol., ii, 438) verify Smoluchowski's theory on the fluctuations in density produced by molecular agitation (compare *Bull. Acad. Sci. Cracow*, 1907, December).

W. G.

Significance of Ionic Volume for the Action of Electrolytes on Colloidal Systems. **G. R. MINES** (*Kolloid-Zeitsch.*, 1914, **14**, 167—168).—The observed differences in the activity of simple and complex cations towards colloidal substances are attributed partly to differences in ionic volume which give rise to variations in the surface density of the electric charge; and partly to variations in the specific inductivity capacity of the colloidal particles.

The volumes of the La^{+++} and $\text{Co}(\text{NH}_3)_6^{+++}$ ions are approximately in the ratio 1: 13, and in view of this difference in ionic size, it is not surprising to find that these ions exhibit considerable differences in their behaviour towards colloidal substances. In equivalent solutions, it is to be expected that the complex ion will exert an influence on a much larger number of colloidal particles, and if the ion serves as nucleus in the coagulation of the colloid, it may be anticipated that the complex will tend to form larger molecular aggregates.

H. M. D.

Measurement of the Tyndall Effect in Colloidal Solutions. **WERNER MECKLENBURG** (*Kolloid-Zeitsch.*, 1914, **14**, 172—181).—A photometric apparatus is described which has been designed for the production and measurement of the intensity of the Tyndall effect in colloidal solutions. The intensity of the light emitted from the Tyndall beam in a direction perpendicular to the beam itself is compared with the intensity of the incident light by reflecting a portion of this and reducing its intensity by an arrangement of Nicol prisms until it becomes equal to that of the light emitted by the Tyndall beam. The intensity of the Tyndall beam diminishes as the length of its path in the colloidal solution increases, but by taking a series of observations at different points in the path of the beam, it is possible to obtain the intensity of the light emitted by the Tyndall beam at the point at which the light enters the solution. The graphically extrapolated intensity

is found to be characteristic of a given solution, and for one and the same substance is proportional to the number of colloidal particles in unit volume.

The Tyndallmeter, as the instrument is called, may be used in the comparison of different solutions of the same colloidal substance, in the investigation of the processes which occur during coagulation, and in the examination of polluted waters. H. M. D.

New Determination of the Avogadro Constant from the Brownian Movement of Small Mercury Particles Suspended in Water. IVAR NORDLUND (*Zeitsch. physikal. Chem.*, 1914, **87**, 40—62).—The Avogadro constant has been determined from the Brownian movement of submicroscopic mercury particles. The particles were produced by electric disintegration, and the movement, as well as the rate of fall through the liquid medium, were determined photographically at intervals of one-sixtieth of a second, which were automatically made. The temperature of the experiments was carefully regulated, and did not vary more than $3/100^{\circ}$ in any series of measurements. The measurements were made in narrow quartz glass cells, and the retarding influence of the walls on the Brownian movement and on the velocity of deposition of the particles was compensated by multiplying the viscosity η of the dispersion medium by the factor $1/n$, where

$$n = 1 - \{9P(16A + 9P)/16(A - 2P)(8A + 9P)\} \cdot \log_e(16A - 7P)/25P,$$

P being the radius of the particles and A the distance apart of the walls of the cell. The value $N = 5.91 \times 10^{23}$ is obtained as a mean of twelve determinations which lie between 4.57×10^{23} and 7.00×10^{23} , the most generally accepted value for N being 6.06×10^{23} (Millikan). The law $(\text{displacement})^2 = \text{time} \times \text{constant}$ is confirmed in many cases.

J. F. S.

The Vertical Partition of Particles in the Brownian Movement. B. ILJIN (*Zeitsch. physikal. Chem.*, 1914, **87**, 366—368).—The partition of particles in emulsions of gamboge in water and gum arabic in castor oil and water, with respect to their vertical concentration, has been investigated. It is shown that the partition of the particles with the height follows the theoretical law of Perrin within the experimental error (Perrin, A., 1910, ii, 493).

J. F. S.

The Mechanism of the Chemical Reaction. GEORGES BAUME (*Compt. rend.*, 1914, **158**, 1177—1179).—A theoretical paper in which the author further develops the theory of "quanta" already put forward by him (compare A., 1913, ii, 1038). W. G.

Reaction Velocity and Activation. M. TRAUTZ (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), **11**, 310—314).—A theoretical paper, in which the author shows that there is a general relation between the absolute value of the chemical reaction velocity and the temperature quotient.

T. S. P.

Retardation of the Decomposition of Hydrogen Peroxide in Presence of Colloidal Platinum by Indifferent Narcotics. OTTO MEYERHOF (*Pflüger's Archiv*, 1914, **157**, 307—325).—Compare this vol., ii, 450).—Experiments have been made to determine the influence of various narcotics (alcohols, ketones, urethanes) on the rate of decomposition of hydrogen peroxide in presence of colloidal platinum. In general, the results show that the activity of members of homologous series increases with the molecular weight, and it would seem, therefore, that the retardation effects are similar to those which have been observed in the inversion of sucrose by invertase, and also in connexion with respiration. The most clearly marked influence of homology on the retardation is found in the case of the aliphatic alcohols.

According to ultramicroscopic observations, the retarding influence of narcotics is not determined by a reduction in the number of the colloidal particles of the catalyst. There was also no evidence that the colloidal solution became less stable after the addition of the narcotic.

H. M. D.

Action of Light on Chlorine Water. ALFRED BENRATH and HERBERT TUCHEL (*Zeitsch. wiss. Photochem.*, 1914, **13**, 383—398).—The rate at which chlorine water is decomposed under the influence of light has been investigated in a series of experiments, in which the effect of the addition of hydrochloric acid and of various metallic chlorides was also examined. The source of light was a quartz mercury lamp, and during the period of insolation the solution was subjected to a continuous rotary movement in order to eliminate disturbances from any inequalities in the concentration which might be set up in consequence of the greater amount of decomposition in the outer layers of the solution. The progress of the reaction was followed by measurement of the electrical conductivity by means of two electrodes inserted in the insolation tube.

On the assumption that the change in conductivity is proportional to the change in the concentration of the chlorine, it is found that the data agree with the unimolecular formula $k = 1/t \cdot \log a/(a-x)$. In the case of pure chlorine water, the whole of the chlorine disappears in the photochemical change, but in solutions which contain hydrochloric acid or metallic chlorides, the reaction comes to an end before the whole of the chlorine has been decomposed. When the reaction is incomplete, the value of a is given by the concentration of the decomposable chlorine, and not by the total chlorine in the original solution.

If the concentration of the added hydrochloric acid is greater than about $0.5N$, no decomposition is observed on exposure to light. In the less concentrated acid solutions, the observed rate of decomposition indicates that k is practically unaffected by the acid present. On the other hand, the coefficient has a higher value in presence of certain chlorides. According to the data for $1N$ -solutions, sodium, potassium, and calcium chloride have a greater influence on the reaction velocity than the chlorides of barium,

magnesium, and strontium. The greater the influence of a salt on the proportion of chlorine which remains undecomposed, the less is its influence on the reaction velocity. This is clearly shown by the data for the alkaline earth metal chlorides.

From experiments at 5° and 30°, it is found that the reaction velocity increases in the ratio 1:1·395 for a rise of 10°.

H. M. D.

The Temperature-coefficient of Chemical Reactions. A. SKRABAL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913 (1914), ii, 306—309).—Mainly a theoretical paper, in which the author shows that it is possible to have reactions for which the temperature quotients are very large. Such reactions generally proceed with extremely small velocity, which is usually incapable of measurement.

The author has succeeded in carrying out measurements on the reaction $3\text{I}_2 + 6\text{OH}' = 3\text{H}_2\text{O} + 5\text{I}' + \text{IO}_3'$, and shows that the results are in accordance with his theory.

The relations holding between the temperature and the temperature quotient are also discussed.

T. S. P.

Dynamics of the Time Reaction between Aqueous Carbonic Acid and Bases. A. THIEL and R. STROHECKER (*Ber.*, 1914, **47**, 1061—1068).—In a previous communication (A., 1913, ii, 396) it has been shown that the slow neutralisation of an aqueous solution of carbonic acid by bases is probably dependent on the reaction represented by the equation $\text{CO}_2 + \text{OH}' \rightarrow \text{HCO}_3'$, and is not conditioned by the rate of hydration of carbon dioxide to carbonic acid. The reaction should therefore be bimolecular.

The authors have succeeded in measuring the velocity of reaction, using a colorimetric method with α -naphtholphthalein as indicator, and find that it is really proportional to the concentrations of the free carbon dioxide and of the hydroxide ion, but also inversely proportional to the concentration of the hydrogen carbonate ion, the proportionality factor being 0·38 at 4°.

The bases used in the investigation were sodium hydroxide, potassium hydroxide, and tetraethylammonium hydroxide.

T. S. P.

Kinetics of the Change of Halogen-alkylamines into Heterocyclic Compounds. III. The Change β -Bromoethylamine into Dimethyleneimine Hydrobromide. H. FREUNDLICH and W. NEUMANN (*Zeitsch. physikal. Chem.*, 1914, **87**, 69—86. Compare also Freundlich and Krestovnikov, A., 1911, ii, 266, and Freundlich and Richards, A., 1912, ii, 633).—The transformation of β -bromoethylamine into dimethyleneimine hydrobromide has been carried out in the presence of sodium hydroxide solution, and the velocity of the reaction determined. It is shown that the reaction is unimolecular, and that the temperature-coefficient is 4·9 for 10° over the range 0—10°. Measurements were made at 0°, 15·65°,

and 26°. The reverse reaction was carried out in hydrogen bromide solution at 25°. This reaction is bimolecular, but is complicated by the formation of piperazine to a small extent, consequently the reaction constant is somewhat uncertain. The temperature-coefficient of this reaction is less than that of the preceding reaction. The equilibrium between dimethyleneimine hydrobromide and β -bromoethylamine was determined from both sides, but the value of k obtained (3·95) does not agree with that calculated from the two velocity constants (0·1). J. F. S.

The Equilibrium and the Velocity of Transformation of Fumaric and Maleic Acids under the Influence of the Light from a Quartz Mercury Lamp. ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1914, **87**, 333—356. Compare Ciamician and Silber, A., 1904, i, 161; Stoermer, A., 1911, i, 295).—It has previously been shown that fumaric acid is converted into maleic acid by ultraviolet light (*loc. cit.*). The present investigation has as its object the determination of the equilibrium which exists between the two acids and the velocity of transformation in either direction. The transformation was carried out in aqueous solutions of the acids of 0·084*N*; these were subjected to the action of the light from a quartz mercury lamp in vessels of glass and of quartz. Other experiments were carried out with the solid acids. The method of analysis of the acids depended on the measurement of the molecular conductivity, and by means of empirical extrapolation formulæ the content of the solution on both acids could be calculated. In the solid condition fumaric acid is not converted into maleic acid by ultraviolet light, whilst maleic acid is converted into fumaric acid only to the very slightest extent. In aqueous solution equally, whether the solution was contained in glass or in quartz vessels, an equilibrium between the two acids could be reached from either side. The equilibrium was displaced somewhat toward the maleic acid side with increasing concentration; thus at 45—50° with 1/10*N*-solution the equilibrium mixture contained 75% of maleic acid and in 2/5*N*-solution 79% of maleic acid. The velocity of transformation was much greater in quartz vessels than in glass vessels, whilst the position of the equilibrium is uninfluenced; warming of the material before subjecting it to the light has no influence on the velocity of transformation. It is shown in an empirical manner that, under the present experimental conditions, between the concentrations 0·02*N* to 0·08*N* the velocity of transformation of fumaric acid into maleic acid increases as the 2/5 power of the concentration of the fumaric acid, and the opposite reaction as the 7/20 power of the maleic acid. An empirical formula is given, which allows the velocity to be expressed as a function of the excess of one of the acids above that required for equilibrium. It is shown that the decomposition of maleic and fumaric acids with the loss of carbon dioxide, as shown by Berthelot and Gaudechon (A., 1911, ii, 170), does not take place under the present conditions to a measurable amount in forty-eight hours.

J. F. S.

Retardation of Ferment Reactions by Indifferent Narcotic Substances. OTTO MEYERHOF (*Pflüger's Archiv*, 1914, **157**, 251—306).—The retarding influence of indifferent narcotics on the rate of inversion of sucrose by invertase has been examined, with the result that the members of homologous series are found to arrange themselves in the same order as that which has been previously observed in the retardation of respiration and alcoholic fermentation. In the homologous series of the aliphatic alcohols, ketones and urethanes, the retarding influence increases with increasing molecular weight.

In respect of the action of invertase, it has been found that the retardation effect increases with decreasing sucrose concentration for most of the substances investigated. Purification of the invertase or addition of egg albumin has no appreciable influence on the retardation. If the invertase is adsorbed by colloidal ferric hydroxide and the precipitate distributed through the sucrose solution, inversion takes place at the same rate as if the invertase were added to the solution in the ordinary way. In general, the retardation effects observed with adsorbed invertase are the same as those found for the unadsorbed ferment.

Other experiments indicate that the degree of dispersity of egg-albumin solutions is not appreciably affected by the addition of narcotics.

From observations on the retardation of respiration in sea urchin's eggs, and of the rate at which oxygen is absorbed by mechanically disintegrated eggs, it has been found that higher concentrations of the various narcotics are required to produce a given retardation in the second process. Since acetone egg powder is affected to a still smaller extent, it would seem that the narcotic influence is largely determined by the vitality of the cells.

H. M. D.

Forces between Atoms and Chemical Affinity. SIR J. J. THOMSON (*Phil. Mag.*, 1914, [vi], **27**, 757—789).—On the assumption that the forces exerted by an atom are the same as those which may be brought into play if each atom contains an electrical doublet, the moment of which is characteristic of the atom, the author shows that chemical compounds may be divided into two classes. In the one class, the component atoms are electrically neutral, whilst in the other they are either positively or negatively charged. The properties are strikingly different according to whether a compound forms a member of the one or of the other class. This difference is to be expected in view of the circumstance that the poles of the doublets are more widely separated in the case of compounds of the second class.

The above views are applied to the consideration of the chemical effects which are produced by the electric fields, of the number of molecules which may enter into combination, and of the conditions which determine the existence of a chemical compound and give rise to the effect of valency.

H. M. D.

The Atomic Theory. I. The Partition of the Particles in a Kinetic Field. RICHARD LORENZ and W. EITEL (*Zeitsch. physikal. Chem.*, 1914, **87**, 293—304. Compare Smoluchowski, *Boltzmann Festschrift*, 1904, 626).—A mathematical paper in which the formula of Smoluchowski, giving the probability of a given volume v in a large volume V containing n molecules out of N contained in the whole volume, is developed, without the use of simplifying assumptions.

J. F. S.

The Atomic Theory. II. The General Formulae for the Partition of Particles in a Kinetic Field. RICHARD LORENZ and W. EITEL (*Zeitsch. physikal. Chem.*, 1914, **87**, 434—440. Compare preceding abstract).—The formulae for the partition of particles deduced by the authors (*loc. cit.*) and Smoluchowski (*Boltzmann Festschrift*, 1904, 626) have been applied by Svedberg (A., 1910, ii, 772) to observations in the kinetic field of colloidal systems, and found not to be applicable. He uses, therefore, modified formulae, which the authors deduce mathematically in the present paper.

J. F. S.

Electron Conception of Valence. STUART J. BATES (*J. Amer. Chem. Soc.*, 1914, **36**, 789—793).—A series of objections is raised to the electron theory of valence. The author acknowledges that the theory has been of value for the classification and relation of compounds and of reactions (compare Nelson, Beans, and Falk, this vol., ii, 44), but points out that the actual movement of the electron is not necessarily involved in the conclusions drawn, and suggests that some other assumption might lead to a similar classification.

E. G.

Flask with Ground-in Distilling Arrangement (Still-head). GEORG WEMPE (*Zeitsch. angew. Chem.*, 1914, **27**, 240).—Ground into the neck of a conical flask is a still-head, which consists essentially of a bulb, from the top of which passes a tube bent in such a way that it can be fitted into a condenser. It can be used for separating a solvent and solute in organic work, the solute remaining in the flask without being contaminated, as it would be if a cork or bung were used to fit in the still-head.

T. S. P.

The Relation of Pulsation to Filtration. ROBERT A. GESELL (*Amer. J. Physiol.*, 1914, **34**, 186—202).—Solutions were filtered through various membranes under constant and pulsatile pressure. Pulsation favours filtration, and so also does stirring. The composition of the filtrate is not influenced, except when colloids (globulins) are used; more globulin passed the membrane during periods of constant than during periods of pulsatile pressure.

W. D. H.

A Durable Gas Generator. U. KREUSLER (*Zeitsch. anal. Chem.*, 1914, **53**, 234—241).—A somewhat complicated form of gas generator is described, which has been found to give satisfactory results

in the generation of hydrogen sulphide, hydrogen, and carbon dioxide for general laboratory work. The acid is admitted to the vessel in which the gas is generated through an adjustable conical glass valve, and the regulation of the gas pressure as well as the removal of the waste liquor is effected by means of a Liebig condenser, the inner tube of which terminates within the outer tube. The side-tube at the lower end of this outer tube is connected laterally with a flask which communicates with the lower end of the gas generating cylinder.

H. M. D.