

General and Physical Chemistry.

The Emissivity of Metals and Oxides. I. Nickel Oxide (NiO) in the Range 600° to 1300°. G. K. BURGESS and P. D. FOOTER (*Physikal. Zeitsch.*, 1914, 15, 721—723).—The emissive capacity of nickel oxide for monochromatic red light of wave-length $\lambda = 0.65 \mu$ has been found to decrease with rise of temperature between 700° and 1300°. From data obtained at 938°, 1058°, 1159°, and 1255°, it increases with increasing wave-length between $\lambda = 0.5$ and $\lambda = 0.7 \mu$. The curves showing the relationship between the emissive capacity and the wave-length indicate the existence of a broad absorption band in the ultra-red region.

The total emission of the oxide was also measured by means of a radiation pyrometer. Between 700° and 1200° the total emission increases approximately as a linear function of the temperature, but between 1200° and 1300° the rate of increase is appreciably smaller. H. M. D.

Optical Properties of Yttrium Platinocyanide. S. BOGUSŁAWSKI (*Ann. Physik*, 1914, [iv], 44, 1077—1105).—The interference phenomena exhibited by sections of crystals of yttrium platinocyanide are described and explained. Measurements have also been made of the optical constants. H. M. D.

The Spectrum of Elementary Silicon. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1914, [A], 90, 512—520).—Measurements have been made of the wave-lengths of lines in the spark spectrum of silicon between $\lambda 2124$ and $\lambda 6371$. In the final observations, silicon electrodes were available which contained as much as 99.56, 99.86, and 99.98% of silicon, the impurities present being titanium, iron, and aluminium. These electrodes were used in correcting the lines given by less pure samples of silicon which were employed in the earlier experiments. It is pointed out that the use of silicon electrodes is rendered difficult by the rapid formation of a coating of oxide, which causes the spark to become much less luminous. This difficulty was overcome by frequently removing the electrodes and grinding the surfaces with an emery wheel.

The wave-length numbers are compared with and discussed in reference to the data obtained by previous observers. H. M. D.

Ultra-red Spectra. II. A Direct Measurement of the Magnitude of Energy Quanta. NIELS BJERRUM (*Ber. Dcut. physikal. Ges.*, 1914, 16, 640—642. Compare A., 1912, ii, 1114).—By application of the theory of quanta, it is shown that the frequency of molecular rotation can be obtained from the formula $\nu = n \cdot h / 2\pi^2 J$, in which J is the moment of inertia, n an integer, and h is the fundamental quantum of energy. The rotation frequencies calculated from this formula are in satisfactory agree-

ment with the values found by von Bahr (A., 1913, ii, 810) in experiments on the ultra-red absorption of hydrogen chloride. From this it follows that the energy of rotation of the hydrogen chloride molecules is represented by $nh\nu$, and that the same unit is involved in the changes of both rotational and vibrational energy.

H. M. D.

Spectrum Analysis by the Secondary Rays from Rontgen Rays and its Application to the Case of Rare Substances. MAURICE DE BROGLIE (*Compt. rend.*, 1914, 159, 304—305).—Using the method already described (compare this vol., ii, 598), the author has determined the number N , as calculated by Moseley's formula, indicating the position of the element in the periodic table, in the case of gallium and germanium, tin and antimony, and lanthanum, using rays belonging to series K . The values obtained correspond well with the positions generally assigned to these elements.

W. G.

The Ultraviolet Spectrum of Aqueous Solutions of Nitric Acid, Metallic Nitrates, and in Particular of Copper Nitrate. G. MASSOL and A. FAUCON (*Compt. rend.*, 1914, 159, 174—175. Compare Hartley, T., 1902, 81, 556; 1903, 83, 221).—Contrary to the results obtained by Hartley (*loc. cit.*), the authors find that copper nitrate falls into line with other metallic nitrates in giving the absorption band of nitric acid, provided that a sufficient thickness of solution is used. The band is, however, less sharply defined, an aqueous solution of copper nitrate being more transparent to the rays between λ 3150 and 2800 than solutions of the other nitrates.

W. G.

The Constant Presence of Rare Earths in the Scheelites, Revealed by Cathodic Phosphorescence. CH. DE ROHREN (*Compt. rend.*, 1914, 159, 318—320).—The author has examined a number of specimens of scheelite (calcium tungstate) under the conditions given by Urbain and Scal for fluorides (compare A., 1907, ii, 30), and has found bright and dark rays in the spectra of cathodic phosphorescence similar to those attributed by them to the rare earths. All the specimens of scheelite examined contained the rare earths, the relative proportions of these elements varying considerably from one specimen to another. All the rare elements to which this method is applicable were found in one specimen or another, and all the spectral phenomena observed could be explained by the known rare elements.

W. G.

Ultraviolet Spectrum of Neoytterbium. J. BLUMENFELD and G. URBAIN (*Compt. rend.*, 1914, 159, 401—405).—The authors have mapped the arc spectra of the two extreme fractions of the series of eight giving neoytterbium by the method previously described (compare this vol., ii, 731). These two spectra are identical save for a few rays in the one fraction, due to thulium, and a few in the other due to lutecium. There are five hundred rays between

the limits λ 2300 and 3500, and these are given in a list, with their intensity appended to them. W. G.

The Absorption of Ultraviolet Rays by the Chloro-derivatives of Methane. G. MASSOL and A. FAUCON (*Compt. rend.*, 1914, **159**, 314—316. Compare Hartley, T., 1881, **39**, 153; Liveing and Dewar, A., 1883, 837; Martens, A., 1902, ii, 117).—The authors have examined three specimens of carbon tetrachloride having respectively b. p. $76.2^\circ/762.4$ mm., $76^\circ/758$ mm., $76.7^\circ/760$ mm. Of these, the first two specimens gave broad absorption bands in the ultraviolet, whilst the third showed no absorption band. Specimen 2 was then submitted to fractional distillation, and a number of fractions were obtained boiling from 61.4° to 76.3° , all of which showed an absorption band. A final fraction was obtained, b. p. $76.4^\circ/758$ mm., which gave no absorption band, and was shown to be pure carbon tetrachloride. The others contained carbon disulphide as an impurity, and this produced the absorption band.

Neither chloroform nor dichloromethane gave absorption bands in the ultra-violet. All three chloro-derivatives are colourless, and transparent to the visible and ultraviolet rays, only absorbing the rays of very short wave-length. The transparency for the latter rays diminishes as the number of chlorine atoms in the molecule increases. W. G.

The Fluorescence Excited in Gases by Ultra-Schumann Waves. W. STEUBING (*Physikal. Zeitsch.*, 1914, **15**, 742—744).—In a previous paper (this vol., ii, 401), Wood and Hemsalech have put forward the view that ultra-Schumann waves are emitted by the spark discharge, and that these give rise to the fluorescence of the gases in the surrounding atmosphere. The author criticises this view, and maintains that no satisfactory proof has yet been given (1) that the fluorescence spectrum is different from that of the exciting spark discharge; (2) that scattering of the light emitted by the spark discharge is eliminated by the experimental arrangement adopted by Wood and Hemsalech; and (3) that ultra-Schumann waves are actually emitted by the spark. H. M. D.

Theories of Rotational Optical Activity. G. BRUHAT (*Phil. Mag.*, 1914, [vi], **28**, 302—304).—A theoretical note in which the theories put forward by Drude and Lorentz on the optical rotatory power are discussed (compare also Livens, A., 1913, ii, 543). It is shown that the two theories hold equally from the point of view of the observable phenomena of anomalous rotatory dispersion and circular dichroism, and their comparison can only be made on the results expected for the dependence of the rotation on the concentration and on the nature of the solvent. Drude's theory points out that the rotatory power is independent of these two factors, whilst Lorentz's theory makes it depend on the mean index of refraction of the active medium according to the relationship $[\omega] = k(\epsilon^2 - 1)[\alpha(\epsilon^2 - 1) + 1]$. This theory does not therefore provide for cases like that of sucrose, in which $[\omega]$ remains constant

at $1/200$, whilst the factor $(\epsilon^2 - 1)(\epsilon^2 + 2)$ varies about $1/3$. The author also cites other reasons why the Drude theory is to be preferred before that of Lorentz.

J. F. S.

Thermodynamics of Photochemical Equilibrium. A. SCHIDLÖF (*Arch. Sci. phys. nat.*, 1914, [iv], **38**, 31—35. Compare this vol., ii, 601).—A continuation of the theoretical paper previously published (*loc. cit.*). It is shown that a photochemical equilibrium is only dependent on the factor ν/T , in which ν is the frequency of the light and T the temperature of the reaction. A number of corrections in the equations previously published are given.

J. F. S.

The Photochemical Properties of Coloured Resinates. J. LARGUIER DES BANCELS (*Compt. rend.*, 1914, **159**, 316—317. Compare A., 1912, ii, 882).—Coloured resinates when exposed to light slowly lose their solubility in benzene. This process is accelerated by the presence of small quantities of mineral salts. Of the chlorides and nitrates of a large number of metals tried, only those of uranium, zinc, and cadmium exert any marked influence, the effect produced being, within certain limits, proportional to the amount of active salt present. The action of uranium is much more powerful than that of zinc or cadmium, which are of the same order. To produce the same effect in the same time, the concentration of zinc or cadmium nitrates requires to be twenty times that of uranium nitrate. The results obtained with uranium and zinc salts are not due to their hydrolysis in aqueous or alcoholic solution giving an acid solution. Certain salts, such as those of copper, iron, chromium, and thorium entirely modify the properties of the resinates, rendering them insoluble, or producing a precipitation which interferes with the experiment.

W. G.

The Magnetic Spectrum of the β -Rays Excited in Metals by Soft X-Rays. H. ROBINSON and W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], **28**, 277—281).—A preliminary account is given of experiments designed to throw light on the connexion between the energy of the β -ray and the frequency of the X-ray exciting it, which may be expected to be connected with it by the relation $E = h\nu$, where E is the energy, ν the frequency, and h is Planck's constant. A nickel anticathode was employed, on account of the relative simplicity of the X-rays from this element. The elements iron and lead have so far been employed as generators of β -rays. The magnetic spectra of the β -rays consisted of bands, not lines; this is ascribed to the production of β -rays at different depths below the surface of the generating metal. The evidence so far obtained points to β -rays being generated which are characteristic both of the element forming the anticathode and of that forming the generator, but it cannot be decided yet whether the simple quantum theory will serve to explain the connexion between the complete β -ray spectrum and that of the X-rays.

F. S.

Spectrum of β -Rays Excited by γ -Rays. SIR ERNEST RUTHERFORD, H. ROBINSON, and W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], **28**, 281—286).—The investigation deals with the velocities of β -rays excited by penetrating γ -rays in various metals, principally lead, and the connexion, if any, between these velocities and those of the primary β -rays accompanying the γ -rays. A fairly thick glass tube containing radium emanation was used as the source of γ -rays, surrounded by a cylinder of the generating metal. A thickness of 0.14 mm. of lead or gold sufficed to obliterate the lines in the magnetic spectrum of the primary β -rays. The bands observed in the spectrum are due under these conditions to β -rays generated in the metal cylinder. They are sharply defined at the edge corresponding with the greater velocity and due to β -rays escaping from the outer surface, and gradually fade in intensity towards the other edge, owing to the loss of velocity of the β -rays which come from the interior.

The most prominent groups of β -rays excited in lead were compared with the strongest groups of primary rays from radium-*B*, having velocities between 0.6 and 0.8 that of light, for which an identity is to be expected on the view that radium-*B* is isotopic with lead. It was found that, within the limits of experimental error, the velocities of the β -rays were the same in each case.

Comparative measurements were made with cylinders of aluminium, silver, gold, and lead around the source. With the first, no groups of β -rays could be detected amidst the general fog; with silver, the lines were faint and difficult to measure; with lead and gold, well-marked lines of similar intensity were obtained. These lines are certainly due to the conversion into β -rays of some of the more penetrating γ -rays of radium-*B*, and their greater intensity with heavy metals is due to the much greater absorption of the γ -rays in these metals than in those of smaller atomic weight. With the silver, comparison with lead revealed no certain difference in the velocity of the three strong groups of rays, but the velocities of a number of the β -rays excited in gold were of the order of 2% higher than those given by lead. F. S.

Excitation of γ -Rays by β -Rays. H. RICHARDSON (*Proc. Roy. Soc.*, 1914, [A], **90**, 521—531. Compare Chadwick, A., 1912, ii, 1025).—The nature of the radiations excited when the β - and γ -rays of radium-*B* and radium-*C* impinge on different substances has been investigated with special reference to the bearing of the results on the type of radiation emitted by different metals on which radium-*C* is deposited. The experiments show that the excitation of characteristic radiations is mainly, if not entirely, due to the β -rays and not to the γ -rays. The amount of γ -radiation excited by the α -rays of radium-*C* is negligible in comparison with that exerted by the β -rays.

From an examination of the radiations emitted by about twenty different elements, it is found that the only radiations excited are those which fall into the *K* and *L* groups found by Barkla. The mass-absorption coefficients for these radiations agree very well with

the numbers obtained previously by Barkla and Chapman (*Proc. Roy. Soc.*, 1912, [A], **86**, 439) for the absorption of the characteristic radiations excited by *X*-rays.

In addition to the penetrating type of radiation for which the absorption coefficient $\mu=0.115$, radium-*C* has been found to emit a small amount of soft radiation similar in type to that emitted by radium-*B*, and for which $\mu=40$ (in aluminium). When radium-*C* is deposited on different metals, a soft radiation is given out which consists of the characteristic radiation of the metal excited by the β -rays of radium-*C*, together with the soft radiation emitted by radium-*C* itself.

H. M. D.

The Spectrum of the Penetrating γ -Radiation from Radium-*B* and Radium-*C*. SIR ERNEST RUTHERFORD and E. N. DA C. ANDRADE (*Phil. Mag.*, 1914, [vi], **28**, 263—273).—Previous results for the wave-lengths of the soft γ -rays ($\mu=40(\text{cm.})^{-1}$ Al) from radium-*B* between the angles of reflection from rock-salt of 8° to 16° showed two lines at 10° and 12° corresponding with the "*L*" series for lead. By the same method the more penetrating rays, $\mu=0.5$ of radium-*B*, and $\mu=0.115$ of radium-*C*, have been examined, and lines found with angles of reflection from rock-salt between $0^\circ 44'$ and $4^\circ 22'$, those greater than $1^\circ 24'$ belonging mainly to radium-*B* and the others to radium-*C*. The chief lines are at $1^\circ 0'$ and $1^\circ 40'$, the latter probably a close doublet, $1^\circ 37'$ and $1^\circ 43'$.

A new transmission method was devised to determine these very high-frequency rays with greater accuracy, in which the cone of rays, passing normally through a rock-salt crystal on to a photographic plate beyond, was deprived by reflection of those rays striking the crystal at the reflection angle, leaving blank absorption lines on the corresponding part of the plate, whilst the reflected rays formed dark, reflected lines on another part of the plate. From the position of either the absorption or reflection line and the geometry of the arrangement, the reflection angle could be determined with considerable accuracy. The results are expressed in the following table:

Old reflection method.	New transmission method.		Mean wave-length. ($\times 10^{-9}$ cm.).
	Absorption lines.	Reflection lines.	
$0^\circ 44'$	$0^\circ 42'$	$0^\circ 43'$	0.71
$1^\circ 0'$	$1^\circ 0'$	$1^\circ 0'$	0.99
$1^\circ 11'$	$1^\circ 10'$	$1^\circ 10'$	1.15
$1^\circ 24'$	$1^\circ 24'$	$1^\circ 25'$	1.37
{ $1^\circ 37'$	$1^\circ 37'$	$1^\circ 36'$	1.59
{ $1^\circ 44'$	$1^\circ 44'$	$1^\circ 44'$	1.69
$2^\circ 0'$	—	$2^\circ 0'$	1.96
—	$2^\circ 20'$	$2^\circ 20'$	2.29
$2^\circ 28'$	—	—	2.42
$2^\circ 40'$	—	—	2.62
$3^\circ 0'$	—	$3^\circ 0'$	2.96
$3^\circ 18'$ *	$3^\circ 18'$ *	—	3.24
$4^\circ 0'$ *	—	—	3.93
$4^\circ 22'$	—	—	4.28

* Possibly second order.

The wave-length of the most penetrating ray, 0.71×10^{-9} cm., is seven times shorter than any previously measured, the "K" line of silver being 0.56×10^{-8} cm., and it is very surprising that the architecture of the crystal is sufficiently definite to resolve such short waves, especially when the thermal agitation of the atoms is remembered. Putting the rock-salt crystal in liquid air did not improve the definition of the lines.

The penetrating γ -rays from radium-B of wave-lengths 1.59 and 1.69 ($\times 10^{-9}$ cm.) probably belong to the "K" series for lead, and their wave-lengths agree fairly with that obtained by extrapolation of Moseley's "K" series from aluminium to silver, but the strong line of radium-C, of wave-length 0.99, cannot be the "K" series line for bismuth, the wave-length of which would be only a few per cent. higher than that of lead, and probably belongs to a new series not yet observed, which may be called the "H" series.

A method is given for calculating approximate wave-lengths of γ -rays from the values of the absorption-coefficients, μ , in aluminium. The "hardening" of the γ -rays of radium-C by passage through lead is ascribed to the weeding out of the rays of wave-lengths 0.99 and 1.15, leaving only that of wave-length 0.71.

F. S.

X-Radiation Similar to that from Radium. F. DESSAUER (*Physikal. Zeitsch.*, 1914, 15, 739—741).—In general the hardness of X-rays is very much less than that of γ -rays, the absorption-coefficients for the former being approximately from ten to eighty times as large as for the latter. An examination of the composition of X-rays has shown, however, that these contain a small proportion of extremely hard rays which resemble closely, and in fact are probably identical with, the γ -rays emitted by radioactive substances. The curve obtained by plotting the intensity of the X-rays as a function of the absorption-coefficient shows that the intensity falls at first very quickly, with diminution in the absorption-coefficient, but at about $\mu = 0.4$ (in aluminium) the rate of decrease in the intensity with diminution of the absorption-coefficient becomes very much smaller. For values of μ less than about 0.35, the curve is but very slightly inclined to the abscissa as compared with its inclination at values of μ from 0.40 to 0.55.

This relationship indicates that X-ray tubes may possibly be utilised as a powerful source of highly penetrating γ -radiation, and may find application for this purpose in medicine.

The factors which exert an influence on the composition of X-rays have been systematically investigated. The proportion of highly penetrating rays is found to increase with decreasing frequency of the discharge, with increase of the potential, and with increasing current density at the cathode. The hardness also appears to increase when the temperature of the cathode rises (within certain limits) and when that of the anti-cathode falls.

H. M. D.

The X-Ray Spectrum of Nickel. W. F. RAWLINSON (*Phil. Mag.*, 1914, [vi], 28, 274—277).—A detailed investigation of the X-ray

spectrum of nickel, which had previously been investigated by Bragg (*Proc. Roy. Soc.*, 1913, [A], **89**, 246). The angles of reflection from crystals of rock salt, heavy-spar, and potassium ferrocyanide of the radiations from a nickel anti-cathode were measured. It is shown that the strong α - and β -lines are close doublets, and have angles of reflection as follows: $\alpha=17^{\circ}6'$, $17^{\circ}9\cdot6'$; $\beta=15^{\circ}22'$, $15^{\circ}25'$. These lines were not completely resolved in the first-order spectrum. In addition to the strong α - and β -lines, evidence was obtained of the existence of a series of faint lines between the α - and β -lines. It is shown that in the case of elements belonging to the *K* series of Barkla, a very large proportion of the radiation appears to be concentrated in the α - and β -lines. The absorption of the radiation was measured by means of two electroscopes, and it is shown that with a tube of 30,000 volts 79% of the radiation was absorbed exponentially with a value $\mu/\rho=55\cdot5$ in aluminium. The remaining 21% was absorbed approximately exponentially with a value of $\mu/\rho=10\cdot36$. The radiation became increasingly penetrating as the voltage was raised, and on the assumption that absorption occurred exponentially, it was found that $\mu/\rho=3\cdot25$ at 42,000 volts and $2\cdot54$ at 51,000 volts. J. F. S.

Velocity of Sound in Argon and the Influence of Röntgen Rays. FRANZ SRIEDER (*Ber. Deut. physikal. Ges.*, 1914, **16**, 615–616).—The results of measurements of the velocity of sound in argon by Kundt's method indicate that this is not influenced to a measurable extent by the action of Röntgen rays on the gas. This is contrary to the results obtained by Küpper (*Ann. Physik*, 1914, [iv], **43**, 905) in experiments with polyatomic gases. H. M. D.

The Amount of Radium and Radium Emanation Present in the Waters of Several Western Springs. R. W. BOYLE and D. McINTOSH (*Trans. Roy. Soc. Canada*, 1913, **7**, iii, 163).—A determination of the radioactivity of the water of the undermentioned Canadian springs by the usual methods has given the following results, expressed in millionths of a milligram of radium per litre: Sinclair, 4·0; Fairmount, 3·5; and Banff, uncertain. In all three cases traces of radium itself were also indicated. G. F. M.

Thermionic Currents in a High Vacuum. J. E. LILIENTHAL (*Physikal. Zeitsch.*, 1914, **15**, 744–746).—A reply to a paper with the same title by Langmuir (this vol., ii, 412), in which the author claims priority in respect of certain observations connected with thermionic currents in high vacua. H. M. D.

Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles. W. I. PAVLOV (*Proc. Roy. Soc.*, 1914, [A], **90**, 398–411).—The ionising properties of positive ions have been examined by a direct method. The results indicate that the positive ions emitted by heated sodium phosphate give rise to negative ions by collision with gas mole-

cules. The curves obtained by plotting the ionisation of the gas against the velocity of the positive ions are of the same form for hydrogen, oxygen, and nitrogen, and appear to approach the velocity axis asymptotically.

With a modified form of apparatus, it was found that the ionising potential for positive ions in hydrogen is about 10 volts, which is of the same order of magnitude as the ionising potential for negative corpuscles. Whereas, however, the ionisation velocity curves are straight lines when the ionisation is due to negative corpuscles, the curves are markedly convex to the velocity axis when the ionisation is brought about by positive ions.

The values obtained for the ionising potential of negative corpuscles in hydrogen and helium by Franck and Hertz (A., 1913, ii, 174) have been confirmed by a different method of measurement.

H. M. D.

Action of a Wehnelt Cathode. FRANK HORTON (*Phil. Mag.*, 1914, [vi], 28, 244—252).—Experiments have been carried out to determine whether the emission of electrons from lime in a Wehnelt cathode depends on the nature of the substance on which it is heated, and further experiments have been made to test the separation of calcium and oxygen by the passage of a thermionic discharge from lime, and to determine the connexion between the recombination of these elements and the electron emission. As a result of the experiments, the author comes to the conclusions: (1) That the electron emission from a Wehnelt cathode has its origin in the lime itself, and the lime does not merely serve to help the electrons to escape from the metal. (2) When an electric current passes through lime at a high temperature, the amount of oxygen liberated is only a very small fraction of what would be expected if the conductivity of the lime were entirely electrolytic. It is suggested that the conductivity is entirely electrolytic, and that the products of electrolysis diffuse through the lime and recombine. It appears unlikely, however, that such recombination should occur so rapidly and completely, through a layer of solid lime, especially as the charged oxygen atoms would be liberated on the vacuum side of the oxide layer, and with a strong electric field tending to drag them away from the cathode. (3) The chemical combination of calcium and oxygen does not by itself give rise to any detectable electron emission. From these results it appears improbable that either the theory of Fredenhagen (A., 1913, ii, 903) or that of Gehrtz (A., 1913, ii, 1005) can furnish an explanation of the activity of the Wehnelt cathode.

J. F. S.

The Ionisation of Platinum by Cathode-Rays. NORMAN CAMPBELL (*Phil. Mag.*, 1914, [vi], 28, 286—302).—It was found that the ionisation produced by cathode-rays in falling on platinum can be very greatly reduced by prolonged heating of the metal in a vacuum or in oxygen. The heating first produces no effect, then there is a sudden large change, followed by a slow change, of

which the end is never reached. It is probable that ultimately the platinum would not be ionised at all by cathode-rays of less than 40 volts' speed. The metal can be put back into its initial state by bombardment with cathode-rays of 100 volts' speed in a pressure of gas below 0.01 mm., but mere contact of the gas or vapours does not restore it appreciably. This restored condition, however, is much less permanent than initially, and a few minutes heating, instead of a few hours, brings the sudden change.

Thus the same treatment which reduces greatly thermionic and photoelectric effects reduces also the ionisation produced at a metal surface by cathode-rays. An explanation of the effects is offered on the view that hydrogen is present in the metal in two forms, first, condensed on the surface, and, secondly, dissolved in the interior, the sudden diminution of the ionisation by heating corresponding with the abolition of the surface layer and the further gradual diminution to the progressive removal of the dissolved gas. To explain the temporary restoration of the surface by the electric discharge, recourse is had to a surface "double layer." F. S.

The Positive Ionisation from Heated Platinum. CHARLES SHEARD (*Phil. Mag.*, 1914, [vi], 28, 170—187).—The increase of positive thermionic currents from platinum wires in high vacua, produced either by heating the wire, earthed, to a higher temperature than that at which the ionisation is subsequently measured, or by heating it, charged to a negative potential, to a temperature sufficient to cause it to discharge negative electricity, has been re-examined in dry air at atmospheric pressure. Testing the ionisation always at 628°, and heating the wire, earthed, to various temperatures, revealed two maxima, one after previous heating at 654° and the other at 756°. Experiment showed that the negative emission from the wire when heated and charged negatively became appreciable at 760°. The results are interpreted on the theory that, on heating the wire, decomposition of a molecule *AB* occurs with production of two ions, *A* positively and *B* negatively charged, *A* being expelled or stored up, later to be expelled when an electric force is applied. At higher temperature *B* loses its electron. Various effects result in accordance with a number of possibilities, which are too numerous to be considered in an abstract. It is necessary to assume the presence of at least two substances capable of so producing ions on heating.

By heating the wire in the flame of a Bunsen burner, an increased positive emission was also obtained, probably in part due to the removal of a surface material incapable of producing ions and in part due to the hydrogen absorbed, owing to its affinity for electrons. Heating in carbon dioxide decreased, if anything, the positive emission. The decay with time of the positive currents at different temperatures showed the existence of two sources of ions, the first source decaying according to an exponential law and the second increasing to a maximum before decaying. This results in the ionisation-time curves showing a formal resemblance to the decay curves of the radium active deposit. F. S.

Emission of Electricity from Various Substances at High Temperatures. G. W. C. KAYE and W. F. HIGGINS (*Proc. Roy. Soc.*, 1914, [A], **90**, 430—437. Compare A., 1912, ii, 525; 1913, ii, 661).—The emission of electricity by various substances has been investigated at temperatures of 2000—2500° by experiments in a carbon-tube furnace. The effect due to the carbon was eliminated by difference measurements. The substances examined included the oxides of calcium, strontium, barium, magnesium, silicon, aluminium, and iron, and the metals tin, aluminium, iron, copper, and brass. With the exception of brass, all these substances were found to give off large quantities of negative electricity during the volatilisation which occurred at the temperature of the experiments. Without the application of any extraneous potential difference, currents of the order of 4 amperes per cm.² were obtained with barium oxide and alumina. The corresponding value for tin was 2 amperes, and for iron 1, whilst brass gave a current of 0.5 ampere in the opposite direction, indicating the emission of large quantities of positive electricity. H. M. D.

Absorption of Gases in the Discharge Tube. F. H. NEWMAN (*Proc. Roy. Soc.*, 1914, [A], **90**, 499—506).—Experiments have been made on the absorption of gases by the electrodes in discharge tubes, the main object being to ascertain whether there is any connexion between the amount of gas absorbed and the quantity of electricity passing during the discharge.

The liquid alloy of sodium and potassium absorbs nitrogen and hydrogen, whether used as cathode or anode, but the quantity of gas absorbed, relatively to the quantity of electricity passing, is greater when the alloy is made the cathode. Mercury behaves similarly towards oxygen. In all cases the ratio of the absorption to the quantity of electricity passing increases as the pressure of the gas in the discharge tube is reduced.

It is suggested that the gases are transformed into active modifications under the influence of the electric discharge. The active forms then enter into combination with the electrode substances. This hypothesis is supported by the fact that the known active modification of nitrogen is absorbed when passed over sodium-potassium alloy. The greater absorption which is observed when the metals are used as the cathode is probably due to the combination of the positive rays with the metal.

Experiments in which molten cadmium, zinc, bismuth, and lead were tested for absorption of nitrogen gave negative results with the ordinary discharge. H. M. D.

Conductivity. II. Conductivity of Some Formates and of Hydrogen Chloride in (Anhydrous) Formic Acid. Cases of Apparent Agreement of Strong Electrolytes with the Mass Law. H. I. SCHLESINGER and A. W. MARTIN (*J. Amer. Chem. Soc.*, 1914, **36**, 1589—1620).—Schlesinger and Calvert (A., 1912, ii, 26) have shown that solutions of ammonia in anhydrous formic acid are excellent conductors, and that ammonium formate,

although highly ionised, obeys the law of mass action. A study has now been made of the behaviour of sodium, potassium, and phenylammonium formates in anhydrous formic acid. Determinations of the conductivities and freezing points of hydrogen chloride in the same solvent have also been carried out.

The formates in anhydrous formic acid obey the law of mass action up to concentrations of 0.3—0.6 molar if the degree of ionisation is calculated from the conductivity values which have not been corrected for viscosity. The ionisation constants are as follows: sodium formate, 0.816; aniline formate, 0.814; potassium formate, 1.02; and ammonium formate, 1.23. The same is true of solutions of hydrogen chloride, the ionisation constant of which is only 0.04. At higher concentrations than 0.3—0.6 molar the formates show deviation from the mass law, the degree of ionisation being less than it should be. The results also indicate that the greater the value of the ionisation constant, the higher is the concentration at which the deviation begins; thus, ammonium formate begins to deviate above 0.55 molar, potassium formate at above 0.45 molar, and sodium and aniline formates at about 0.3 molar. This suggests that a relationship exists between the degree of ionisation and the volume of the non-ionised molecule.

When the conductivities are corrected for the viscosity of the solutions and the ionisation constants calculated from these corrected values, the agreement with the mass law disappears. Evidence is adduced to show that the uncorrected conductivities of these solutions should be used for the calculation of the degree of ionisation.

The results obtained by Zanninovich-Tassarini (A., 1896, ii, 352) on the conductivities and freezing-point depressions of solutions of hydrogen chloride in formic acid have been found to be incorrect.

E. G.

The Acid Dissociation Constants of the Carbohydrates. L. MICHAELIS (*Biochem. Zeitsch.*, 1914, 65, 360—362).—In the former series of measurements of the acid dissociation constants (Michaelis and Rona, A., 1913, ii, 379) it was found that maltose had a higher value than might have been expected. It is now shown that the preparation used was not pure. A preparation was obtained, therefore, by the slow precipitation of a saturated solution of the sugar in 70% alcohol by ether vapour. For this, the value of k found was 9.0×10^{-13} . This is only slightly greater than that found for the reducing mono- and di-saccharides.

S. B. S.

Potential of Silver in Non-aqueous Solutions of Silver Nitrate. VERNETTE L. GIBBONS and F. H. GETMAN (*J. Amer. Chem. Soc.*, 1914, 36, 1630—1655).—A résumé is given of previous work on the potentials of metals in aqueous and non-aqueous solutions of their salts, and an account is furnished of an investigation of the behaviour of silver in non-aqueous solutions of silver nitrate.

The conductivities of solutions of silver nitrate in ethyl alcohol, methyl alcohol, acetone, aniline, and pyridine have been deter-

mined for concentrations between 0.1*N* and 0.0001*N*. It has been found that the conductivity curve for solutions in aniline approaches a second maximum as the solutions become more dilute. The results also indicate a relationship between the dielectric constant and the normalities of all the conductivity curves. Measurements have been made of the transport numbers of silver nitrate in ethyl alcohol, methyl alcohol, and pyridine. The *E.M.F.* has been determined for a large number of concentration cells in the different solvents, and for these experiments a special form of apparatus was employed, which was free from defects due to capillarity and constant communication of the two liquids. Calculations of the electrode potential of silver gave the following values: in ethyl alcohol, 0.8314; in methyl alcohol, 0.8298; in acetone, 0.9022; and in pyridine, 0.3711. The data obtained in these experiments indicate that the abnormalities observed in non-aqueous solutions of silver nitrate are due to the combination of the solvent and solute to form complex compounds which undergo gradual dissociation. E. G.

Volta Effect and Unimolecular Layers. J. GUYOT (*Compt. rend.*, 1914, 159, 307—311).—The apparent potential difference at the contact of a metal and pure water diminishes notably, and may become inverted by depositing on the surface of the water very thin layers of certain insoluble organic compounds. As each drop of the latter is placed on the water the diminution effect increases, until the surface of the water is entirely covered. At this stage the surface tension is equal to that of pure water, but, on the addition of more drops, the surface tension falls rapidly, whilst the diminution in the Volta effect becomes less and less, and finally disappears. The author has measured this Volta effect in the case of a number of glycerides and their corresponding acids, esters of dibasic acids, dibasic acids, esters of monobasic acids and their corresponding alcohols, metallic salts, an aldehyde, a benzene hydrocarbon, and some aromatic hydroxy- and alkoxy-compounds. The results obtained are practically the same, whether the pure substance is used or its solution in benzene or toluene. W. G.

Variation of Electrical Potential Across a Semi-permeable Membrane. F. G. DONNAN and G. M. GREEN (*Proc. Roy. Soc.*, 1914, [A], 90, 450—455).—In a previous paper (A., 1911, ii, 848) it was shown that the potential difference between two differently concentrated solutions of an electrolyte, separated by a membrane which is impermeable to the electrolyte, but permeable to the solvent, can be represented by the formula $\pi = RT/nF \cdot \log c_1/c_2$, in which c_1 and c_2 are the molar concentrations of the K^+ ions of the electrolyte kA . In the derivation of this formula, it was assumed that the membrane is permeable to other salts with the same cation K^+ , although impermeable to the salt kA .

Measurements have now been made of the potential difference between two differently concentrated solutions of potassium ferrocyanide, separated by a membrane of colloidal copper ferrocyanide.

In these experiments, $1N$ -solution was combined with solutions varying from $0.1N$ to $0.01N$, and in a second series a $0.1N$ -solution was combined with solutions varying from $0.05N$ to $0.005N$.

On comparing the observed potential differences with those calculated from the above formula, it is found that there is a fairly constant deviation of the order of 25% in all the measurements which involve the $1N$ -solution. A much closer agreement is exhibited by the results for pairs of solutions in which the $0.1N$ -solution is the stronger, although the percentage deviation increases as the ratio of the concentrations increases. When the assumptions involved in the calculation of the potential difference are taken into account, it would seem that the experimental data afford evidence of the correctness of the above formula in its application to the case investigated.

H. M. D.

Thermodynamics of Normal Cells. ERNST COHEN and W. D. HELDERMAN (*Chem. Weekblad*, 1914, **11**, 740—746).—A comparison of the results given by von Steinwehr in his paper on the Weston cell (this vol., ii, 622) with those previously obtained by Cohen (A., 1900, ii, 703).

A. J. W.

Electrolytic Deposition of Metals in Valve Cells. GÜNTHER SCHULZE (*Ann. Physik*, 1914, [iv], **44**, 1106—1120).—The action of an alternating current on the deposition of copper from a copper sulphate solution, in which a tantalum electrode is immersed, has been examined with special reference to the valve effect. When the tantalum forms the cathode, about 35% of the total copper is deposited in such a condition that it is redissolved in the succeeding phase of the current discharge when the tantalum forms the anode. The remainder separates as a fine powder, and settles at the bottom of the containing vessel. In the initial period of this phase, the soluble copper is redissolved, and the cell then ceases to transmit the current in this direction.

The proportion of soluble copper which is deposited during the passage of the current through the solution to the tantalum is practically independent of the applied potential difference, the current density (at higher densities), the concentration of the electrolyte, and the thickness of the active tantalum layer. It increases with the temperature and with diminution in the current density (at low densities), and also increases as the strength of the acid in combination with the copper decreases.

The proportion of soluble copper is influenced to a large extent by the addition of other electrolytes to the solution, this influence being determined by the valve potential of the added electrolyte. The lower this valve potential, the greater is the diminution in the quantity of deposited copper.

From experiments with solutions of the nitrates, sulphates, and acetates of the heavy metals, it has been found that the proportion of the heavy metal, which is deposited in a soluble form by the same alternating current, varies with the nature of the acid radicle, but in all three cases the numbers obtained afford a series in which the metals are arranged in the same order.

Similar phenomena are exhibited with an aluminium electrode, but the valve-action effects are not so clearly developed in this case.

H. M. D.

Concentration Cells Built up from Ammoniacal Solutions of Silver Salts. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, **28**, 222—227).—It is shown that the *E.M.F.* of concentration cells of the type $\text{Ag} \mid \text{ammoniacal silver chloride (1)} \mid \text{ammoniacal silver chloride (2)} \mid \text{Ag}$, in which the two solutions have the same ammonia and different silver chloride concentrations, can be calculated from the formula $96540E = 2v/u + v \cdot RT \cdot \log C/c$, in which C is the silver chloride concentration in the stronger, c that in the more dilute, solution.

The *E.M.F.* of cells in which the two solutions have the same silver chloride concentration and contain different quantities of ammonia is similarly given by $96540E = nRT \cdot \log A/a$, in which A and a are the free ammonia concentrations of the concentrated and dilute solutions respectively, and n is the ratio of ammonia to silver in the complex silver salt in the solutions. The calculated *E.M.F.*'s are in satisfactory agreement with the experimental data recorded in the literature if it is assumed that $n = 2$. H. M. D.

Indices of Migration of the Ions and the Transport of Ammonia in Ammoniacal Solutions of Silver Nitrate. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, **28**, 215—222).—Measurements of the relative mobilities of the positive and negative ions show that the proportion of the current carried by the negative ion increases somewhat when ammonia is added to an aqueous solution of silver nitrate. From experiments with solutions obtained by the addition of ammonia to silver nitrate in the molar ratios 2:1 and 1:1, it has been found that the change in the ammonia concentration at the electrodes indicates respectively the transport of somewhat less than 2 and 1 mols. of ammonia for each silver ion. It is suggested that the complex ions involved in the transport of the electric charge are those represented by the formulæ $\text{Ag}^+, 2\text{NH}_3$ and $\text{Ag}^+, \text{NH}_3, \text{H}_2\text{O}$, and that the corresponding ion in pure aqueous solution is $\text{Ag}^+, 2\text{H}_2\text{O}$. H. M. D.

Indices of Migration of the Ions and the Transport of Ammonia in Ammoniacal Solutions of Copper Sulphate. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1914, **28**, 227—229).—The relative mobilities of the ions in aqueous solutions of copper sulphate are practically unaltered on the addition of ammonia. The change in the ammonia concentration resulting from the passage of the current indicates that at least four, and possibly five, molecules of ammonia are associated with the copper ion in the ammoniacal solutions. H. M. D.

Preparation of Alloys for Magnetic Researches. J. DE FREUDENREICH (*Arch. Sci. phys. nat.*, 1914, [iv], **38**, 36—45).—Alloys of iron with nickel and cobalt, corresponding approximately with

the formulæ Fe_2Ni and Fe_2Co , have been prepared by melting the two metals together in a magnesite crucible in an electric resistance furnace. Attempts to prepare these alloys by the thermite process from iron oxide and the second metal gave products which contained about 2% of aluminium and 2% of silicon. Such alloys had a magnetic saturation which was considerably smaller than the correct value for the pure alloys, and since no relationships could be deduced between the magnetic saturation and the impurities, the alloys were valueless for the purpose of the author. The magnetic saturation of the ferrocobalt alloy is 10% larger than that of pure iron, whereas the alloys prepared by the thermite process were only 6.5% larger.

J. F. S.

Magnetic Susceptibility and Electrolytic Dissociation. A. QUARTAROLI (*Gazzetta*, 1914, **44**, ii, 43—63).—The method previously described (this vol., ii, 619) has been applied to the study of the magnetic susceptibility of a number of solutions of iron, manganese, nickel, and cobalt salts, either alone or in the presence of mannitol or ammonium chloride, citrate, or tartrate.

The results show that, although an undeniable relation exists between electrolytic dissociation and magnetic susceptibility, the latter does not depend merely on the free ions of the magnetic elements. Where complex ions are present, the susceptibility may be even greater than with the simple salts. Additional support is thus afforded by the general rule that the contribution of atoms to the physical constants of compounds is a variable dependent on the other atoms present, and probably also on the order of arrangement.

T. H. P.

Photographic Analysis of Explosions in the Magnetic Field. HAROLD B. DIXON, C. CAMPBELL, and W. E. SLATER (*Proc. Roy. Soc.*, 1914, [A], **90**, 506—511).—The explosion-waves in a series of gas mixtures have been photographed as the waves entered, traversed, and emerged from a magnetic field, and also when they travelled through the same tube in the absence of the magnetic field. The mixtures examined were: (1) cyanogen and oxygen with varying proportions of nitrogen; (2) hydrogen and oxygen in different proportions; (3) acetylene and oxygen; (4) carbon disulphide and oxygen; (5) carbon monoxide and oxygen. In no case do the photographs show any influence of the field on the explosion-wave phenomenon, and since the mechanism of a compression-wave affords a satisfactory explanation of the observed effects, the authors draw the conclusion that the velocity of the explosion-wave is not connected with the ionising action of electrons.

H. M. D.

The Dilatation of Ferro-nickels over a Wide Temperature Interval. P. CHEVENARD (*Compt. rend.*, 1914, **159**, 175—178).—A study of the dilatation and contraction of alloys of iron and nickel, varying from pure iron to pure nickel, over a temperature

range from -195° to 750° . The difference between the linear dimensions of bars of the alloys before and after heating are a measure of the amplitude of the irreversible transformation. These differences gradually tend towards zero on passing from iron to the alloy Fe_3Ni , which is apparently the limit of irreversible alloys. The alloys between Fe_2Ni and FeNi_2 have abnormal, quasi-reversible properties. For the alloy FeNi_2 , the dilatation takes place according to a parabolic law between 0° and 800° .

W. G.

Determination of the Specific Heat of Chlorine. HERMANN SCHMIDT (*Physikal. Zeitsch.*, 1914, 15, 720).—The author refers to his previous measurements of the velocity of sound in gases, in which the position of the stationary waves in a Kundt tube was made evident by the ionisation of the gas.

H. M. D.

Molecular Complexity at the Melting Point. D. E. TSAKALOTOS (*J. Chim. phys.*, 1914, 12, 461—463).—A theoretical paper in which it is shown that the fatty acids mixed with water constitute binary systems which do not follow the general law put forward by Thole, Mussell and Dunstan (T., 1913, 103, 1108) that binary systems which have positive viscosity curves have also fusion curves which exhibit one or more maxima. The viscosity curves of the lower fatty acids and water are entirely positive, but the fusion curves show no maxima. The author explains the anomaly by the assumption that the molecular compounds formed between the acid and water exist only in the liquid state, and are dissociated as the mixture approaches its freezing point. An associated liquid is also considered as a binary system the constituents of which are alike, and that in certain cases the complex molecules dissociate as the freezing point is reached, in the same way as in the above-mentioned cases.

J. F. S.

Unimolecular Layers and Superfusion. HENRI LABROUSTE (*Compt. rend.*, 1914, 159, 306—307).—In the case of substances such as trilaurein and tribenzoin, which exhibit marked superfusion, the matter obtained by joining together unimolecular layers appears in the liquid state if the substance can exist superfused at the experimental temperature. Fused or superfused substances can be spread out on water having a temperature considerably lower than the melting point of these substances provided that the temperature of the water is higher than the lowest temperature at which it is possible to obtain the substance in the superfused state. These rules do not apply to those substances, such as camphor, which spread out spontaneously on water, even in the solid state, owing to their volatile or soluble nature.

W. G.

An Exact Vapour Pressure Formula. IVAR W. CEDERBERG (*Physikal. Zeitsch.*, 1914, 15, 697—705).—According to van der Waals, the relation between the vapour pressure p of a liquid and

the temperature T may be approximately represented by the formula $\log \pi_0/p = a(\theta_0/T - 1)$, in which π_0 is the critical pressure, θ_0 the critical temperature, and a a constant. It has already been pointed out that a is not constant, but is a function of the temperature. For a number of substances, the curves which are obtained by plotting a as a function of T are found to be convex to the temperature axis, and approximately symmetrical with reference to a line drawn through the minimum point on the curve at right angles to the temperature axis. Where this is not the case, the curve may be made symmetrical by an alteration of the critical pressure to an extent which falls within the limits of experimental error. On the assumption that this curve is symmetrical in all cases, it is suggested that the dependence of a on the temperature is represented by $a = \alpha \cdot \beta^{(T/\theta_0 - v)^2}$, in which α is the minimum value of a , β is a constant, and v is the reduced temperature corresponding with the minimum value of a . The resulting formula, $\log \pi_0/p = \alpha \cdot \beta^{(T/\theta_0 - v)^2} \cdot (\theta_0/T - 1)$, is found to afford an exact representation of the vapour pressures of water and benzene from the lowest temperatures up to the respective critical temperatures.

Since the van der Waals' equation may be regarded as a special form of the reduced vapour-pressure equation $p/\pi_0 = F(T/\theta_0)$, it was to be expected that the constants in the above equation would, at least in part, be found to have the same value for different substances. In point of fact, the value of β is approximately equal to 2 and v to $\frac{3}{4}$ for non-associated substances, and for this group of liquids the vapour-pressure formula may be simplified by the introduction of these values. The constant α varies, however, from one substance to another. It is shown that α is connected with the latent heat of vaporisation by means of the formula $\alpha = \frac{3}{4} M \lambda / p(V - v)$, in which M is the modulus of Briggs' logarithms, λ the molecular heat of vaporisation, V the molecular volume of the saturated vapour, and v that of the liquid at the temperature ($v = \frac{3}{4}$) corresponding with the minimum value of a .

H. M. D.

An Apparatus for Boiling-point Determination without Thermometer Correction. THEODOR PAUL and KARL SCHANTZ (*Ber.*, 1914, **47**, 2285—2288).—An apparatus is described embodying the principles of Beckmann's boiling-point apparatus and Kahlbaum's still-head; the condenser can, by rotating, be moved from a reflux position to one for direct distillation. Without disconnecting the apparatus in any way, it is therefore possible to determine the boiling point of a mixture first at constant composition and then during distillation. For details the original paper should be consulted.

D. F. T.

Advantageous Form of Still for the Exact Measurement of Boiling Point during Fractional Distillation. THEODORE W. RICHARDS and FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1914, **36**, 1787—1791).—Apparatus is described which has been devised for

the exact determination of boiling points. Its essential feature is that the whole stem of the thermometer is maintained at the temperature of the vapour, and the boiling point of the actual distillate can thus be accurately ascertained.

It consists of a flask and a wide tube held parallel to the neck, and connected with the latter by two side-tubes at the top and bottom. The upper side-tube, which forms the exit tube for the vapour, is joined to the upper end of the neck of the flask. The lower side-tube, which serves to return the prematurely condensed liquid to the flask, is a constricted continuation of the end of the wide tube; it is bent into the form of a shallow U, and fused into the neck of the flask at a point a few cm. above the bulb. The wide tube is open at the top, where it is so constricted as to receive and hold closely a Beckmann thermometer at a point near the zero mark. The thermometer can be made to fit without grinding, as a liquid seal will collect at this point and prevent the escape of vapour, but for use with hygroscopic liquids a ground joint must be employed. The wide tube and upper connecting tube are encased in a thick shell of asbestos.

In a second form of the apparatus, suitable for use with small Anschütz thermometers, the upper end of the wide tube is fitted with a glass stopper provided with a hook, from which the thermometer can be suspended.

The apparatus is of simple construction, efficient, and convenient in use, and can be easily cleaned. E. G.

Theory of the Fractional Distillation of Mixtures of Water and Alcohol. E. CHENARD (*Bull. Soc. chim.*, 1914, [iv], 15, 646—649).—A study of the conditions governing fractionation by condensation, which requires, as essential, the continuous removal of the condensed liquid from contact with the vapours producing it. The apparatus consisted of an unpolished copper tube 35 cm. long and 1 cm. internal diameter, bent slightly downwards and fitted midway with a tube for collecting the condensed liquid and exhausting the apparatus. A thermometer at each end of the tube gave the temperatures between which condensation occurred. The ratio of condensed liquid (p) to the total weight of vapour (P) passing through the tube varied with the velocity of flow of the vapour through the tube. This ratio, p/P , was higher with a low velocity, as was also the ratio of condensed alcohol to total alcohol. W. G.

Laboratory Fractionating Apparatus. HENRI VIGREUX (*Bull. Soc. chim.*, 1914, [iv], 15, 682—685. Compare Hildt, this vol., ii, 103).—A comparison of the effectiveness of the Chenard and Vigreux fractionating columns for separating such mixtures as water and alcohol or benzene and toluene by fractional distillation. Length for length, the Vigreux column is far more efficient than the Chenard. W. G.

Heat of Formation of Solid Solutions. H. W. FOOTE and BLAIR SAXTON (*J. Amer. Chem. Soc.*, 1914, **36**, 1704—1708).—An account is given of determinations of the heats of solid solution of sodium chlorate in silver chlorate, and of silver chlorate in sodium chlorate. The method employed consisted in determining the heats of solution in water of the mixed crystals and of mechanical mixtures of the same empirical composition. The difference between these two values gives the heat of formation of the mixed crystals from the single salts. Four samples of mixed crystals were prepared by means of Foote's data (A., 1892, ii, 453). Two of the samples were on the sodium chlorate side, and crystallised as cubes, whilst the other two contained an excess of silver chlorate and were tetragonal.

The results show that both the molecular heats of formation of the solid solutions are small and of opposite sign. The values for the isometric crystals are almost constant, showing that there is little or no heat of dilution, but those for the tetragonal crystals show a small variation, indicating that in this case there is a small heat of dilution. The amount of silver chlorate which can be taken up by sodium chlorate to form mixed crystals increases with the temperature, and the process is accompanied by absorption of heat, whereas in the case of the tetragonal crystals the reverse is true. In the relation of the heat of solution to the temperature-coefficient of solubility, Le Chatelier's law is therefore applicable to solid solutions as well as to solutions of other types. E. G.

A Regularity between Molecular Heat of Combustion and its Bearing on the Constitution of the Hydrocarbons. GERVAISE LE BAS (*Chem. News*, 1914, **110**, 26—27, 37—38).—The molecular heat of combustion of gaseous, liquid, and solid paraffins is proportional to the number of valency units in the hydrocarbon molecule. From the data for the gaseous paraffins this ratio is equal to 26·5, which is regarded as the effective combustion value of the hydrogen atom. The effective combustion value for combined carbon is therefore $4 \times 26\cdot5 = 106\cdot0$. In the case of the olefines and acetylenes, the observed heats of combustion are greater than those calculated from the effective heat values of carbon and hydrogen, the differences corresponding with the double and triple bonds being +15·8 and +44·3 cal. respectively.

The heats of combustion of *cyclopropane* and *cyclobutane* are also greater than the calculated values to the extent of 15·3 and 18·0 cal., whilst for *cyclopentane* and *cyclohexane* the observed and calculated values are in satisfactory agreement. It is supposed that this corresponds with the stability of the various ring systems.

The data for benzene and its derivatives indicate that these are saturated compounds, whilst *cyclohexadiene* and *cyclohexene* behave like unsaturated hydrocarbons. The fact that benzene behaves like a saturated hydrocarbon on combustion is discussed

with reference to the question of its constitution. Since no double bonds are present, it is suggested that the unsaturation is distributed uniformly between all the carbon atoms in the molecule as represented by the formula



H. M. D.

Calculation of Constants for the Heats of Combustion of Hydrocarbons. H. STANLEY REDGROVE (*Chem. News*, 1914, 110, 73—74).—Polemical. The method of procedure, adopted by Le Bas (preceding abstract) in deducing constants from the heats of combustion of the hydrocarbons, is subjected to criticism. The relation between the heat of combustion of the saturated hydrocarbons and the valency number, according to which the constant for carbon is exactly four times the constant for hydrogen, is, in the author's opinion, accidental in character. If a general relationship were involved, it would hold for compounds containing other elements, which is not the case.

H. M. D.

Heat of Vaporisation of Normal Liquids. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1914, 36, 1620—1630).—The accuracy of the various equations which have been proposed for representing the variation of heat of vaporisation with temperature has been tested by comparison with the experimental results obtained for octane, methyl butyrate, carbon tetrachloride, and fluorobenzene by Young. For the first three compounds, the author's equation (this vol., ii, 101) and that of Mills (*A.*, 1907, ii, 226) show the best agreement with Young's figures, whilst in the case of fluorobenzene the experimental results are shown to be inaccurate.

It is pointed out that no conclusions can be drawn as to the relative theoretical merits of the different formulæ, and that at present they are merely of service as checks on the experimental data.

E. G.

Influence of Temperature on the Density and Electrical Conductivity of Aqueous Salt Solutions. II. HEINRICH CLAUSEN (*Ann. Physik*, 1914, [iv], 44, 1067—1076. Compare *A.*, 1912, ii, 119).—The density and electrical conductivity of aqueous solutions of rubidium chloride, bromide, iodide, nitrate, and sulphate, and also of caesium chloride, have been measured at 6°, 18°, and 30°. The experimental data are interpreted in accordance with the views put forward by Heydweiller (*A.*, 1910, ii, 106; 1912, ii, 433), and afford further support for the theory that the difference in the density of solution and solvent is determined by coefficients characteristic of the ionised and non-ionised molecules.

H. M. D.

Electrical Conductivity and Viscosity of Solutions of Sodium Iodide and Potassium Iodide in Mixtures of Ethyl Alcohol and Water. E. P. WIGHTMAN, P. B. DAVIS, A. HOLMES, and HARRY C. JONES (*J. Chim. phys.*, 1914, **12**, 385—427).—The viscosity and fluidity of $N/8$ -solutions of sodium iodide and potassium iodide in ethyl alcohol, and in mixtures of ethyl alcohol and water from 100—0%, have been determined at temperatures 15°, 25°, and 35°. Conductivity determinations have been made of $N/8$ - and $N/128$ -solutions of potassium iodide in alcohol-water mixtures from 0·0—96·09% alcohol at 20°, and a further series of $N/8$, $N/32$, $N/128$, and $N/1024$ in similar alcohol-water mixtures at the same temperature. There is a slight increase in the viscosity of alcohol-water mixtures when sodium iodide or potassium iodide is dissolved in them to form a $N/8$ -solution in all cases from 100% alcohol to 60% alcohol; below this concentration there is a slight diminution in the viscosity. On elevation of temperature, the point where the fluidity curve of the solution cuts that of the solvent is displaced, and the displacement is to be attributed to a change in the association of the solvent. The change in the association is greater for water than for alcohol. The viscosity changes are to be explained by the theory previously put forward by Jones and his collaborators (A., 1906, ii, 737). A continuous diminution in the electrical conductivity of solutions of potassium iodide and sodium iodide occurs on passing from pure water to pure alcohol, the diminution being most noticeable in those solutions containing a high percentage of water, and least noticeable in those containing a small percentage of water. This is probably to be explained by the fact that the association of alcohol is changed only very slightly by the addition of small quantities of water, whilst the association of water is strongly affected by the addition of small quantities of alcohol. Since viscosity and association are closely connected, it is to be taken that the same explanation will apply to the viscosity changes, or, to express it differently, in mixtures of alcohol and water there is a far larger change in the viscosity of the water than in that of the alcohol. The decrease in the conductivity of potassium iodide with increase in the percentage of alcohol is more rapid than the corresponding decrease for sodium iodide in the same solvents, due, no doubt, to the greater atomic volume of the potassium iodide (compare Jones and Veazey, A., 1907, ii, 438; 1908, ii, 259, 260). Hydration has practically no influence on the conductivity at any temperature, however; with the elevation of temperature the dissociation of feebly hydrated ions produces a slight increase in the temperature-coefficient of most solutions containing water. Alcohol solutions have temperature-coefficients which are linear functions, and consequently indicate that no "alcoholation" has occurred. The conductivity curves, which appear to be non-symmetrical, become symmetrical if they are prolonged up to 100%, and then they form symmetrical curves with the point of symmetry at 80% alcohol instead of 50%. On raising the temperature, the curves tend to become linear functions, which is to be attributed to the fact that

under similar conditions the fluidity curves also tend to become linear. J. F. S.

Stalagmometric Estimations of Small Hydroxyl Ion Concentrations. JULIUS GRÖH and IRENE D. GÖTZ (*Biochem. Zeitsch.*, 1914, **66**, 165—172).—By means of a Donnan stalagmometer, the surface tension at the interface of a solution of 0.25% stearic acid and aqueous solutions of alkalis was measured. It was found that a calibration curve could be obtained for concentrations of pure sodium hydroxide solutions between the concentrations $2 \cdot 10^{-4}$ and $25 \cdot 10^{-4}$ *N*. The method is more sensitive when the alkaline solution contains neutral salts (for example, potassium chloride in about 0.3*N* concentration). In this case measurements could be made over the range of $5 \cdot 10^{-5}$ to $6 \cdot 10^{-4}$ *N*. The method is still more sensitive when the hydroxyl ions arise from the hydrolytic dissociation of weak salts, when concentrations of OH ions to $2 \cdot 10^{-7}$ *N* affect the tension at the interface. It was found, however, that it was not possible to employ the changes in the tensions at the interfaces to determine the hydrolysis constant, owing to disturbing influences (possibly adsorption phenomena).

S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. V. The Relationship between Physiological and Physico-chemical Action of Neutral Salts. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 173—190).—Capillary-active substances, such as ethyl alcohol, phenol, thymol, menthol, camphor, quinol, α -naphthol, sodium glycocholate, albumose, and caseinogen, lower the surface tension of water more in the presence than in the absence of salts when the solutions are not saturated with the substances. These phenomena run parallel with the physiological activities of the substances. The surface tensions of the salt solutions saturated with these substances are, however, not smaller than those of the salt-free solutions. The surface tension of saturated ammonium sulphate solution is not lowered by thymol, camphor, menthol, or glycocholic acid. The various phenomena are best explained on the assumption of hydrate formation by salts.

S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. VI. The Action of Phenol on the Surface Tension of Protein Solutions. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 191—201).—The surface tension of solutions of serum, various proteins, peptones, and ereptone are lowered more by phenol than is that of pure water. The same phenomenon is shown by *p*-cresol and chloral hydrate, but not by ethyl alcohol, propyl alcohol, triacetin, and camphor. This lowering is not caused by the concentration at the surface of the phenol, but by that of the protein. The diminution of the bactericidal activity of phenol by serum, as observed by Ehrlich and Bechhold, can be explained by means of the surface-tension theory.

S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. VII. Pharmacological Activity and the Lowering of Surface Tensions. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 202—206).—The measurements of the surface tensions of a number of phenol solutions show the general relationship between the capacity of substances to lower the surface tension of water and their pharmacological action as indicated by Traube and others. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. VIII. Some Complexes of Protein and Starch with other Colloids. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 207—217).—Soaps diminish the surface tension of water less in the presence of proteins than in their absence. The effect of the proteins is increased if the mixtures are kept some time before the stalagmometric measurements are made. Similar phenomena were observed with starch solutions, and with mixtures of albumoses and peptones with proteins. The results are explained on the assumption of the formation of colloidal complexes. Bile salts are bound by proteins, but not by starch. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. IX. Colloidal Complexes of Cholesterol. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 218—224).—The stalagmometric measurements indicate the formation of colloidal complexes in soap-cholesterol and soap-protein mixtures, which change with changing hydroxyl ion concentration. A complex, but not quite similar to these, is formed with lecithin and cholesterol. No evidence of a complex between saponin and cholesterol could be obtained. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. X. The Action of Certain Narcotics on Lecithin Solutions. L. BERCZELLER (*Biochem. Zeitsch.*, 1914, **66**, 225—230).—Narcotics increase the surface tension of lecithin solutions. After narcosis, the surface tension of the urine is often lowered by non-volatile products. S. B. S.

The Adsorption Isotherm in the Region of very Small Concentrations. G. TRÜMLER (*Kolloid. Zeitsch.*, 1914, **15**, 10—18).—The question of the validity of the exponential adsorption formula at very small concentrations has been examined by experiments on the adsorption of fluorescein from aqueous solution by animal charcoal. The concentration of the fluorescein was determined spectrophotometrically in the case of the more concentrated solutions (0.05—0.0005 gram per litre), and by measurement of the intensity of the fluorescence in the case of the more dilute solutions (0.0005—0.000005 gram per litre).

From observations on the rate of adsorption, it was found that the initial stage in which the fluorescein is rapidly absorbed is succeeded by a period of relatively slow fall in the concentration

of the fluorescein solution. No definite condition of equilibrium was attainable, and on this account the experiments were arranged so as to afford a measure of the initial rapid absorption. This method of procedure is justified by the probability that the slow absorption is due to a secondary change not directly connected with the true adsorption.

The experimental results are in satisfactory agreement with the requirements of the formula $x = a \cdot c^n$ if $a = 0.25$ and $n = 0.18$. It would thus appear that there is no measurable lower limit of concentration at which the exponential formula loses its validity as a means of expressing the adsorption from solution. H. M. D.

Dissociation of Hydrogen into Atoms. I. IRVING LANGMUIR and G. M. J. MACKAY (*J. Amer. Chem. Soc.*, 1914, **36**, 1708—1722).—In earlier papers (A., 1912, ii, 231, 826, 1162) it has been shown that hydrogen, particularly at low pressures, is readily dissociated into atoms by metallic wires at very high temperatures. It has now been found, however, that there is good reason for suspecting that the actual values recorded for the degree of dissociation are much too high, and this was thought to be due to an incorrect assumption as to the diffusion-coefficient of hydrogen atoms through molecular hydrogen.

Experiments have therefore been carried out by methods which do not necessitate any assumption as to the magnitude of the diffusion-coefficient. Single-loop filaments of pure tungsten wire were mounted in large, cylindrical lamp-bulbs. The temperatures were determined by means of the relation $T = 11230/7.029 - \log H$, where H is the intrinsic brilliancy of the filament in international candle-power per sq. cm. of projected area. On this scale, the m. p. of tungsten is 3540° (abs. temp.), which is regarded as more probable than the lower values usually assigned to it. The temperatures were also determined by measuring the resistance, and also by matching the colour of the emitted light against that of a standard provided with a blue screen. The three methods nearly always gave concordant results.

Measurements have been made of the total losses of heat from tungsten wires in hydrogen at pressures ranging from 10 mm. up to ordinary atmospheric pressure, and also at very low pressures from 0.01 to 0.2 mm. Experiments have also been made with nitrogen in order to compare the loss of heat in this gas with that in hydrogen.

The results obtained show a striking difference in the effects in the two gases. In the case of nitrogen, the values for the power consumption decrease steadily at all temperatures as the pressure is reduced, and in hydrogen at temperatures up to 1500 — 1700° a similar decrease occurs. At higher temperatures in hydrogen, however, the power consumption is much greater at low pressures than at atmospheric pressure. At very high temperatures, that part of the loss of heat which depends on the dissociation of the hydrogen increases very rapidly, and becomes 50 or 100 times as large as the possible experimental error. E. G.

Osmotic Data in Relation to Progressive Hydration. W. R. BOUSFIELD (*Proc. Roy. Soc.*, 1914, [A], **90**, 544—548).—A theoretical paper in which it is shown that the formula connecting the osmotic pressure with the vapour-pressure lowering of a solution may be deduced on the basis of a definition of osmotic pressure which does not permit of the assumption that this varies with hydrostatic pressure. The expressions given previously for the osmotic data in terms of progressive hydration (T., 1914, **105**, 609) can now be written in the simpler and more accurate form

$$P/R'T = \Delta/F' = \delta p/p = i/h - n,$$

in which P is the osmotic pressure in atmospheres, Δ the freezing-point lowering, $\delta p/p$ the relative lowering of the vapour pressure, h the total number of molecules of water per molecule of solute, n the number of molecules of water combined with one molecule of solute, and i is the ionisation factor. The values of the constants are $R' = 4.557$ and $F' = 103.6$.
H. M. D.

Attempt at a Physical Explanation of the Semipermeability of Living Cells to Ions. PIERRE GIRARD (*Compt. rend.*, 1914, **159**, 376—379).—If between an acid solution of barium chloride and pure water, each containing an electrode, a goldbeater skin 0.1 mm. in thickness intervenes, chlorine diffuses through into the water five times faster than the barium. If, on the other hand, an alkaline solution of barium chloride is used, it is the barium which diffuses the faster. If the thickness of the membrane is increased to 0.5 mm., the passage of the two ions equalise one another. In the system electrode—acid solution of barium chloride—water—electrode, the algebraic sum of the differences of potential is equal to +0.075 volt. The interposition of the thin membrane between the water and the barium chloride inverts the sign of the sum of the potential differences, and it becomes equal to -0.025 volt, this inversion favouring the passage of the chlorine ions. The author considers that it is this state of polarisation of the membrane which gives it its relative semipermeability, this being relative only on account of the progressive lowering of the state of polarisation. He is of the opinion that the above process is analogous to that which takes place in living cells. W. G.

The Most Simple Method of Crystallographic Description. E. VON FEDEROV (*Zeitsch. Kryst. Min.*, 1914, **54**, 17—45).—For many years the author has been endeavouring to perfect a system whereby the crystalline form of a substance may be made to serve for its identification. In the course of this work, the difficulties incidental to the measurement of crystals, and the recording of the data necessary for their complete description, have been reduced to a minimum. The usual method of describing crystals is held to be very inconvenient, and such descriptions often contain numerous errors.

A special universal goniometer, designed for rapid rather than specially accurate work, is described. The necessary angles are measured with this instrument, and from them a gnomostereo-

graphic projection is made upon a specially prepared diagram. By the method of zonal calculation, involving the employment of bipolar spherical co-ordinates, all other angles on the crystal can be calculated by simple addition or subtraction of natural co-tangents. The author appeals to crystallographers to employ his method of description in order to facilitate the tabulation of data for his tables for crystallochemical analysis. E. H. R.

The Theoretical and Experimental Investigation of Crystal Structure. P. GROTH (*Zeitsch. Kryst. Min.*, 1914, **54**, 65—73).—A historical sketch of the development of the modern theory of crystal structure is given, followed by a description of the recent work of W. H. Bragg and W. L. Bragg, and a discussion of their results. It must now be concluded that molecules as such do not exist in crystals, but only in amorphous substances. Barlow and Pope came to the same conclusion in an entirely different manner. Polymorphism can no longer be explained by the difference in size between the molecules of the two modifications. Among other important questions which now arise is that of the difference between chemical and physical isomerides. In future, the "topic parameters" will be replaced by the actual dimensions of the space-unit of the crystal. E. H. R.

Chemical Significance of Crystalline Form. WILLIAM BARLOW and WILLIAM JACKSON POPE (*J. Amer. Chem. Soc.*, 1914, **36**, 1675—1686, 1694—1695).—The authors reply to the objections raised by Richards (A., 1913, ii, 483) to their views on the relationship between crystal structure and chemical constitution, and point out that their method of quantitative treatment for the elucidation of this relationship has proved so fertile in co-ordinating chemistry and crystallography as to be incapable of being affected by such adverse criticism. E. G.

Further Remarks Concerning the Chemical Significance of Crystalline Form. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1914, **36**, 1686—1694).—A reply to Barlow and Pope (preceding abstract). E. G.

An Association of Crystals of Unlike Symmetry. A. DUFFOUR (*Compt. rend.*, 1914, **159**, 260—263).—A study of mixed crystals of the isodimorphous dichromates of potassium and ammonium. From solutions containing less than 65% of ammonium salt, triclinic crystals, similar to those of the potassium salt, separate; when this proportion is exceeded, monoclinic crystals are formed, isomorphous with the ammonium salt, together with an unstable form of the potassium salt. From a solution containing 60% of ammonium dichromate, monoclinic crystals are first deposited. Subsequently, triclinic crystals grow upon the former, which themselves gradually disappear. From the regular manner in which the triclinic crystals become orientated upon the monoclinic variety, the author is led to modify the axial ratios of the

triclinic potassium salt. There is now seen to be a close morphotropic resemblance between the two kinds of crystal, which would account for the regular manner of growth of the one upon the other. E. H. R.

Mixed Crystals of Ammonium Chloride with Manganese Chloride. H. W. FOOTE and BLAIR SAXTON (*J. Amer. Chem. Soc.*, 1914, **36**, 1695—1704).—Although several investigators have studied the products which are formed when mixed solutions of ammonium and manganese chlorides are allowed to crystallise, the extent of mixed crystal formation and the conditions under which mixed crystals are produced instead of double salts have not hitherto been determined.

A study of this subject has now been carried out by the solubility method employed by Foote (A., 1912, ii, 847) in investigating the mixed crystals of ammonium chloride with nickel and cobalt chlorides. Determinations have been made of the solubility of various mixtures of ammonium and manganese chlorides at 25°, and both the residues and solutions have been analysed.

The results show that ammonium chloride and the double salt $2\text{NH}_4\text{Cl} \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (Saunders, A., 1892, 781) form two series of mixed crystals, α and β , there being a gap between the limiting composition of each type. An investigation of the heats of formation of the mixed crystals has shown that that of the β -crystals is positive, whilst that of the α -crystals is negative. The β -crystals are to be regarded as a solid solution of ammonium chloride in the double salt, and the α -crystals as a solid solution of the double salt in ammonium chloride. E. G.

Reversible Transformation of Emulsoid Solutions of Gum Arabic and Gelatin into the Suspensoid Condition and the Properties of these Systems. O. SCARPA (*Kolloid. Zeitsch.*, 1914, **15**, 8—10).—When ethyl alcohol is added gradually to an aqueous solution containing about 2% of gum arabic or gelatin, the liquid becomes opalescent, and ultramicroscopic observation indicates that the emulsoid has been transformed into a suspensoid. The change in question is reversible.

The colloidal particles of the suspensoid system move towards the positive pole in an electrical field, indicating that both gum arabic and gelatin are electro-negative colloids. The suspensoid solution of gum arabic is coagulated on the addition of most salts, acids, and bases, but a perfectly clear, non-opalescent solution is obtained by the addition of mercuric chloride. The opalescent solutions of gelatin are precipitated by mercuric chloride, copper sulphate, and ferric chloride, but most other electrolytes convert the suspensoid into an optically clear solution. The coagulation is in most cases reversible, and this holds also for the product which separates at the positive pole when an electric field is applied.

H. M. D.

Adsorption, Imbibition, and Osmotic Pressure of Colloids. M. POLÁNYI (*Biochem. Zeitsch.*, 1914, **66**, 258—268).—By means of a

thermodynamic cycle, the following relationships were deduced. When a gel is in equilibrium with a solution, $u = c/RT \cdot d\pi/dc$, where u is the amount of the dissolved substance concentrated in the gel, c the concentration of the solution, π the imbibition pressure of the gel, and R and T have the ordinary significance. The statement that has often been made, but not verified, that substances which favour imbibition are positively adsorbed, whereas those which inhibit imbibition are negatively adsorbed, is a strict law if certain premises are made. Such premises are fulfilled when the separation of the adsorbed substance can take place continuously, and the adsorption process is a reversible one. Accepting the same premises, substances which increase the osmotic pressure of colloids are positively adsorbed by the colloids, whereas those which diminish the osmotic pressure are negatively adsorbed. The following equation expresses the relation of a colloid to the solution, $v' = c/RT \cdot dp/dc$, where v' is the concentration of the substance in the colloid and p the osmotic pressure of the colloidal solution.

S. B. S.

Contraction Phenomena. RAPHAEL ED. LIESEGANG (*Kolloid. Zeitsch.*, 1914, **15**, 18—23).—An account is given of a number of peculiar structures, the development of which is attributed to the contraction in gels and other systems in which chemical interaction is accompanied by the formation of precipitation membranes. The formation of completely enclosed cavities and of cavities communicating with the exterior may result in this way, and the importance of these effects in the interpretation of certain geological configurations is emphasised.

H. M. D.

Reversible Reactions of Water on Iron and Ferrous Oxide. G. CHAUDRON (*Compt. rend.*, 1914, **159**, 237—239. Compare Sainte-Claire Deville, *ibid.*, 1870, **70**, 105; Preuner, A., 1904, ii, 317).—A study of the equilibrium between iron and water at temperatures between 300° and 1000°. An apparatus similar in principle to that of Sainte-Claire Deville's (*loc. cit.*) was used, the source of heat being an electric furnace. The equilibrium was determined for the system iron, water, hydrogen, ferrous oxide, and for the system ferrous oxide, water, hydrogen, magnetic oxide of iron. There are two series of equilibria: (1) iron and ferrous oxide; (2) ferrous oxide and magnetic oxide of iron.

W. G.

Mechanism of Irreversible Phenomena Deduced from the Boltzmann-Gibbs Law of Distribution. R. MARCELLIN (*J. Chim. phys.*, 1914, **12**, 451—460).—A theoretical paper in which results deduced by another method (A., 1911, ii, 27) are now obtained from the law of distribution of Boltzmann-Gibbs. It is shown (1) that a physico-chemical complex in process of transformation is made up of two systems which are changing in opposite directions, and consist of a system I, the mass of which is constantly increasing, and a system II, the mass of which is constantly decreasing. The velocity of change which is observed experiment-

ally is the resultant of these two changes, and is given by the formula $V = M[\exp(-A_1/RT) - \exp(-A_2/RT)]$, in which M is a constant depending on the temperature and the nature of the substance of the reacting system, A_1 and A_2 are respectively the affinities of the systems I and II, and V is the velocity at the time t . The velocity with which the opposing systems are destroyed is given as a function of the temperature by the expression $d \log_e v / dT = A/RT^2 + \alpha/RT + \beta/R$, in which the constants α and β are small in comparison with A . From the fact that a reaction does not take place instantaneously, the conclusion is to be drawn that the molecules capable of transformation are in an exceptional condition (critical condition), which is different from the mean condition. The energy necessary for converting a molecule in the mean condition into one in the critical condition is given by the expression $E = RT^2 \cdot d \log_e v / dT$. J. F. S.

Velocity of Catalysis of Butyric Acid by means of Thoria.

A. KOEHLER (*Bull. Soc. chim.*, 1914. [iv]. 15, 649—657).—A study of the conditions governing the catalytic influence of thorium oxide on the conversion of butyric acid into butyrene by heat, the catalyst being distributed on the surface of glass balls in a copper tube. The results show that the amount of acid converted into ketone in a given time by a given weight of thorium oxide is constant and independent of the velocity of flow of the acid vapour. The velocity of decomposition is also independent of the weight of the catalyst used, the surface being constant, but it is apparently a function of the surface offered by the catalyst, and is probably proportional to this surface. The velocity of decomposition diminishes on diluting the acid with an inert vapour, when this dilution passes a certain limit. W. G.

The Question of Associate Atoms. F. H. LORING (*Chem. News*, 1914, 110, 25—26).—It is supposed that the atoms of certain elements, the atomic weights of which seem to be invariable, are in reality composite, and contain two or more associate atoms in perfectly definite proportions. H. M. D.

Theory of Valency and Molecular Structure. WILLIAM C. ARSEM (*J. Amer. Chem. Soc.*, 1914, 36, 1655—1675).—The theory put forward in this paper is based on the conception of molecules and atoms as systems of moving electrons, and of valency as a consequence of the relative stability of these systems. For example, a binary molecule composed of two univalent atoms is regarded as a stable system formed of two systems of moving electrons, the dynamic equilibrium being such that one electron oscillates periodically from one system to the other, and is common to both systems, neither of which is complete in itself. The oscillating electron is termed the "valence electron." Valency is thus the property or power which an atom possesses of sharing a certain number of electrons with one or more other atoms in such a way that the atoms so united form a complete or perfect electron system

which is electrically neutral. This theory is developed and applied to the explanation of the mechanism of chemical reactions, tautomerism, conductivity of metals, association, and dissociation and conductivity in electrolytes and gases. E. G.

An Efficient Stirring Apparatus. WILHELM GLUUD and RICHARD KEMPF (*J. Soc. Chem. Ind.*, 1914, **33**, 680).—The aim of the construction is to meet as many needs as possible with one apparatus. It consists of a flask of 1500 c.c. capacity, constricted somewhat at the base so as to be equally efficient for small quantities of liquid. It is fitted with a hollow, ground-glass stopper, through which the stirring rod passes, with a condenser, and with a dropping funnel. The absence of rubber stoppers makes it suitable for nitrations, etc., and the whole apparatus may be heated in an oil bath without risk of fracture. A pear-shaped trap, which is filled with paraffin oil or other suitable liquid, is fused on to the stirring rod in the flask, and an extension of the stopper dips into it, so as to seal off the interior of the flask from the metal fittings of the stopper and upper portion of the stirring rod. The apparatus is easily detachable for cleaning purposes. G. F. M.
