

## General and Physical Chemistry.

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### Measurements in the Arc Spectrum of Iron for the Purpose of Determining Tertiary Normals.

SOPHIE HOELTZENBEIN (*Zeitsch. wiss. Photochem.*, 1917, **16**, 225—251).—Making use of a concave grating, 4 metres radius and 3960 lines per centimetre, the author has re-measured the iron arc spectrum over the range  $\lambda\lambda$  5658—4859 in the third order spectrum,  $\lambda\lambda$  4315—3513 in the fourth order spectrum, and  $\lambda\lambda$  3513—2987 in the fifth order spectrum. Long tables of the wave-length and intensity of the measured lines are given, and an accuracy of about 0.001 Å. is claimed for the values of the wave-lengths. A comparison of the present results with those of Gale and Adams (*Astrophys. J.*, 1912, 35) and St. John and Ware (*ibid.*, 1912, **36**, 14, 203) has been made, and it is shown that very many lines may be used as tertiary normals, and further, that among the lines chosen as tertiary normals very great divergencies are to be observed in the values of the different observers, and consequently more work is necessary before the tertiary normals can be finally chosen. J. F. S.

**Series System in the Spectrum of Gold.** W. M. HICKS (*Phil. Mag.*, 1919, [vi], **38**, 1—31).—A theoretical discussion of the series systems of the gold spectrum. It is shown that a *D* set corresponding with order  $m=1$  exists, which extends far in the ultra-red, and the satellite mantissa of which conforms to the general rule of being a multiple of  $\Delta$ . Gold, therefore, does not constitute an exception, as formerly appeared to be the case. It is indicated that summation lines for the *P* and *S* series exist. In general, such lines for *S* and *P* will lie far down in the ultra-violet, and this is, no doubt, one reason why they have not been previously recognised. The evidence given in the paper must be supported by further numerical coincidences obtained in other spectra before it is to be regarded as conclusive, but it is sufficient to render it extremely probable. The more accurate determination of the  $\delta$  depending on  $81\delta = \Delta = 113951 - 6p$ , where 0.1p Ångström is an observational error, has been carried out. This result gives  $\delta = 1406.802 - 0.074p$ . Taking the ratio of  $\delta : (W/100)^2$ , where *W* is the atomic weight, to be  $361.75 + 0.05q$ , the resulting value of the atomic weight of gold is  $197.2024 - 0.0052p - 0.0136q$ . J. F. S.

**The Constitution of the Atom and the Properties of Band Spectra.** H. DESLANDRES (*Compt. rend.*, 1919, **169**, 593—599. Compare this vol., ii, 310).—A mathematical discussion in which the author shows that band spectra may be considered as formed by longitudinal and transverse vibrations, the exact part which each plays not being, as yet, fully determined. Two formulæ are deduced which account for the known facts, their

interpretation admitting of longitudinal and transverse vibrations in the atom and molecule, analogous to those in solids. W. G.

**The Conditions of Excitation of Fluorescence.** L. BRUNINGHAUS (*Compt. rend.*, 1919, **169**, 531—534).—The phenomena of phosphorescence and fluorescence are characterised by the fact that the maximum effect is obtained when the solution is very dilute and the exciting radiation only very feebly absorbed.

W. G.

**Photochemical Change in the System  $\text{SO}_2\text{Cl}_2 = \text{SO}_2 + \text{Cl}_2$  under the Influence of Light Rays of Definite Wave-length.**

M. LE BLANC, K. ANDRICH, and W. KANGRO (*Zeitsch. Elektrochem.*, 1919, **25**, 229—251).—A long series of experiments are described which are designed to furnish answers to the questions arising from the following case. Given an homogeneous gaseous system,  $A + B \rightleftharpoons C$ , which is sensitive to light and such that the absorption spectra of  $A$ ,  $B$ , and  $C$  respectively do not overlap one another, and which has a zero velocity when in the dark, does the whole system become sensitive to light if it is subjected to light which is absorbed by only one constituent, and, if so, to what extent does the reaction proceed in the direction of  $C$ ? The case  $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$  has been examined with the object of answering the questions. The absorption spectra of sulphur dioxide, chlorine, and sulphuryl chloride have been determined at a series of pressures, and it is shown that chlorine absorbs all light from the visible region to the middle ultra-violet, and has a maximum at  $340 \mu\mu$ ; sulphur dioxide has an absorption maximum at  $290 \mu\mu$  and a minimum at  $240 \mu\mu$ ; sulphuryl chloride vapour absorbs light from  $300 \mu\mu$  upwards. Experiments on the decomposition of sulphuryl chloride by light at a series of temperatures, the formation of gaseous sulphuryl chloride, and the formation of liquid sulphuryl chloride are described. It is shown that in the reaction  $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$  the formation of secondary products does not occur to the extent of 10%. The illumination of sulphuryl chloride by light, which is practically only absorbed by this substance, brings about quantitative decomposition at both  $55^\circ$  and  $100^\circ$ . The concentration has apparently no influence on the course of the reaction. When the system  $\text{SO}_2 + \text{Cl}_2$  is illuminated with light which is absorbed by sulphur dioxide, only a slight reduction of pressure takes place; this is not due to the formation of sulphuryl chloride, but to a side reaction. When the same system is illuminated by light which is only absorbed by chlorine, the formation of sulphuryl chloride takes place until, after a time, a stationary condition is set up. The velocity and also the position of the stationary condition depend, at constant temperature, on the presence of a small quantity of water, and the higher the temperature the earlier the stationary condition is reached. In a number of cases a reversal is noted, so that the stationary condition does not come at the end of diminution of pressure, but of an increase in pressure. At the temperatures  $105^\circ$  and  $125^\circ$ , at which the equili-

brium in the dark is known, the stationary condition lies more to the side of sulphuryl chloride than in the non-illuminated reaction. Under none of the experimental conditions do the two points coincide. The lower the temperature the further apart are the end-points of the illuminated and the non-illuminated reactions. The temperature-coefficient of the formation of sulphuryl chloride from chlorine and sulphur dioxide by light which is only absorbed by chlorine is small, and has little influence on the course of the reaction.

J. F. S.

### Photochemical Reactions of Compounds of Less Common Elements. II.

ALFRED BENRATH (*Zeitsch. wiss. Photochem.*, 1917, **16**, 253—261. Compare A., 1915, ii, 504).—An aqueous solution of ammonium molybdate when diluted with an equal volume of either ethyl alcohol or methyl alcohol and exposed to sunlight changes to blue after a short exposure and a reddish-brown substance is deposited on the side of the flask on which the light falls. This compound has the formula  $(\text{NH}_4)_2\text{MoO}_4 \cdot 2\text{MoO}_3 \cdot 2\text{MoO}_2 \cdot 6\text{H}_2\text{O}$ . In this formation only the complex added group,  $\text{MoO}_3$ , and not the neutral ammonium molybdate is reduced. Colloidal molybdic acid is rapidly reduced by alcohol to the blue oxide,  $\text{Mo}_3\text{O}_8$ . Neutral sodium tungstate is only slowly reduced by alcohol in sunlight, so that after a period of five months' exposure to light only a faint blue colour is produced. On the other hand, suspensions of tungstic acid and acidified solutions of tungstates become deep blue in colour when mixed with alcohol and exposed to sunlight for a few hours. The greenish-yellow powder deposited when uranyl chloride dissolved in ether is exposed to sunlight has been examined and found to have the formula  $\text{UOCl}_2$ , and the similar precipitate obtained by exposing an aqueous solution of uranyl nitrate containing a little alcohol to sunlight is  $\text{UO}_2(\text{NO}_3)_2$ .

J. F. S.

### The Relation between Uranium and Radium. VII.

FREDERICK SODDY (*Phil. Mag.*, 1919, [vi], **38**, 483—488. Compare Soddy and Hitchens, A., 1915, ii, 726).—The subsequent growth of radium in the old uranium preparations, since they were last tested in 1915, has confirmed the earlier result that the growth is proceeding according to the square of the time, and that the product of the two periods of average life of ionium and radium is, to an accuracy of some 5%, 237,500,000 years. Assuming the period of radium to be 2375 years, that of ionium is 100,000 years. It is not to be expected that this period will be determined with much greater accuracy, as the result of subsequent measurements upon these preparations.

F. S.

### Electrical Conductivity and Other Properties of Saturated Solutions of Copper Sulphate in the Presence of Sulphuric Acid.

H. M. GOODWIN and W. G. HORSH (*Chem. and Met. Eng.*, 1919, **21**, 181—182).—The specific electrical conductance at 25° of saturated solutions of copper sulphate contain-

ing sulphuric acid from 0.15 to 3.6 equivalents per litre has been determined, using the customary Wheatstone bridge arrangement with alternating current. The solutions were rotated in a constant temperature bath and the measurements continued until constant, which indicated saturation. The constant of the conductivity cell was determined by measuring the conductivity of normal potassium chloride solution and a solution of sulphuric acid of maximum conductivity. The results, accurate to 0.5%, show that the conductivity increases, following a straight-line law with increasing concentration of sulphuric acid. The solubility of copper sulphate in the presence of sulphuric acid is determined by electro-analysis. The concentration of copper sulphate at the saturation point falls continuously with increase of concentration of sulphuric acid up to 4 equivalents per litre. The acid content of the solutions was determined by titrating with standard sodium hydroxide solution in the presence of copper sulphate, using methyl-orange as an indicator. The density of the solutions was measured by means of a Mohr-Westphal balance. The density first falls with increasing sulphuric acid content and then increases rectilinearly with a minimum at about 0.5 equivalent per litre. T. H. B.

**Applicability of the Precipitated Silver-Silver Chloride Electrode to the Measurement of the Activity of Hydrochloric Acid in Extremely Dilute Solution.** G. A. LINHART (*J. Amer. Chem. Soc.*, 1919, **41**, 1175—1180).—Measurements of the *E.M.F.* of cells of the type  $\text{Ag}, \text{AgCl} | \text{HCl} | \text{H}_2\text{Pt}$  have been carried out for concentrations of hydrochloric acid varying between 0.04826*N* and 0.000136*N*. The cell was made up in a single vessel, consisting of a bulb of about 1200 c.c. capacity fitted with fairly narrow tubes at the top and bottom. The bottom tube contained the silver-silver chloride electrode, and here a current of hydrogen entered just above the electrode; the top tube contained the hydrogen electrode of iridium coated platinum, and above the electrode was an exit tube for the hydrogen. The silver-silver chloride electrode consisted of a layer of fine-grained electrolytic silver covered with a layer of precipitated silver chloride. After filling, the cell was placed in a thermostat and kept at a temperature of  $25^\circ \pm 0.01^\circ$  for three to four days to come to equilibrium, and then the *E.M.F.* measurements were made over a considerable period of time until constant values were obtained. The following values of the *E.M.F.* for a hydrogen pressure of 1 atm. are obtained:  $\text{HCl}$ , 0.04826*N*, 0.3874 volt; 0.00965*N*, 0.4658 volt; 0.004826*N*, 0.5002 volt; 0.001000*N*, 0.5791 volt; 0.000483*N*, 0.6161 volt; 0.000242*N*, 0.6514 volt; and 0.000136*N*, 0.6805 volt. The *E.M.F.* is calculated to molecular concentration of hydrogen and chloride ions on the assumption of complete ionisation; these values extrapolated at infinite dilution yield the value 0.2234 volt, from which the degree of dissociation is calculated for each dilution. J. F. S.

**Transport Number of Chromic Ions in Violet Chloride Solutions.** KARL HOPFGARTNER (*Monatsh.*, 1919, **40**, 259—269).—The transport number of the chromic ion in hydrochloric acid solu-

tions of violet chromic chloride has been determined by the Hittorf method. The determinations were effected with solutions of three concentrations (1.00, 0.32, and 0.075 equivalent). The transport numbers found were  $0.318 \pm 0.005$ ,  $0.357 \pm 0.003$ , and  $0.414 \pm 0.005$  respectively, which extrapolate to the value 0.446 for the concentration zero, and lineally extrapolate to 0.430. From these values the mobility of the chromic ion is estimated by various methods as 53, 49.5, and 46.3, and of these the first value is probably too high. The results indicate that the chromic ion is surrounded by a fairly large water sheath, although the various methods of calculating the magnitude of this give results which vary considerably.

J. F. S.

**Anodic Peroxidation of Manganese in an Acid Medium in Presence of Silver Salts.** ARMANDO RUSCONI (*Arch. farm. sper. sci. aff.*, 1919, **27**, 94—96).—When 30% sulphuric acid containing a small proportion (0.05%) of manganous sulphate is electrolysed in a U-shaped voltameter with a potential difference of 5—6 volts, the formation of traces of permanganic acid at the anode is observable after a few minutes. If, however, the solution contains also a few drops of saturated silver sulphate solution, the formation of permanganic acid at the anode is immediate and rapid. Similar results are obtained if the sulphuric acid is replaced by concentrated sodium hydrogen sulphate solution (compare Marshall, A., 1901, ii, 156; Scagliarini and Casali, A., 1913, ii, 181).

T. H. P.

**Flowing Metal Vapour Arcs.** EMIL PODSZUS (*Zeitsch. Elektrochem.*, 1917, **23**, 179—181).—A metallic vapour arc is described which will burn steadily and continuously in any atmosphere. The lamp consists of a large globe of glass or quartz open at the bottom and fitted with a narrow exit tube at the top. The wide opening at the bottom stands in an iron dish containing mercury, and through the bottom of which are three openings. A narrow glass tube for admitting gas passes through the first; the second opening admits the cathode vessel, and the third the anode vessel. The cathode vessel is made of iron, and down the middle of it a tube of boron nitride passes; covering the top of the cathode is a plate of tungsten perforated by a narrow opening in the centre. The object of the boron nitride tube and the tungsten plate is to stabilise the arc and to prevent fluctuations of the mercury or amalgam which constitutes the cathode. The anode is a tungsten rod. The arc is struck by lowering the anode until it touches the cathode and then drawing it away. The arc produced is a thin, quiet flame, which is affected in colour by the gases in the globe and by the metal used as cathode. In hydrogen the light is greenish-white; in nitrogen bluish-white. All compound gases introduced into the arc were reduced; thus the solid element was obtained from boron trichloride and titanium tetrachloride, whilst calomel was also produced.

J. F. S.

**A New Method for the Rapid Determination of Critical Temperatures. Application to Carbonyl Chloride.** L.

HACKSPILL and MATHIEU (*Bull. Soc. chim.*, 1919, **25**, 482—485).—A simple apparatus for the determination of critical temperatures consists of a cylinder of aluminium or copper about 25 cm. long and 5 cm. in diameter wound throughout its entire length with nickel wire, by which it is heated electrically. The liquid to be examined, contained in a thick glass tube, is placed in a hole in the axis of the cylinder, and can be viewed through a longitudinal slit in the cylinder. A second hole parallel to the first is provided for a thermometer. The critical temperature of carbonyl chloride was found to be  $183 \pm 0.5^\circ$  with this apparatus.

E. H. R.

**The Critical Temperature as a Single Function of the Surface Tension. II.** MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1919, **17**, 325—328. Compare this vol., ii, 183). The author deduces, on theoretical grounds, the equation, previously put forward (*loc. cit.*), connecting the surface tension with the critical temperature. The relationship is verified in the case of a number of organic liquids.

J. F. S.

**The Equation of State of Ethyl Formate.** E. ARIÈS (*Compt. rend.*, 1919, **169**, 602—605).—The equation of state of ethyl formate, like that of ethyl acetate (compare this vol., ii, 360), satisfactorily represents the thermal properties of this fluid, except in so far as concerns the heat of vaporisation and the density of the vapour over a temperature range extending from the critical temperature to  $35^\circ$  below it.

W. G.

**Standardisation of the Sulphur Boiling Point.** E. F. MUELLER and H. A. BURGESS (*J. Amer. Chem. Soc.*, 1919, **41**, 745—763).—The boiling point of sulphur as a standard temperature has been investigated and the conditions under which it should be determined examined. The suggestion that the reflecting power of the inner surface of a radiation shield may influence the temperature assumed by a resistance thermometer is confirmed. A number of shields, both of glass and porcelain, have been examined, and several satisfactory forms are described. The influence of the type of boiling apparatus on the observed temperature is found to be very small. The presence of 0.05% of arsenic in the sulphur has no effect on the boiling point, but 0.10% raises the boiling point  $0.02^\circ$ , 0.05% of selenium, together with 0.10% of arsenic, raises the boiling point  $0.08^\circ$ , and 0.10% of arsenic and 0.10% of selenium raises the boiling point  $0.09^\circ$ . The boiling point of pure sulphur at 760 mm. pressure is  $421.73^\circ$ . The vapour pressure over the range 700 mm. to 800 mm. has been redetermined, and from these values an equation for calculating the boiling point at various pressures is deduced. This has the form  $t = 444.60 + 0.0910(p - 760) - 0.000049(p - 760)^2$ . A resumé of the conditions to be observed in determining the boiling point of sulphur for standardisation purposes is appended to the paper.

J. F. S.



**Determination of Boiling Points of Solutions.** F. G. COTTRELL (*J. Amer. Chem. Soc.*, 1919, **41**, 721—729).—A modified boiling-point apparatus is described for solutions whereby the conditions obtaining in the determination of the boiling point of pure liquids are imitated. In the present method, the Beckmann thermometer is placed in the vapour phase and the bulb coated with a thin film of the boiling liquid. The coating of the bulb with the boiling solution is effected by means of a narrow glass tube, which is placed in the liquid; this tube is funnel-shaped at the bottom and sealed at the top, but with a lateral hole just above the bulb of the thermometer. When the liquid boils, bubbles of vapour pass up the tube and carry boiling liquid into a cup through a loosely fitting opening in which the stem of the thermometer passes, the liquid flows over the bulb, and slowly drips back into the solution. It is claimed that this arrangement entirely removes errors due to superheating and yields accurate results extremely readily. J. F. S.

**Laws of Concentrated Solutions. VI. The General Boiling-point Law.** EDWARD W. WASHBURN and JOHN W. READ (*J. Amer. Chem. Soc.*, 1919, **41**, 729—741).—The boiling points of concentrated solutions of naphthalene and diphenyl in benzene have been determined by means of the Cottrell boiling-point apparatus (preceding abstract). In the determinations, two pieces of apparatus were used, in one of which the pure solvent was kept continually boiling, and in the other the solution, so that the elevation of the boiling point was read directly and was independent of slight pressure changes. The apparatus was further modified by the addition of a side-tube, from which quantities of the solution were extracted for analysis. In the present case, the analysis consisted in determining the density of the solution at 25° and calculating the composition by means of an empirical equation connecting density and composition. The boiling-point law for ideal solutions and the connexion between the boiling-point elevation and the barometric pressure are considered. It is also shown how the molecular weight of a dissolved substance which undergoes solvation may be calculated from the elevation of the boiling point. J. F. S.

**Molecular-weight Determination by Direct Measurement of the Lowering of the Vapour Pressure of Solutions.** ROBERT WRIGHT (T., 1919, **115**, 1165—1168).

**The Evaporation of Concentrated and Saturated Solutions of Ammonium Nitrate, Vapour Pressures, Heats of Solution, and Hydrolysis.** E. B. R. PRIDEAUX and R. M. CAVEN (*J. Soc. Chem. Ind.*, 1919, **38**, 353—355r).—The vapour pressures of 47·8%, 60·4%, and saturated solutions of ammonium nitrate have been measured between 40° and 100°. In 60·4% solutions, which are about saturated at the ordinary temperature, the pressure still rises rapidly with rise of temperature, but the

pressures of saturated solutions are low, being no more than 17 cm. at 100°. The heats of evaporation, calculated from the vapour pressures, are, in the case of unsaturated solutions, about 50 cal. lower than that of water at the same temperature, and appear to reach a maximum at some temperature between 60° and 70°. The maximum is more pronounced with saturated solutions, occurring at about 60° with a latent heat of 400 to 450 cal.

When ammonium nitrate solutions are evaporated in contact with iron, there is considerable loss of ammonia and corrosion of the iron by the hydrolytic nitric acid. In acid-resisting vessels or vessels of aluminium, the loss of ammonia through hydrolysis is almost entirely obviated.

E. H. R.

**Improved Apparatus for the Estimation of Vapour Pressures.** ALLAN MORTON (*J. Soc. Chem. Ind.*, 1919, **38**, 363—364r).—Difficulties having arisen in the determination of the vapour pressures of certain organic liquids on account of the solvent action of these liquids on the lubricants employed for the stopcocks, an apparatus was devised in which taps were entirely avoided. The apparatus took the form of a U-shaped barometer with a bottom mercury reservoir. To the top of each barometer tube was fused a capillary tube, which was bent downwards with its end dipping into a mercury cup. The mercury having been thoroughly cleaned and dried, a sample of the liquid of which the vapour pressure was to be determined was placed in one of the two mercury cups, and, by suitable manipulation of the bottom reservoir, drawn up into one of the arms of the barometer. The difference between the mercury levels in the two arms was a measure, of course, of the vapour pressure.

E. H. R.

**The Vapour Pressures of Mixtures of Ether and Sulphuric Acid.** ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, **14**, 280).—A correction to some remarks made by the author in a discussion on a paper by F. H. Campbell (*A.*, 1916, ii, 83).

E. H. R.

**Use of Coal as a Substitute for Talcum to Induce Rapid Boiling.** E. C. KENDALL (*J. Amer. Chem. Soc.*, 1919, **41**, 1189—1190).—Small, compact pieces of anthracite serve excellently for bringing about rapid boiling of liquids and solutions, and also for preventing the bumping in Kjeldahl flasks. Powdered anthracite has not the same action, and anthracite which has been kept in water for some time loses its efficacy, but after baking for some time the efficacy is regained.

J. F. S.

**The Occlusion of Gases by Metals. Introductory Address to General Discussion.** SIR ROBERT HADFIELD (*Trans. Faraday Soc.*, 1919, **14**, 173—191).—A historical account of the subject, with special reference to the effect of occluded gases in steel castings. A bibliography is appended.

E. H. R.



### General Remarks on Occlusion of Gases in Metals.

ALFRED W. PORTER (*Trans. Faraday Soc.*, 1919, **14**, 192—197).—The term "occlusion" probably covers a number of different phenomena which may take place either singly or in conjunction. These can be enumerated under six heads: first, chemical combination of gas with metal, for example, hydrogen with sodium, potassium, or palladium; secondly, simple solid solution, either separately or in conjunction with the first; thirdly, solid solution in contiguous phases; fourthly, solution accompanied by surface adsorption; fifthly, surface condensation under molecular forces, unaccompanied by solution; sixthly, inclusion, as when large or minute bubbles become entangled in the molten, viscous mass. The work of earlier investigators on occlusion, particularly the occlusion of hydrogen by palladium, is discussed from the point of view of this classification of the phenomena. The influence of condensed gases on the Volta effect is also discussed. E. H. R.

### The Physical Properties of Metals as Affected by their Occluded Gases.

COSMO JOHNS (*Trans. Faraday Soc.*, 1919, **14**, 198—201).—To explain the profound effect of occluded gases on the physical properties of metals, for instance, the rendering brittle of iron or copper by hydrogen, the following theory is proposed. As a working hypothesis, it is assumed that hydrogen is soluble in the molten metals, but insoluble in the solid, and the theory is adopted that the tenacity of solid metals and the strength of the crystal boundaries are due to the presence of amorphous material, that is, an under-cooled liquid, which serves to cement the crystal grains which compose the solid mass. This intercrystalline matter must contain more hydrogen in solution than the solid metal can hold, and it is therefore at the crystal boundaries that the change in properties occurs, and the brittleness of the whole mass is explained. Relatively small quantities of gas dissolved in the intercrystalline material might thus cause profound changes in the properties of the metal.

The carbon monoxide and carbon dioxide found occluded in steel are probably formed by interaction of dissolved oxide of iron and carbon at the particular temperature when iron oxide, being thrown out of solution as freezing progresses, becomes concentrated in the mother liquor between the growing crystals and reacts with the carbon which has not suffered the same concentration. The gases would thus become concentrated in the intercrystalline layers, and would have the same effect as the hydrogen in copper and iron. Such data as are available on the physical properties of metals or alloys all refer to metals containing unknown quantities of occluded gases, which may profoundly modify their properties, and consequently knowledge of the properties of pure metals, if such can be obtained, is lacking. E. H. R.

### Theories of Occlusion: the Sorption of Iodine by Carbon.

J. W. MCBAIN (*Trans. Faraday Soc.*, 1919, **14**, 202—212).—The term "sorption" is employed to include the phenomena of adsorp-

tion, absorption or true solid solution, and chemical reaction, all of which may accompany the fixation of a gas by a solid, and the occlusion of gases by metals is considered as a special instance of the process of sorption. The three processes involved in the phenomenon of sorption differ widely in their time relationships. True adsorption is nearly instantaneous, whilst absorption should obey Fick's diffusion law, commencing with a very high velocity for the first few moments and rapidly falling off with time. Chemical reaction may show the most varied time relationships, since it often proceeds vigorously in surface films as well as in solid solution. Since the occlusion of gases is hastened by rise of temperature, it is reasonable to conclude that the phenomena involved are largely those of diffusion, that is, of absorption rather than adsorption, whilst chemical reaction may play a prominent part.

It was shown by Davis (T., 1907, **91**, 1666) that the sorption by carbon of iodine dissolved in benzene, toluene, and other solvents consists of a surface condensation and a diffusion into the interior. The surface condensation is nearly instantaneous, whilst the diffusion proceeds for weeks or months. After an interval of eleven years, the experiments set up by Davis have been re-examined, and the sorption due to the slow diffusion of the iodine into the charcoal is found to be still continuing. Fresh experiments extending over four years have also confirmed Davis's results.  
E. H. R.

**Balanced Reactions in Steel Manufacture.** ANDREW McCANCE (*Trans. Faraday Soc.*, 1919, **14**, 213—223).—A discussion of the equilibrium conditions in the open-hearth furnace during the manufacture of steel. The distribution of ferrous oxide between the steel and the slag and the influence of the furnace gases are particularly considered.  
E. H. R.

**A Few Suggestions on the Theories of Occlusion of Gases by Metals.** J. H. ANDREW (*Trans. Faraday Soc.*, 1919, **14**, 232—239).—From a consideration of the experimental evidence available, it is concluded that the occlusion of hydrogen by palladium is dependent on the presence of the active, amorphous form of the metal. Palladium in the crystalline state, free from contamination by the amorphous phase, is inactive towards hydrogen in the cold, but can be rendered active by continually pumping in and extracting gas from the metal, this treatment giving rise to the amorphous form. An amorphous layer of the metal will act as a vehicle for conveying the gas into the crystalline metal, the adsorbed layer of gas acting as a layer of extreme concentration and exerting the same effect as a high external pressure. In the occlusion of hydrogen by iron, the amorphous phase, in this case the intercrystalline cement, probably plays a prominent part. For instance, when a piece of wrought iron is immersed for some time in a saturated solution of sodium hydroxide at 100°, the mass becomes brittle, because the gas is absorbed

more rapidly in the amorphous intercrystalline layers than by the crystals themselves, and the expansion of these layers forces the crystals apart and weakens their cohesion. After remaining longer in the sodium hydroxide, the iron loses its brittleness, because the hydrogen gradually diffuses into the crystals from the intercrystalline cement. Electrolytic iron, being already saturated with hydrogen, is unaffected by sodium hydroxide. It is concluded that diffusion and occlusion are more or less identical, and can be explained by simple physical laws without reference to chemical combination.

E. H. R.

**Solutions.** A. REYCHLER (*J. Chim. Phys.*, 1919, **17**, 209—265).—A theoretical paper in which many of the properties of solutions are considered. On the basis of Perrin's value of  $N$ , the Avogadro number, it is calculated that the mean kinetic energy of one molecule at  $0^\circ$  is  $0.5 \times 10^{-13}$  ergs, and that the charge  $e$  of one electron is  $4.2 \times 10^{-10}$  electrostatic units. An explanation of the mechanism of osmotic pressure is evolved, and a method of interpreting certain anomalies observed in osmotic pressure values is indicated. The author has developed the formulæ for calculating molecular weights from boiling-point elevations and freezing-point depressions on the basis of the vapour pressure formula. The nature of ionisation is considered, and it is shown that the ionic equilibrium is a condition of balance between the disruptive forces of the water and the attractions of the ions for one another, which, being of an electrical character, are never entirely eliminated, since they can act over a distance. A connexion is established between ionisation and an adsorption phenomenon. The reasons for the variation of the index in the dissociation laws of Storch and Noyes are considered.

J. F. S.

**Unique Case of a Liquid that Exhibits a Minimum Solubility in an Unstable Region.** MARSTON TAYLOR BOGERT and JACOB EHRLICH (*J. Amer. Chem. Soc.*, 1919, **41**, 741—745).—On cooling a clear solution of the monohydrate of 3:5-dimethoxyacetophenetidide in boiling water, there appeared a cloud of minute drops, which disappeared on further cooling, with the formation of a clear solution; from this, on continued cooling, white crystals eventually separated. To ascertain the nature of this behaviour, the solubility of this compound has been determined over the temperature range  $21.8$ — $173.6^\circ$ . It is shown that the solubility increases with rise of temperature up to  $87.5^\circ$ , when the solid in contact with the solution melts. The solubility of the liquid hydrate increases more rapidly with further rise of temperature. Below  $87.5^\circ$ , the solubility of the liquid hydrate decreases with falling temperature until a point somewhere between  $68.5^\circ$  and  $58.1^\circ$  is reached, when it again increases. Hence the liquid hydrate has a minimum solubility at about  $63^\circ$ . The following solubilities in molecular percentages are recorded. (1) The solid hydrate:  $21.8^\circ$ , 0.010;  $39.4^\circ$ , 0.020;  $57.0^\circ$ , 0.046;  $69.5^\circ$ , 0.076;  $72.8^\circ$ , 0.091;  $77.1^\circ$ , 0.120;  $80.2^\circ$ , 0.151;  $84.2^\circ$ , 0.203;  $86.0^\circ$ , 0.237;

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86.9°, 0.257. (2) The liquid hydrate: 35.6°, 0.301; 45.6°, 0.257; 58.1°, 0.237; 68.5°, 0.237; 84.3°, 0.257; 99.8°, 0.303; 111.1°, 0.361; 118.4°, 0.407; 129.2°, 0.499; 173.6°, 2.041. J. F. S.

**Intermediate and Complex Ions. V. The Solubility Product and Activity of the Ions in Bivalent Salts.** WILLIAM D. HARKINS and H. M. PAINE (*J. Amer. Chem. Soc.*, 1919, **41**, 1155—1168. Compare A., 1917, ii, 77).—In previous papers (*loc. cit.*) it is shown that salts of tri-ionic and higher types ionise in steps and give, even in 0.1*N*-solutions, a large number of intermediate ions. In the present paper, the ionisation of salts composed of a bivalent cation and anion are considered. For this purpose, the solubility of calcium sulphate in water, and in solutions of copper sulphate, magnesium sulphate, and potassium nitrate, has been determined at 18° and 25°. The equivalent conductivity of various concentrations of the four salts and of the solutions of calcium sulphate in the others has been determined at the same temperatures, as well as the densities. The results show that the solubility relations of calcium sulphate when common ions are added are very similar to those of the higher type salts. This indicates the probability that complex ions, such as  $\text{Ca}(\text{SO}_4)_2$  and  $\text{Ca}_2\text{SO}_4$  are present in the solutions. These complex ions differ from what are usually considered under this title, since they are present to a considerable extent in dilute solutions, so in this sense they are more like intermediate ions. If it is assumed that such complex ions are absent, the solubility product, calculated on this basis, is found to increase with great rapidity as the concentration increases; thus, if the total ion concentration increases from 0.02*N* to 0.10*N*, the solubility product is trebled, so, if only simple ions are present, this activity decreases very rapidly with an increase in concentration. On the other hand, the solubility found for the un-ionised part, on the basis of this assumption, remains much more constant than in the case of uni-univalent salts. The change in the slope of these curves is in the direction which is to be expected if complex ions are present. The percentage concentration of such complexes is much higher in copper sulphate solutions than in magnesium sulphate solutions at the lower concentrations. J. F. S.

**Reciprocal Solubility of Mixtures of Water, Alcohol, and Ether.** A. BOUTIN and A. SANFOURCHE (*Bull. Soc. chim.*, 1919, [iv], **25**, 458—463).—The solubility of water in ether varies but little with temperature, but that of ether in water falls from 12.2% at -3.3°, the freezing point of water saturated with ether, to 4.0% at 35°. By adding one constituent to mixtures of the other two of known composition at 15° until two layers were just formed or just disappeared, limiting values were obtained for a series of ternary mixtures of varying composition. The results are conveniently plotted on a triangular diagram, each corner representing 100% of one constituent. A curve is obtained dividing the triangle into two zones, the one representing homogeneous and the other

heterogeneous mixtures. By drawing tangents to the curve from the points representing pure ether and pure water, the homogeneous zone is divided into six areas. One of these represents mixtures which cannot be made heterogeneous by addition of one constituent; two represent those which can only be made heterogeneous by addition of ether; two others represent those which can only be made heterogeneous by addition of water; whilst the last area represents mixtures which can be separated into two layers by either water or ether. No homogeneous mixture can be made heterogeneous by addition of alcohol alone. E. H. R.

**Crystal Lattices and Bohr's Atom Model.** L. VEGARD (*Ber. deut. physikal. Ges.*, 1919, **21**, 383—385).—A short criticism of a paper by Born and Landé (this vol., ii, 188), in which the author states that some of the views expressed in the paper, and others attributed to Sommerfeld (A., 1918, ii, 303) were in reality put forward by him at an earlier date (A., 1918, ii, 93, 94, 144), and in consequence he claims priority. J. F. S.

**Crystal Lattices and Bohr's Atom Model.** M. BORN and A. LANDÉ (*Ber. deut. physikal. Ges.*, 1918, **21**, 385—387. Compare preceding abstract).—An answer to Vegard's criticism (*loc. cit.*), in which the authors allow the priority claim in some respects, but maintain their own in others. J. F. S.

**An Experiment Relating to Atomic Orientation.** T. R. MERTON (*Phil. Mag.*, 1919, [vi], **38**, 463—464).—On the two assumptions, first, that the axes at right angles to the planes of the rings of electrons in the atom are orientated in a regular manner in a crystal structure, and, secondly, that the direction of expulsion of  $\alpha$ - and  $\beta$ -particles from a radioactive atom is also related in some regular manner to this atomic axis, there should be a difference in the  $\alpha$ - and  $\beta$ -activities of different faces of certain crystals of radioactive substances. The  $\alpha$ -activities of three different faces of large crystals of uranium nitrate have been tested and found to be the same within the error of measurement, so showing that at least one of the two assumptions is incorrect. It is considered the more probable that the  $\alpha$ -rays are shot out of the nucleus without regard to the orientation of the atomic axis. F. S.

**Colloid Chemistry and its General and Industrial Applications. Second Report.** F. G. DONNAN, W. C. M. LEWIS, E. F. ARMSTRONG, ADRIAN J. BROWN, C. H. DESCH, E. HATSCHEK, H. R. PROCTER, W. RAMSDEN, A. S. SHORTER, H. P. STEVENS, and H. B. STOCKS (*Rep. Brit. Assoc.*, 1918, 1—172).—The present report consists of articles on the following subjects: (i) Peptisation and precipitation (pp. 15), Wilder D. Bancroft; (ii) Emulsions (pp. 5), E. Hatschek; (iii) The Liesegang phenomenon (pp. 5), E. Hatschek; (iv) Electrical endosmose, I. (pp. 14), T. R. Briggs; (v) Electrical endosmose, II. (pp. 14), T. R. Briggs: this article deals with de-watering of peat and clay, electrical tanning, preservation of

timber, manufacture of bricks and electro-therapeutics; (vi) Colloid chemistry in the textile industries (pp. 18), W. Harrison; (vii) Colloids in agricultural phenomena (pp. 12), E. J. Russell; (viii) Sewage purification (pp. 15), E. Ardern; (ix) Colloid problems in dairy chemistry (pp. 22), W. Clayton; (x) Colloid chemistry in physiology (pp. 38), W. M. Bayliss; (xi) Administration of colloids in disease (pp. 18), A. B. Searle.

J. F. S.

**Vibration and Syneresis of Silicic Acid Gels.** HARRY N. HOLMES, WILFORD E. KAUFMANN, and HENRY O. NICHOLAS (*J. Amer. Chem. Soc.*, 1919, **41**, 1329—1336).—The tones produced by vibrating silicic acid gels have been investigated. Silicic acid gels were made which on tapping in thin-walled glass tubes produced a tone two octaves above middle *C*. Such gels vibrate as rigid solids, but tension is an important factor. That the gels are under considerable tension is shown by their great contraction in vaselined tubes. Contracted gels removed from vaselined tubes have a lower vibration frequency than similar gels adhering to the walls of tubes of equal diameter. Since vibration frequency varies inversely as the diameter of the gel column, tension must exert some influence on pitch. Vibration frequency varies directly as the concentration of silicic acid, increases with excess of mineral acid, and decreases with excess of organic acids. Syneresis (separation of aqueous solutions from highly hydrated gels) increases with increase in concentration of silicic acid, increases with excess of mineral acids, and decreases with excess of organic acids. For acid gels the factors which increase vibration frequency also increase syneresis. Vibration and syneresis are directly related to tension, but basic gels are abnormal in this respect. Syneresis varies directly as the free surface. When gels contract in vaselined tubes far more liquid separates than from equal volumes of gel in plain tubes to which the gel adheres.

J. F. S.

**Influence of the Age of Ferric Arsenate on its Peptisation.** HARRY N. HOLMES and PAUL H. FALL (*J. Amer. Chem. Soc.*, 1919, **41**, 713—717).—Determinations have been made of the amount of a 5*N*-solution of ferric chloride solution required to peptise 1.32 grams of ferric arsenate of various ages. The arsenate was prepared in bottles by adding 3 c.c. of 5*N*-ferric chloride solution to 17.6 c.c. of *M*/5-disodium arsenate solution and shaking vigorously for three minutes. The samples were then preserved, and after measured intervals were treated with ferric chloride solution and vigorously shaken until, by the trial method, the minimum quantity of ferric chloride required for peptisation was found. The experiments were made with ferric arsenate of ages varying up to fifty-six days. It is shown that the amount of ferric chloride required increases rapidly if the precipitate is allowed to age before peptisation—up to an age of one or two days. After this there is only a very small increase in the amount of ferric chloride needed even if the precipitate is kept a month before peptisation. The explanation of this behaviour is found in a decrease in hydration



of the precipitate—rapid during the first day and slow afterwards; also in the formation of larger aggregates with a consequent decrease in the external surface of the particles. Both influences retard diffusion of a solution of a peptising agent and greatly check the rate of peptisation. A few experiments, using ammonium hydroxide and sodium hydroxide as peptising agent, led to similar results.

J. F. S.

**Jellies [formed] by Slow Neutralisation.** HARRY N. HOLMES and PAUL H. FALL (*J. Amer. Chem. Soc.*, 1919, **41**, 763—764).—Clear gels of ferric arsenate, peptised by ferric chloride, can be prepared by entirely filling a bottle with the sol, covering the neck with a piece of gold-beaters' skin, and placing in a tube attached to the neck 2 c.c. of *N*-ammonium hydroxide, 2 c.c. of saturated calcium hydroxide solution, or 2 c.c. of sodium acetate solution. The base diffuses through the membrane and neutralises the free acid slowly enough to allow of the formation of a perfect gel structure.

J. F. S.

**Calculation of the Equilibrium Constants in the Deacon Process.** W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1917, **23**, 177—179).—A theoretical paper, in which, making use of known data and the dissociation constants of water and hydrogen chloride, the author shows that the equilibrium constants of the Deacon process are given by the expression  $\log K_p = 6034/T - 6.972$ . This expression is trustworthy between 300° and 1800°, and the values are nearly correct at temperatures in the region of the atmospheric temperature.

J. F. S.

**Influence of Substitution in the Components on the Equilibrium of Binary Solutions. VII. Binary Solutions Equilibria of  $\alpha$ - and  $\beta$ -Naphthylamine respectively with Nitro-derivatives of Benzene.** ROBERT KREMANN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 723—753. Compare this vol., ii, 275).—Fusion curves have been produced for the binary systems formed between  $\alpha$ - and  $\beta$ -naphthylamine respectively and the three dinitrobenzenes, 2:4-dinitrotoluene, 1:3:5-trinitrobenzene, the three mononitrophenols, and 2:4-dinitrophenol respectively. It is shown that neither  $\alpha$ - nor  $\beta$ -naphthylamine forms compounds with *o*-dinitrobenzene or *o*-nitrophenol;  $\beta$ -naphthylamine forms no compounds with 2:4-dinitrotoluene. Equimolecular compounds are formed between  $\alpha$ -naphthylamine and *p*-dinitrobenzene (m. p. 81.8°), *m*-dinitrobenzene (m. p. 63.8°), 2:4-dinitrotoluene (m. p. 62°), *m*-nitrophenol (m. p. 56.3°), *p*-nitrophenol (m. p. 68.2°), and 2:4-dinitrophenol (m. p. 104.5°). A compound of unknown and undetermined composition is indicated in the system  $\alpha$ -naphthylamine-trinitrobenzene. Equimolecular compounds are formed between  $\beta$ -naphthylamine and *p*-dinitrobenzene (m. p. 91°), *m*-dinitrobenzene (m. p. 53.3°), 1:3:5-trinitrobenzene (m. p. 161°), *m*-nitrophenol (m. p. 63.5°), *p*-nitrophenol (m. p. 81.5°), and 2:4-dinitrophenol (m. p. 72.3°). In the case of the

compounds with the dinitrobenzenes, the range of existence is greater for the compounds with  $\alpha$ -naphthylamine than for those with  $\beta$ -naphthylamine.

J. F. S.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. VIII.** ROBERT KREMANN and WILHELM CSANYI (*Monatsh.*, 1916, **37**, 755—760. Compare preceding abstract).—Fusion curves have been produced for the binary systems formed between  $\beta$ -naphthylamine and the three dihydroxybenzenes. It is shown that  $\beta$ -naphthylamine forms equimolecular compounds with resorcinol (m. p.  $77.6^\circ$ ) and catechol (m. p.  $81.3^\circ$ ). A compound (m. p.  $141.7^\circ$ ) is formed between two molecules of  $\beta$ -naphthylamine and one molecule of quinol.

J. F. S.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. IX. A Comparative Determination of the Degree of Dissociation of some Additive Compounds in the Molten Condition.** ROBERT KREMANN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 761—774. Compare preceding abstracts).—The degree of dissociation of the equimolecular compounds, formed by naphthalene,  $\alpha$ -naphthylamine,  $\beta$ -naphthylamine, and aniline with various other substances, has been calculated. The calculation was carried out by means of the formula of van Laar,  $\alpha_0 = (RT_0^2/Q_0)[x^2(1+x)]/[4(T_0-T)]$ , in which  $T_0$  is the melting point of the pure compound,  $\alpha_0$  the degree of dissociation,  $T$  is the melting point of a mixture of the compound and its components in a concentration  $x$ , and  $Q_0$  is the total heat of fusion which is made up of the real heat of fusion  $q_0$  and the heat of dissociation  $\lambda$ .  $Q_0$  is determined experimentally from the initial direction of the fusion curve of the compound and an indifferent substance by means of the expression  $(dT/dx) = -RT_0^2/(q_0 + \alpha\lambda) = -RT_0^2/Q_0$ . As indifferent substances, *p*-nitrotoluene and nitrobenzene were used in the experiments. The following values of  $\alpha_0$  were obtained: naphthalene-*m*-dinitrobenzene, 0.93; naphthalene-*p*-dinitrobenzene, 0.87; naphthalene-2:4-dinitrotoluene, 0.86; naphthalene-2:4-dinitrophenol, 0.83;  $\alpha$ -naphthylamine-*m*-dinitrobenzene, 0.53;  $\alpha$ -naphthylamine-2:4-dinitrotoluene, 0.58;  $\alpha$ -naphthylamine-*m*-nitrophenol, 0.55;  $\alpha$ -naphthylamine-*p*-nitrophenol, 0.56;  $\alpha$ -naphthylamine-2:4-dinitrophenol, 0.28;  $\beta$ -naphthylamine-*m*-dinitrobenzene, 0.88;  $\beta$ -naphthylamine-*m*-nitrophenol, 0.55;  $\beta$ -naphthylamine-*p*-nitrophenol, 0.54;  $\beta$ -naphthylamine-2:4-dinitrotoluene, 0.61; aniline-*m*-dinitrobenzene, 0.23; aniline-2:4-dinitrotoluene, 0.67; aniline-phenol, 0.44; and aniline-*m*-cresol, 0.10.

J. F. S.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XIX. The Binary Systems of Antipyrine with Phenols and their Derivatives.** ROBERT KREMANN and OTFRIED HAAS (*Monatsh.*, 1919, **40**, 155—188. Compare this vol., ii, 275).—By means of melting-point curves, the binary systems, antipyrine and phenolic sub-

stances, have been investigated with the object, as in the previous communications, of ascertaining the influence of substitution on the tendency of organic substances to form molecular compounds. In the present papers, the systems antipyrine with phenol, salicylic acid,  $\alpha$ -naphthol,  $\beta$ -naphthol, *o*-nitrophenol, *p*-nitrophenol, *m*-nitrophenol, 2:4-dinitrophenol, pyrogallol, catechol, quinol, and resorcinol have been examined and the fusion curves constructed. It is shown that an equimolecular compound is formed between antipyrine and salicylic acid, phenol,  $\alpha$ -naphthol, and  $\beta$ -naphthol respectively. In the case of the nitrophenols, antipyrine, as in other cases, forms no compounds with *o*-nitrophenol, but with *p*-nitrophenol three molecular compounds are formed, namely, two molecules of antipyrine with one molecule of *p*-nitrophenol, and one molecule of antipyrine with one and two molecules, respectively, of *p*-nitrophenol. In the cases of *m*-nitrophenol, pyrogallol, and 2:4-dinitrophenol, only the melting-point curves of the pure components could be observed, owing to the extreme slowness of the crystallisation of the melt lying between them. There is little doubt that in these cases one or more molecular compounds exist, but they could not be obtained. Catechol forms three molecular compounds with antipyrine, one molecule of the phenol to one and two molecules of antipyrine respectively, and two molecules of the phenol to one molecule of antipyrine. In the case of quinol, two compounds are formed, two molecules of antipyrine to one and three molecules, respectively, of quinol. J. F. S.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XX. The Binary Systems of Acenaphthene with some Nitro-derivatives of Benzene.** ROBERT KREMANN and OTFRIED HAAS (*Monatsh.*, 1919, 40, 189—204. Compare preceding abstract).—Fusion curves have been constructed for the binary systems formed between acenaphthene and the three dinitrobenzenes, 2:4-dinitrotoluene, the three nitrophenols, 2:4-dinitrophenol, and picric acid respectively. The systems acenaphthene-*o*-dinitrobenzene and acenaphthene-*p*-dinitrobenzene form no compounds, but simple eutectics; *m*-dinitrobenzene, on the other hand, forms an equimolecular compound (m. p.  $70\cdot1^\circ$ ). In the case of dinitrotoluene, an equimolecular compound is also formed (m. p.  $57\cdot5^\circ$ ). No compounds are formed between acenaphthene and the three nitrophenols, simple eutectics being formed in each case. An equimolecular compound is formed between 2:4-dinitrophenol and acenaphthene (m. p.  $86^\circ$ ), and a similar equimolecular compound is formed between picric acid and acenaphthene (m. p.  $151\cdot5^\circ$ ).

J. F. S.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXI. The Binary Systems of Trimethylcarbinol with Phenols and Amines respectively.** ROBERT KREMANN and OTTO WLK (*Monatsh.*, 1919, 40, 205—236. Compare preceding abstract).—Fusion curves have

been constructed for the binary systems trimethylcarbinol and the three dihydroxybenzenes,  $\alpha$ -naphthol,  $\beta$ -naphthol, pyrogallol, *p*-toluidine, the three phenylenediamines,  $\alpha$ -naphthylamine and  $\beta$ -naphthylamine respectively. It is shown that two compounds are formed between catechol and trimethylcarbinol, namely, between two molecules of catechol and one molecule of the alcohol (m. p.  $69.7^\circ$ ), and between two molecules of the alcohol and one molecule of catechol (m. p.  $29^\circ$ ). In the case of resorcinol and trimethylcarbinol, two compounds are also formed, an equimolecular compound (m. p.  $45.8^\circ$ ) and a compound between two molecules of the alcohol and one molecule of resorcinol (m. p.  $47.3^\circ$ ). The volatility of trimethylcarbinol rendered the examination of the fusion curve with quinol incomplete, so that nothing can be said of any compounds which may be formed in this case. Pyrogallol,  $\alpha$ -naphthol, and  $\beta$ -naphthol each form a single compound with trimethylcarbinol which melt at  $56.2^\circ$ ,  $1.0^\circ$ , and  $24^\circ$  respectively. Trimethylcarbinol forms no compounds, but only simple eutectics with *p*-toluidine, *m*-phenylenediamine, and *p*-phenylenediamine. Two compounds are formed between trimethylcarbinol and  $\beta$ -naphthylamine, namely, a compound between two molecules of the amine and one molecule of the alcohol (m. p.  $95.5^\circ$ ), and between one molecule of the amine and two molecules of the alcohol (m. p.  $92^\circ$ ). In the case of  $\alpha$ -naphthylamine, three compounds are formed, namely, between two molecules of the amine and one molecule of the alcohol (m. p.  $29.5^\circ$ ), one molecule of the amine and two molecules of the alcohol (m. p.  $24.1^\circ$ ), and between one molecule of the amine and six molecules of the alcohol (m. p.  $16.0^\circ$ ).

J. F. S.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXII. The Binary Systems Triphenylcarbinol with Phenols and Amines respectively.** ROBERT KREMAN and OTTO WLK (*Monatsh.*, 1919, **40**, 237—258. Compare preceding abstracts).—Fusion curves have been constructed for the binary systems triphenylcarbinol and phenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, quinol, catechol, resorcinol, *p*-toluidine,  $\alpha$ -naphthylamine, and  $\beta$ -naphthylamine respectively. It is shown that phenol,  $\alpha$ -naphthol, and  $\beta$ -naphthol form only simple eutectics, and no compounds with triphenylcarbinol. Triphenylcarbinol forms a single compound with two molecules of catechol (m. p.  $82.0^\circ$ ) and with two molecules of quinol (m. p.  $151.6^\circ$ ). In the case of resorcinol, a reddish-brown substance of high melting point separates from the mixture when the concentration of the mixture lies between 25% and 55% of triphenylcarbinol. This compound has not been further examined and is not a molecular compound. No molecular compounds are formed between triphenylcarbinol and *p*-toluidine,  $\alpha$ -naphthylamine and  $\beta$ -naphthylamine, respectively, simple eutectics being formed in each case.

J. F. S.

**Interchange of Bases in Permutite.** GERTRUD KORNFELD (*Zeitsch. Elektrochem.*, 1917, **23**, 173—177. Compare A., 1918, ii, 315).—The replacement of sodium in sodium permutite by silver, and the replacement of silver in silver permutite by potassium, barium, and ammonium have been studied. It is found that shaking permutite with solutions of the various salts for twenty minutes is sufficient to complete the interchange. In all cases except the replacement of silver by barium, the concentration of the solution has no effect on the amount of change. The change between sodium permutite and silver is represented by the equation  $([Ag_p]/[Na_p])^{1.64} \times (Na_L/Ag_L) = 129$ , the indices  $P$  and  $L$  denoting, respectively, permutite and solution. In the case of silver permutite and ammonium nitrate, the reaction is represented by  $(Ag_p/[NH_4]_p)^{1.67} \times ([NH_4]_L/Ag_L) = 37.7$ . The replacement of silver by potassium is given by the equation

$$(Ag_p/K_p)^{2.17} \times (K_L/Ag_L) = \text{const.} = 9.9,$$

and the replacement of silver by barium by the formula

$$1.5 = (Ag_p/\sqrt{Ba_p})^{2.8} \times (\sqrt{Ba_L}/Ag_L).$$

The various theories put forward to explain the above-mentioned interchange are discussed in the paper. J. F. S.

**Wollastonite ( $CaO, SiO_2$ ) and Related Solid Solutions in the Ternary System Lime-Magnesia-Silica.** J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], **48**, 165—189).—A continuation of work previously published (this vol., ii, 401). In the present paper, the solid phases of the ternary system lime-magnesia-silica are examined. The solid phases were obtained by preparing glasses of the desired composition and crystallising at low temperatures. The solids obtained were heated at various temperatures and the changes noted. The results confirm the earlier work with regard to the wollastonite-diopside solid solutions, namely, that wollastonite will take up a maximum of 17% of diopside to form solid solutions. The existence of solid solutions of pseudowollastonite-diopside containing a maximum of 16% of diopside is confirmed. A new compound,  $5CaO, 2MgO, 6SiO_2$ , is described. Solid solutions of åkermanite (or perhaps of an unstable compound,  $3CaO, MgO, 3SiO_2$ ) in both wollastonite and pseudowollastonite are shown to exist. The wollastonite solutions extend to a composition containing between 60% and 70% of åkermanite, and the pseudowollastonite solid solutions extend to a composition containing about 23% of the same compound. It is shown that an area exists in which the wollastonite-diopside, wollastonite-åkermanite, and wollastonite- $5CaO, 2MgO, 6SiO_2$  solid solutions are all capable of existence. The decomposition temperatures on this area between the 17% diopside solid solution and the compound  $5CaO, 2MgO, 6SiO_2$  pass through a minimum. The compound  $5CaO, 2MgO, 6SiO_2$  decomposes at  $1365^\circ$ , and the 17% diopside solid solutions at about  $1340^\circ$ , whilst pure wollastonite undergoes inversion at  $1200^\circ$ .

Further, the inversion temperatures and decomposition temperatures of the solid solutions of silica and the compound  $3\text{CaO}, 2\text{SiO}_2$  were studied. The results are discussed generally, and diagrams and models to represent the system are drawn. J. F. S.

**Graphic Representation of Systems of the Form  $a + b = c$  in Triangular Co-ordinates and a [Method of] Presentation of the Phase Rule.** WA. OSTWALD (*Zeitsch. Elektrochem.*, 1919, 25, 251—254).—A mathematical paper in which the representation of systems of the form  $a + b = c$  on triangular co-ordinates is considered. The use of such a co-ordination system for the general representation of phase-rule problems is discussed. J. F. S.

**Theory of Detonation.** R. BECKER (*Zeitsch. Elektrochem.*, 1917, 23, 40—49).—The theory of detonation is developed mathematically, and from the equations deduced the following values are calculated, which are of the same order as the experimentally determined values: for a detonation temperature of  $2000^\circ$  with glyceryl trinitrate, a detonation pressure of 92,500 atms. is set up and the detonation proceeds through the mass with a velocity of 7230 metres per sec.; for  $2500^\circ$  the corresponding figures are 110,500 atm. and 7930 metres per sec. J. F. S.

**Development of Atomism. I.** M. GIUA (*Gazzetta*, 1919, 49, ii, 1—42).—A historical essay with the headings: Genesis of atomism; precursors of atomism in Greece; doctrine of the elements: Anaxagoras and Empedocles; the atomistic system: Leucippus and Democritus; Plato and Aristotle; atomism of Epicurus; atomistics in the poem of Lucretius; atomistics in the Middle Ages; Arabic atomism. T. H. P.

**Harmony of the Atomic Weights.** EDUARD SCHMIZ (*Ber., Deut. pharm. Ges.*, 1919, 29, 504—518).—The author calculates numerical relationships between the atomic weights of the elements. These relationships are the same as those which exist between the sides, hypotenuse, and radius of the inscribed circle of an isosceles right-angled triangle, and the radius of the circumscribed circle round the squares erected on the sides of the triangle. The ratios of the named lines are  $\sqrt{2}/2 : 1 : (\sqrt{2}-1)/2 : \sqrt{5}/2$ . Thus in twelve cases it is shown that the ratio of the atomic weights of pairs of elements in the same group of the periodic system is  $\sqrt{5} : \sqrt{2}$ ; in nine other cases the ratio is  $\sqrt{5} : \sqrt{5}-1$ . In several cases contiguous elements in the same series exhibit the ratio  $\sqrt{5}/2 : (2\sqrt{2}-1)/2$ . Other relationships of a similar character are also given. J. F. S.

**Law of Multiple Proportions.** E. PUXEDDU (*Gazzetta*, 1919, 49, i, 203—208).—The various forms in which the law of multiple proportions is expressed, including the new statement of this law by Balareff (A., 1918, ii, 15), are discussed. It is shown that the law,



usually illustrated by means of the oxides of nitrogen and by a few other inorganic and organic groups of compounds, possesses an intrinsic significance different from that commonly attributed to it, and that the new mode of enunciating it is a necessary consequence of various principles of general chemistry, and does not correspond exactly with the original enunciation.

T. H. P.

**Determination of Molecular and Atomic Weights; the Density of Gases under Normal Conditions and Critical Constants.** J. J. VAN LAAR (*J. Chim. Phys.*, 1919, **17**, 266—328).

—A critical consideration of the methods of calculating atomic and molecular weights of gases from purely physical data. It is shown that for the majority of gases, on the assumption that  $v = \infty$ ,  $a = a_c(e^{a/RT})/(e^{a/RT_c})$  and  $b = b_c(e^{a/RT})/(e^{a/RT_c})$ , where  $a = RT_c$ . At  $0^\circ R T_0 = 1$  and  $a_0 = (a_c)_\infty e^{RT_c - 1}$  and  $b_0 = (b_c)_\infty \cdot e^{RT_c - 1}$ . On reducing  $a_c$  and  $b_c$  of the volume  $v_c$  to the volume  $v = \infty$ , the values become  $(a_c)_\infty = \phi a_c$  and  $(b_c)_\infty = \phi b_c$ , where  $\phi$  is given by the expression  $\phi = 1 + \epsilon T_c$ , in which  $\epsilon$  has a value  $54 \times 10^{-5}$  for substances with a critical temperature below  $300^\circ$  Abs. and  $43 \times 10^{-5}$  for substances with a critical temperature above  $300^\circ$  Abs. This difference may probably be expressed by an expression of the type  $\phi = 1 + \epsilon T_c - \epsilon' T_c^2$ . The value  $\epsilon = 43 \times 10^{-5}$  may, however, always be used, since the value of  $B_0$  is nearly always relatively very small for substances with a critical temperature below  $300^\circ$  absolute, so that this value has little influence on the value of  $M$ . The function  $e^{a/RT}$  often appears too large for diatomic gases, and in this case it may be retained if  $\alpha = \frac{1}{2} RT_c$  is employed. In the majority of cases where the critical temperature is above  $300^\circ$   $B_0 = b_0 - a_0 = (b_c - a_c) \cdot e^{RT_c - 1} \times (1 + 0.00043 T_c)$ . In this formula  $b_c$  may be calculated from the expression  $b_c = RT_c / 8 p_c$ , and  $a_c$  from  $a_c = RT_c \times b_c \times 27/8 : \lambda$ , where the correcting factor  $\lambda$  is obtained from the formula  $\lambda = 27 / (8\gamma - 1) [\gamma / (\gamma + 1)]^2$  and  $2\gamma = 1 + 0.038 \sqrt{T_c}$ . In the case of abnormal substances  $a_c$  and  $b_c$  may not be calculated by the above simple formulæ, but by means of much more complicated formulæ which are developed in the paper. The formulæ put forward are used to calculate the atomic weights of carbon, xenon, nitrogen, helium, hydrogen, neon, argon, and krypton from physical data, and yield values in excellent agreement with the accepted values.

J. F. S.

**Single Deflexion Method of Weighing.** PAUL H. M.-P.

BRINTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1151—1155).—To use this method, the balance is given a permanent overload on the left arm by screwing the adjusting nut on one end of the beam until, when the beam and pans are released, the pointer swings out 3 to 7 divisions to the right. The pan arrests must be so adjusted that there is no lateral vibration of the pans when released, and the method may not be used with balances in which the beam and pans are released by a single operation, such as the turning of a single

milled head or lever. In making a measurement after freeing the beam, the pans are released by a gentle, steady motion, the pointer swings out to the right, and the turning point of the single swing is taken as the zero of the balance. To obtain the weight of any object, it is counterbalanced by weights until on releasing the pans the pointer swings out to the same point. A number of readings made by the author and by students are given to show that exceedingly rapid weighing to within 0.1 mg. is possible by this method.

J. F. S.

**Self-acting Mercury Pump.** A. STOCK (*Zeitsch. Elektrochem.*, 1917, **23**, 35—40).—A self-acting mercury pump, on the Toepler principle, is described, which permits the collection of the gases pumped off. The movable mercury reservoir is replaced by a strong three-necked bottle into which the foot of the pump enters. The mercury is raised by means of air or carbon dioxide under pressure until the pump is full, then by means of valves actuated by the mercury, the pressure is cut off and the mercury falls again. The pump has the advantage, in addition to the ease of operation, that the mercury does not become contaminated with impurities from rubber connexions between its two main parts.

J. F. S.

**Greaseless Valve for Gas Work.** A. STOCK (*Zeitsch. Elektrochem.*, 1917, **23**, 33—35).—A modification of the floating valve previously described (A., 1915, ii, 339) is given in the paper. This consists of a pair of narrow tubes ground to fit a constriction in each of two parallel tubes. On raising a mercury reservoir connected with the tubes the valves are raised and close the apparatus. The action is similar to that of the valve in a Toepler pump. Three forms of valve are described which are designed for use in working with gases which have chemical action on the lubricant used with glass taps. These valves are made of a porous material which will allow the passage of gases, but not of mercury, so that when the valve is in contact with mercury no gas may pass. The valves are fitted into the glass parts of apparatus by ground joints. These valves may be used in the production of high vacua, and they exhibit no tendency to absorb gases. They are rather slow in action; thus the pressure in a 1350 c.c. flask filled with air was reduced from 760 mm. to 391 mm. in five minutes, to 189 mm. in fifteen minutes, 73 mm. in thirty minutes, and to 0.0006 mm. in ten hours by means of a mercury pump fitted with a double valve of the type described.

J. F. S.

**Gas Washing and Absorption Apparatus.** FRITZ FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 252—256).—The author discusses the properties of some thirty different forms of gas-washing and gas-absorption apparatus which have been described since the first Woulfe's bottle was used for the purpose. He considers that only those forms which have a "serpentine" principle ensure complete washing or absorption of a gas under reasonable conditions.

W. P. S.

**Simple Distillation and Extraction Apparatus.** H. W. VAN URK (*Pharm. Weekblad*, 1919, **56**, 1301—1303).—A description, illustrated by a diagram, of a simple apparatus which may be used alternatively for direct distillation or extraction. W. S. M.

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