

General and Physical Chemistry.

Influence of Simple and of so-called Multiple Union of the Atoms on the Refractive Power of Compounds. Constitution of Benzene and Naphthalene Compounds. By J. W. BRÜHL (*Ber.*, **20**, 2288—2311).—Gladstone showed that the molecular refraction of aromatic compounds is always in excess of the value calculated from Landolt's formula. The author observed a similar excess in the case of all unsaturated compounds which are supposed to contain double union of atoms, the extent of the excess being dependent on the number of double combinations present. The atomic refraction of the saturated carbon-atom $rC' = 2.48$, remains the same whether the four affinities are satisfied by single carbon-atoms or by monatomic substituents. Hence if benzene is represented by nine single carbon combinations it would possess a normal molecular refraction.

The molecular refractions of aldehyde and paraldehyde are 11.50 and 32.40 respectively; the latter number is three times the former less 2.10. This number is nearly the same as that obtained by multiplying the refraction-equivalent of the double combination of oxygen and carbon ($3 \times 0.76 = 2.28$).

Tables are given showing the molecular refraction of hydrocarbons C_5H_{10} , $C_{10}H_{20}$, and $C_{10}H_{16}$. The following conclusions are drawn:—That a so-called double combination of atoms is never optically equivalent to two single combinations, and that in the conversion of the former into the latter the increment of refraction disappears entirely or partially according as all or a portion of the multiple combinations are taken up. The author discusses the constitution of benzene, and considers Kekulé's formula to be established; carvacrol and carvol are probably constituted on the same model. Tables are given showing the refraction-equivalents of naphthalene and some of its derivatives; the numbers point to the presence of five ethylene combinations in naphthalene as shown in Erlenmeyer's formula. N. H. M.

Fluorescence of Spinel. By L. DE BOISBAUDRAN (*Compt. rend.*, **105**, 261—262).—Spinel usually gives a brilliant red fluorescence in a vacuum, but some specimens show a green fluorescence.

If a mixture of magnesia and alumina free from chromium is strongly heated, it yields spinel in fine granules which show no red fluorescence in a vacuum. A feeble green fluorescence is, however, visible, and its spectrum shows the green band observed with the green fluorescence of natural spinel. If the artificial spinel contains 0.1 per cent. of manganese oxide, it shows an intense green fluorescence, the spectrum of which consists of the same band. If 1 per cent. of chromic oxide is added the spinel shows a splendid red fluorescence. It follows that the green fluorescence of natural spinel is due to the presence of manganese, and the red fluorescence is due to the presence of chromium. C. H. B.

Crimson Line of Phosphorescent Alumina. By W. CROOKES (*Proc. Roy. Soc.*, **42**, 25—31).—The author has repeated his previous experiments on this subject (*Phil. Trans.*, 1879, 660; *Ann. Chim. Phys.*, 1859, **57**, 50; *Proc. Roy. Soc.*, **32**, 206), and now gives careful measurements of the spectrum of phosphorescent alumina. This consists of a very faint pair of bands in the red, an intense crimson double line ($\lambda = 6942$ and 6937), a pair of faint and nebulous orange lines ($\lambda = 6707$ and 6598), and a continuous spectrum commencing at $\lambda = 6514$ and shading off into the green. The spectrum is different from that of spinel, first described by Becquerel, which shows a faint double band in the extreme red, a narrow crimson line ($\lambda = 6857$), four hazy red bands, and sometimes a continuous spectrum most intense in the green, and shading off gradually to blue and violet. A detailed description of this is given.

De Boisbaudran (this vol., p. 191) attributes the red fluorescence of calcined alumina, when submitted to the electric discharge in a vacuum, solely to the presence of chromic oxide. The author, however, has obtained the double line from pure alumina, quite free from chromium; and has found, moreover, that the line is reduced in intensity when a little chromium oxide is mixed with the alumina.

Alumina precipitated from its ammoniacal solution by boiling shows no crimson line, but simply a greenish phosphorescence; the red line is fully developed only when the earth is calcined at the highest temperature of the blowpipe flame. The author's previous experiments prove that physical differences may greatly influence the phosphorescence. In view of the possibility of the line belonging to some special variety of the earth, he has submitted pure alumina to three separate processes of fractionation, the operations being repeated 20 to 30 times in each case. Details are not given; but the result was that alumina giving the crimson line became concentrated towards one end of the fractionation, whilst the earth accumulating at the other end phosphoresced either green or hardly at all. Chromium was in no case detected.

It is thus still uncertain whether the line is due to alumina, but capable of being suppressed by the presence of some other earth; or if the line belongs to some accompanying earth; or if it depends on the mode of preparation of the alumina; or, lastly, if the molecule of ordinary alumina is complex and the line belongs to one of its constituents.

CH. B.

Fluorescences of Manganese and Bismuth. By L. DE BOISBAUDRAN (*Compt. rend.*, **105**, 45—48 and 206—208; see also this vol., pp. 3, 4, 89, and 873). The author has continued his researches, and has examined the fluorescences of a mixture of two solid solvents behaving towards one another as moderately active substances, and a third substance strongly fluorescent with one of the solvents only, as represented by a mixture of cadmium sulphate (100 parts), bismuth sulphate (10 parts), and calcium sulphate. With a proportion of calcium sulphate not exceeding 14.8 per cent., the calcium cadmium fluorescence is prevented by the presence of bismuth, although the calcium bismuth fluorescence is not visible. When the quantity of calcium

sulphate exceeds 16.1 per cent., the calcium bismuth fluorescence becomes visible, and increases in brilliancy with the proportion of calcium sulphate.

The author has also investigated the properties of a mixture of two solid solvents, the first of which (α) behaves towards the second (β) as a moderately active substance, and two active substances, one of which fluoresces with both solvents, and the other with only one of them. These conditions are fulfilled by a mixture of calcium, cadmium, bismuth and manganese sulphates. With an excess of calcium sulphate, the calcium manganese fluorescence is strongest, the calcium bismuth fluorescence much weaker, and the cadmium manganese fluorescence is not visible. With an excess of cadmium sulphate, the cadmium manganese fluorescence is predominant, the calcium manganese fluorescence is also visible, but the calcium bismuth fluorescence cannot be recognised.

The author's experiments lead to the following general conclusions. A substance may show strong fluorescence when disseminated through another substance, and yet show no fluorescence with a third substance closely analogous to the second. A substance may fluoresce strongly with one compound of a metal and not at all with another compound of the same metal; or it may show fluorescence of a different character in the second case. Strongly coloured substances prevent the fluorescence of active substances by reason of their strong absorptive power. A substance may behave as a solvent to one active substance; and also behave as a more or less active substance itself when mixed with a third substance. When two active substances coexist in the same solvent their individual fluorescences are reduced in intensity, but their spectral character is not altered. Two more or less active substances in the same solvent may, however, neutralise one another. A substance which is active under certain conditions, but is inert when mixed with a particular solvent, may yet reduce the effect of a substance which is usually active with this solvent. Fluorescence in a given solvent seems as a rule to diminish on the addition of a second solvent which is not so effective with the active substance as the first solvent, but in some cases this effect is very slight. An active substance generally produces a double fluorescence with a mixture of two active solvents, but with certain proportions one of the fluorescences diminishes in a greater ratio than the quantity of the solvent which produces it. With one active substance, and equivalent quantities of two effective solvents, the two fluorescences usually are equal in intensity, but the contrary is observed in certain cases. If two substances are unequally active with a given solvent, and the ratio of the two is kept constant whilst the proportion of the solvent is gradually increased, it is possible in some cases to observe successively (1) the effect of the less active body alone, (2) the coexistence of the two effects with increasing predominance of the effect of the more active substance. When the proportion of the more active substance is increased, its effect alone is observed whatever the nature of the solvent. Certain fluorescences which are masked by others can be seen when the tube is heated, or by observing immediately after the cessation of the electrical discharge, or by modifying the strength of the discharge.

C. H. B.

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New Fluorescences with Well-defined Spectra. By L. DE BOISBAUDRAN (*Compt. rend.*, **105**, 258—261, 301—304, 343—348).—Mixtures of alumina with samarium oxide, Za_2O_3 , or $Z\beta_2O_3$, treated with sulphuric acid and calcined, give fluorescences the spectra of which are characterised by a large number of well-defined lines and bands instead of by one or a few nebulous bands as is usually the case. Calcination at a very high temperature greatly increases the brilliancy of the fluorescences. The positions and characters of the bands and lines are described in detail.

Mixtures of alumina with uranium oxide give no fluorescence at all, and lanthanum and yttrium oxides give no well-marked fluorescences. Alumina and ytterbium oxide give a blue fluorescence, the spectrum of which consists of four bands, which are also observed in the fluorescences of mixtures rich in ytterbium and thulium, or erbium and thulium, and which therefore may be attributed to thulium or to a new element.

Mixtures of alumina with oxides of cerium, erbium, thulium, dysprosium, and gadolinium, have also been examined, and their fluorescences will be described in detail in a subsequent paper.

C. H. B.

Spectra of Didymium and Samarium. By E. DEMARÇAY (*Compt. rend.*, **105**, 276—277).—The author has previously stated that the band at 4690 varies in intensity during the fractionation of praseodymium, and he concluded that the band was not due to praseodymium. The fact is confirmed but the conclusion is withdrawn. The purest fractions of praseodymium containing only small quantities of lanthanum show a strong nebulous band at about 4690, which, however, is very different in character from the band previously referred to, and it follows that there are two bands of very similar wave-length, but of different character, one being due to praseodymium and the other to some other element at present unknown.

Neodymium free from praseodymium and containing only a very little samarium, gave a spectrum in which the following bands not previously described were observed. A somewhat narrow band at about 4640 on the less refrangible side of a nebulous didymium band; a narrow and somewhat feeble band at 4300; and in a nitric acid solution a band at 4760, which really consists of two lines at 4734 and 4768 respectively, the more refrangible being the more intense. This double line is seen with pure neodymium.

The author anticipated Kruss, Nilson, and Gerhardt, in the discovery of the compound nature of samarium (*Abstr.*, 1886, 837; and this vol., p. 551).

C. H. B.

Development of Voltaic Electricity by Atmospheric Oxidation. By C. R. A. WRIGHT and C. THOMPSON (*Proc. Roy. Soc.*, **42**, 212—216).—The authors have observed that when metallic copper immersed in aqueous ammonia is exposed to a limited supply of air, the metal dissolves chiefly as cuprous oxide. This action, which the authors regard as in all cases the primary action, is very slow when the liquid is kept perfectly at rest; but it can be greatly

accelerated by arranging horizontally near the surface of the liquid a plate, termed the "aëration" plate, of platinum or other conductor not acted on under the circumstances, and joining this to the copper by a wire. When connection is made through a galvanometer, it is found that a current is generated during the action. The voltaic element thus formed polarises rapidly unless the external resistance is very high. Its electromotive force varies from 0.5 to 0.6 volt, and increases with the concentration of the ammonia solution, or when sodium or ammonium chloride is added thereto, or when spongy platinum is substituted for the platinum plate. In the latter case, and with strong ammoniacal brine, it may amount to 0.8 volt, nearly equalling that due to the heat of formation of cuprous oxide (40810), or 0.88 volt.

This battery has a close connection with the air battery of Gladstone and Tribe (this Journal, 1873, 582), which consists of copper in solution of cupric nitrate, and an aëration plate formed by a trayful of crystals of silver nitrate. Cuprous oxide is here deposited on the aëration plate, whilst in the author's cell it is formed at the surface of the copper. This has been proved by means of a battery of special construction. After continued action, copper was found only in the liquid surrounding the copper plate.

The authors are continuing these experiments, and have found that metals not otherwise prone to oxidation (mercury, silver) may be similarly dissolved in appropriate liquids.

CH. B.

Alteration of Carbon Electrodes used for the Electrolysis of Acids. By H. DEBRAY and PÉCHARD (*Compt. rend.*, 105, 27—30).—The battery used consisted of four Bunsen cells, and the electrodes had been purified by treatment with chlorine. When hydrochloric acid is electrolysed with carbon electrodes, the gas evolved at the positive pole is a mixture of chlorine, carbonic anhydride, and oxygen; in the case of sulphuric acid it is a mixture of oxygen and carbonic anhydride; and in the case of nitric acid a mixture of nitrogen oxides and carbonic anhydride. In all cases, the positive electrode undergoes disintegration, and the black powder which is formed, after being washed and dried in a vacuum, deflagrates at a temperature below a red heat, with evolution of carbonic anhydride and carbonic oxide. When nitric acid has been electrolysed, the gas also contains nitrogen.

The products were analysed by causing them to deflagrate in a vacuum, and collecting the water and oxides of carbon evolved. The deflagrated matter was then heated to bright redness in a porcelain tube, and the gas given off was collected and analysed.

The amount of water and oxygen contained in the product varies with the nature of the acid electrolysed and its degree of concentration. The proportion of oxygen is sometimes as high as 9 to 10 per cent., and that of water as high as 8 per cent.

In the case of hydrochloric acid, no soluble organic compound is formed.

C. H. B.

Conductivity of Bismuth for Heat in a Magnetic Field. By A. RIGHI (*Compt. rend.*, 105, 168—169).—The conductivity of bis-

ment for heat varies in a magnetic field in the same ratio as its electrical conductivity, and the isothermal lines undergo rotation in the same manner as the equipotential lines. C. H. B.

Comparative Radiation of Fused Platinum and Fused Silver. By J. VIOLETTE (*Compt. rend.*, 105, 163—165).—The total radiation of melting platinum as measured by means of a smoked thermopile is 54 times as great as the total radiation of an equal surface of melting silver. This ratio is much less than that of the luminous intensities of the two metals. C. H. B.

Heat of Formation of Hydrogen Telluride. By BERTHELOT and FABRE (*Compt. rend.*, 105, 92—95).—Tellurides of zinc, iron, and the alkalis do not yield pure hydrogen telluride. Better results are obtained with the tellurides of calcium, barium, and magnesium, especially the latter. Magnesium telluride is obtained by heating a mixture of the two elements to dull redness when combination takes place with great violence. A better method is to pass tellurium-vapour over magnesium heated in an atmosphere of pure hydrogen. The telluride is a white, flocculent substance, which alters very readily on exposure to air, and yields pure hydrogen telluride when treated with hydrochloric acid. The gas is very unstable even in the dark, and decomposes at once in contact with moist air. It is completely absorbed by potash. Its odour is different from that of hydrogen sulphide or selenide, and slightly resembles that of hydrogen arsenide, and its action on the animal economy is very much less irritating than that of the selenide. Its solution in alkalis is colourless, but becomes blue in presence of a trace of oxygen, tellurium being precipitated if the oxygen is in excess.

Hydrogen peroxide decomposes hydrogen telluride with formation of water and liberation of tellurium, but part of the latter undergoes oxidation. The reaction with ferric chloride is, however, very definite, and it was therefore used in the thermochemical measurements. The heat developed by the reaction ($\text{TeH}_2 = 130$) is 58.24 Cal., from which it follows that—



The heats of formation of water, hydrogen sulphide, and hydrogen selenide, are respectively + 59.0, + 4.6, and - 12.3 Cal., and it is evident that in the oxygen-group, as in the chlorine-group, the energy of combination with hydrogen diminishes as the atomic weight of the element rises. C. H. B.

Heat of Formation of Crystalline Tellurides. By C. FABRE (*Compt. rend.*, 105, 277—280).—Tellurides can be prepared by passing the vapour of tellurium over the metal, or by heating the finely-divided metal with tellurium in an atmosphere of hydrogen. Ferrous telluride forms steel-grey crystals which scratch glass; cobalt telluride forms brownish crystals; nickel telluride forms small, reddish-grey crystals; thallium telluride resembles galena in appearance, but rapidly tarnishes in the air and is readily powdered. These tellurides

are not affected by cold hydrochloric and sulphuric acids, but slowly alter in moist air.

All the tellurides dissolve readily in bromine-water and bromine, with formation of hydrogen bromide, a metallic bromide and tellurous acid. This reaction was utilised for the determination of the heats of formation of the tellurides, and the numbers given in the following table are the heats of formation of the crystallised compounds from crystallised tellurium and the solid metal. The heats of formation of the selenides are given for comparison.

	Selenide.	Telluride.
Ferrous	18·44	15·58
Cobalt	18·88	15·30
Nickel	18·42	15·10
Zinc	40·40	37·22
Cadmium	24·20	19·96
Cuprous.....	20·84	14·30
Thallium	17·72	12·24
Lead	15·76	11·42

The heats of formation of the tellurides are lower than those of the corresponding selenides. C. H. B.

Values of the Heats of Combustion of Organic Compounds Determined by Different Methods. By F. STOHMANN (*J. pr. Chem.* [2], 36, 131—141).—A comparison of the results obtained by the author in his various researches with those published by Berthelot in conjunction with Vieille, Louguinine, and Recoura. A determination of the heat of combustion of naphthalene by Berthelot's method of combustion in compressed oxygen has given the value 1231·5 cal.

W. P. W.

Passage from the Benzene Series to the Acetic Series. By BERTHELOT and RECOURA (*Compt. rend.*, 105, 141—145).—A further connecting link between the two series is furnished by the fact that quercite and inosite can both be converted into quinone.

Quercite.—Heat of combustion, 1 gram 4·330 Cal.; per gram-molecule at constant volume, +710·1 Cal.; at constant pressure, 709·8 Cal. Heat of formation (crystallised), +268·2 Cal.

Inosite.—Heat of combustion, 1 gram 3·703 Cal.; per gram-molecule at constant volume and pressure, +666·5 Cal. Heat of formation, +3·115 Cal. These values are slightly higher than those for glucose.

Quinic Acid.—Heat of combustion, 1 gram 4·342 Cal.; per gram-molecule, +833·7 Cal. Heat of formation (crystallised), +238·3 Cal.

The union of quercite with two atoms of oxygen to form inosite would develop +43·3 Cal., a number intermediate between the heat of conversion of benzene into phenol (36·6), and of phenol into quinol (+52·2). The formation of quinic acid and water by the union of quercite and formic acid would develop +53·9 Cal., a number comparable with the heat developed by the similar reaction between phenol and formic acid (+36·6). The conversion of inosite into quinone by removal of 4 mols. water would develop +9·7 Cal., and hence this is a case of dehydration with change of function, but with-

out condensation, accompanied by development of heat. The conversion of quercite into quinone by removal of 3 mols. H_2O would develop +24.9 Cal., and the conversion of quinic acid into hydroxybenzoic acid by a similar reaction would develop +98.7 Cal. The condensation of acetylene to benzene develops +171.0 Cal.

In all cases, the conversion by dehydration of compounds belonging to the acetic acid series into compounds of the benzene series is accompanied by a development of heat, or in other words by a loss of energy, which corresponds with the increased stability acquired by the nucleus of the fundamental hydrocarbon.

C. H. B.

Boiling Points of Salt Solutions. By G. T. GERLACH (*Zeit. anal. Chem.*, **26**, 413—530).—The author has carefully redetermined the boiling points of solutions of about 40 salts, acids, and alkalis, making in each case a series of observations on solutions of different strengths. With the majority, the formation of a crust during ebullition begins a little below the highest temperature attainable. In the case of salts which crystallise with water of crystallisation, the salting out which occurs on further evaporation is accompanied by a fall of temperature, which in some cases is very considerable. The crystalline magma obtained by salting out sodium sulphate at the boiling point has been observed to boil at 72° , while the escaping steam showed 100° . If in a constant amount of water equal quantities of salt are successively dissolved, the differences in the boiling points invariably decrease, but if in the case of salts which crystallise with water of crystallisation, only the anhydrous salt is considered, the differences between the boiling points for equal increments of salt increase at first, and only begin to decrease when stronger solutions with higher boiling points are reached. This points to the existence, in the weak solutions, of compounds of salt and water acting as a single substance, even at the boiling temperature, and to the dissociation of these hydrated molecules at the higher boiling points.

By laying down the boiling points in curves, it is seen that when equal weights of the salts are regarded, the curves for different substances follow no regular law, and frequently cut one another. With equal equivalents (molecular weight divided by the valency of the metal) the curves of salts of the same group and similar constitution never cut.

No direct connection can be traced between the molecular weights of the dissolved substances and the boiling points of their solutions, nor between specific gravity or specific heat and boiling point. On the other hand, in most cases, solutions of highly soluble salts boil at higher temperatures (for equal molecular concentration) than those of lower solubility. Also those salts which in the act of dissolving produce the smallest amount of contraction are almost invariably those which for equal molecular concentration show the highest boiling points. Ammonium salts are the chief exceptions to both these laws.

Tamman's law that for a given temperature the lowering of the vapour-tension produced by dissolving one molecule of a salt in an invariable quantity of water is equal for salts of similar constitution, is not borne out by the author's observations.

M. J. S.

Solidification of Liquids by Pressure. By E. H. AMAGAT (*Compt. rend.*, **105**, 165—167).—The author has examined a large number of organic and inorganic liquids at temperatures between 0° and 50° , and at pressures up to 3000 atmos., but has not observed any signs of solidification. Carbon tetrachloride, however, behaves differently, and solidifies at a high pressure, melting again when the pressure is released. The solid has a very distinct crystalline structure; solidification takes place under a pressure of 210 atmos. at -19.5° , 620 atmos. at 0° , 900 atmos. at 10° , and 1160 atmos. at 19.5° .

Carbon protochloride, C_2Cl_4 , does not solidify under a pressure of 900 atmos. at 0° , but benzene seems to solidify at about 700 atmos. at 22° .

It is probable that every liquid possesses a critical point of solidification analogous to the critical point of gases, that is, a temperature above which no pressure, however great, will convert the liquid into a solid. C. H. B.

Dissociation of some Gases by the Electric Discharge. By J. J. THOMSON (*Proc. Roy. Soc.*, **42**, 343—345).—When the vapour of iodine, at a temperature of 200 — 230° , is subjected in a tube exhausted of air to the action of the sparks from a coil giving a 3-inch spark in air, the pressure as indicated by a sulphuric acid manometer increases at first rapidly, then more slowly, and finally becomes stationary. On stopping the coil, the greater part of this increase is permanent, or at least lasts for some hours. The author attributes it to dissociation of the iodine-vapour. The amount of dissociation has been measured by observing the vapour-density in a special apparatus, sulphuric acid being excluded. The density after sparking then fell to 100, 115, 86, and 84 ($H = 1$) in different experiments. In the last case (temp. = 232°), after standing 24 hours, the dissociation still equalled that produced by Meyer at 1570° . The colour of the dissociated vapour is stated to be a little lighter and less uniform than that of the normal vapour. The electric strength was also reduced.

When bromine-vapour is sparked in a similar way, an increase of pressure also occurs, but disappears rapidly, probably owing to reunion of the separated atoms. Vapour-density determinations also showed that bromine is dissociated by simple heating at a low pressure for a long time. In such determinations, therefore, the vapour should be maintained at constant temperature for some time before observing.

Experiments have also been made with chlorine and nitrogen tetroxide. Ch. B.

Osmotic Equilibrium and the Concentration of Solutions by Gravitation. By GOUY and G. CHAPERON (*Compt. rend.*, **105**, 117—119).—An application of the laws of thermodynamics to the question of osmotic equilibrium.

Demonstration of the Coefficient of Expansion of Gas as a Lecture Experiment. By R. SCHIFF (*Gazzetta*, **17**, 190—191).—In this paper, a simple apparatus is described for demonstrating the law

of the expansion of gases as a lecture experiment. In a graduated tube surrounded with a warming jacket is inclosed 273 c.c. of dry gas; the tube is connected with a piece of flexible tubing, bent in the form of a U, and provided with a mercury reservoir. Previous to the experiment the level of the mercury in both limbs is adjusted, the tube heated with steam, and the level readjusted. If the barometric pressure has remained the same, the reading on the tube will give the coefficient of expansion. V. H. V.

Estimation of Pressure in Closed Tubes. By A. REYCHLER (*Ber.*, **20**, 2461—2462).—In this paper, a simple apparatus is described by means of which the pressure in sealed tubes may be roughly estimated. It consists of a glass tube of small diameter, about 40 cm. long, one end of which is sealed off, and 4—5 cm. length from this end is silvered; the tube is then bent in the form of a U, and filled to a certain height with mercury. The whole is enclosed in the tube in which it is proposed to carry on the reaction at an increased pressure, which forces down the mercury in the open limb, thus causing it to rise in the sealed limb and dissolve off the silver. Then from the rise of level of mercury thus determined and the tension of the vapour of mercury at the temperature of the reaction, the pressure within the tube can be directly calculated. V. H. V.
