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General and Physical Chemistry.

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Change in Colour-tone of Spectral Colours and Pigments by Diminution in Intensity of the Light. By E. ALBERT (*Ann. Phys. Chem.* [2], **16**, 129—160).—The analogy in the changes of spectrum colours and pigments is not complete. No conclusion can be drawn from the alteration of a homogeneous colour with regard to that of the corresponding pigment, the alteration in the latter being the resultant of the changes of the homogeneous colours composing the pigment.

The whole behaviour of homogeneous colours on diminution of light intensity is explained by the Young-Helmholtz theory, through the following assumption:—For a diminution in the intensity of various coloured light there is a different reduction of the sensitiveness, in such a way that the latter diminishes more slowly for rays of smaller than for rays of greater wave-length, no matter in what part of the spectrum they may be.

The author considers that the known facts in connection with this subject are a further confirmation of the Young-Helmholtz theory (compare Chodin (*Sammlung Physiologischer Abhandlungen von Preyer*, **1** Reihe, 7 Heft), Aubert (*Physiologie der Netzhaut*, 125), Helmholtz (*Phys. Optik*, 317); also Purkinje and Dove). T. C.

Relation between the Molecular Refraction of Liquid Compounds and their Chemical Composition. By H. SCHRÖDER (*Ann. Phys. Chem.* [2], **15**, 636—675).—From a careful comparison of the experimental determinations of Landolt and of Brühl, the author draws the following conclusions in regard to the molecular refraction of liquid compounds.

Contrary to the assumption of both Landolt and Brühl, the difference between the molecular refractions of compounds for equal differences in chemical composition is not constant, but increases distinctly, although slightly, with the atomic weight. The influence, therefore, of elementary atoms on the molecular refraction is not constant, but increases with the atomic weight of the compound, thus:—

	Molecular refraction.	Difference.
Formic acid, CH_2O_2	13·61	7·08
Acetic acid, $C_2H_4O_2$	20·69	7·32
Propionic acid, $C_3H_6O_2$....	28·01	7·49
Butyric acid, $C_4H_8O_2$.....	35·50	

The influence of the components, and therefore of the elementary atoms of a compound on their molecular refraction bears a simple relation to one another. Thus the groups CH_2, CO, OH_2, and the O_2 of acid carboxyl exert an equal influence on the molecular refrac-

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tion of compounds containing them. Hence it follows that the atoms of H, C, and O (when combined with hydrogen in hydroxyl) possess the same "refraction-stere," whilst the diatomic O in CO has two refraction-steres. It is worthy of note that the formulæ which represent the refraction-constitution of saturated compounds are identical with those which the author had previously employed to represent the volume constitution. In every case of saturated compounds which has been examined, the elementary atoms have exactly the same number of steres for their volume constitution as for their molecular refraction. The stere in all the groups varies between 2·3 and 2·4.

As regards non-saturated compounds, a pair of doubly linked carbon-atoms (as in the allyl compounds) has twice the refraction-stere of a pair of carbon-atoms in saturated compounds.

The volume constitution and refraction-constitution of non-saturated compounds are no longer the same. The singly linked atoms of C, H, and O carry *one* stere, both in their volume constitution and in their refraction constitution, and a doubly linked oxygen-atom bears two steres in both cases. But whilst the volume-constitution of two doubly linked carbon-atoms is expressed by C^3_2, *i.e.*, three steres, that of the refraction constitution is represented by C^4_2, *i.e.*, four steres.

In aromatic compounds the carbon of phenyl (C_6H_5) has twice as great an influence on the molecular refraction as in saturated compounds. In aromatic compounds, the volume constitution no longer agrees with the refraction constitution, for in the volume-constitution the 6 carbon-atoms of phenyl possess eight steres, whilst in the refraction constitution they have 12.

Brühl has drawn the conclusion that because the molecular refraction is greater by two units for each pair of doubly linked carbon-atoms than the sum of the influence of the elementary atoms according to the ordinary calculation, and, moreover, because the molecular refraction of aromatic compounds is greater by 6 units than calculation would lead us to expect, therefore there are three pairs of doubly linked carbon-atoms in benzene. The author thinks that this conclusion as regards the constitution of benzene is incorrect, even when considered from Brühl's point of view: for in non-aromatic compounds a loss of 2 atoms of hydrogen occurs for each double linking of the carbon-atoms, and consequently if Brühl be correct, there ought to be a loss of only 6 atoms of hydrogen for the three pairs of doubly linked carbon-atoms in benzene, whereas there is really a loss of 8 hydrogen-atoms. In the unsaturated compounds of the fatty series, the optical influence of the hydrogen which has been lost by each double linking of the carbon-atoms is completely compensated by the smaller lowering of the refractive power, whereas in the aromatic compounds the influence of the disposible hydrogen is not completely, but only three-fourths, counterbalanced by the increased action of the carbon.

The author considers that the heats of combustion (Thomsen), the volume-constitution (Schröder), and the refraction-constitution (Schröder) of aromatic compounds are all unanimously in favour of Ladenburg's prism, and not of Kekulé's hexagon as representing the constitution of benzene. T. C.

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Galvanic Polarisation and Smee's Element. By W. HALLOCK (*Ann. Phys. Chem.* [2], **16**, 56—86).—The usual view that the changes in the electromotive force of a Smee's element are due to the action of polarisation is correct. The electromotive force of the polarisation is by no means independent of the nature of the electrodes, nor are we at present in a position to calculate the polarisation from the heat evolved. The electromotive force of polarisation considerably exceeds that, which is necessary for the apparent decomposition, thus confirming the earlier views on this subject (compare *Wiedemann's Galvanismus*, **1**, 681 [1874]). T. C.

Chemical Energy of the Voltaic Pile. By D. TOMMASI (*Compt. rend.*, **94**, 1407—1410).—Joule and Favre have shown that there is a close relation between the energy of the voltaic pile and the heat developed by the chemical reactions taking place in the pile, so that the electromotive force of a couple will be proportional to the heat developed by the chemical action. Favre, however, states (*ibid.*, **69**, 39) that "the heat developed by the combustion of hydrogen in electrolysis is transmissible or not by the circuit, according to the nature of the compound supplying the oxygen necessary for this combustion." According to this, in a zinc-platinum couple with dilute sulphuric acid (Smee's element) the heat developed is 39 cal., but only 29·8 are transmissible by the circuit. Two of these couples, therefore, should not decompose water, for $29{\cdot}8 + 29{\cdot}8 < 69$ cal. The author, however, has shown that decomposition does take place just as if the whole of the heat developed were transmissible, $39 + 39 > 69$ cal. If the water in the voltameter is acidulated with hydrochloric acid decomposition of the water takes place more readily, the thermic equivalent being 66 cal. instead of 69 cal. But even in this case, according to Favre, it ought not to take place, for $29{\cdot}8 + 29{\cdot}8 < 66$ cal.

If in the two Smee's elements graphite plates (previously heated to redness) be substituted for the platinums, decomposition takes place much more rapidly, and this is greatly increased when electrodes of gas-carbon of large surface are employed; yet, according to the views generally received, the chemical action of the pile ought not to be altered.

According to Favre, two zinc-platinum couples with dilute hydrochloric acid should not decompose water acidulated with sulphuric acid, whilst it should do so if acidulated with hydrochloric acid, for

$$33{\cdot}4 + 33{\cdot}4 < 69 \text{ cal. } (H_2SO_4).$$
$$\text{whilst } 33{\cdot}4 + 33{\cdot}4 > 66 \text{ cal. } (HCl)$$

This is in fact what actually takes place, but if graphite or, better, gas-carbon is substituted for the platinum of the couples, dilute sulphuric acid is decomposed. This cannot be explained on Favre's hypothesis, but is strictly in accordance with thermic considerations—

$$34{\cdot}2 + 34{\cdot}2 + 1{\cdot}4^* > 69 \text{ cal.}$$

Again, according to Favre, a zinc-platinum couple with hydrochloric

* The electromotive force of an amalgamated zinc-couple is greater than that of a zinc-couple by about 0·7 cal.

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acid should not decompose water acidulated with hydrochloric acid for

$$29{\cdot}9 + 29{\cdot}9 < 66 \text{ cal.}$$

It does take place, however, and even dilute sulphuric acid which absorbs 69 cal. is decomposed by a zinc and gas-carbon couple. If the water in the voltameter is acidulated with hydrobromic acid, this is decomposed and not the water, hydrogen being evolved at the negative, and bromine at the positive electrode. This is easily explained: for whilst water absorbs 69 cal. when decomposing, hydrobromic acid absorbs only 59 cal., and the author has previously drawn attention to the fact that of two compounds, that one is decomposed by preference which requires less thermic energy. C. E. G.

Electromotive Force of a Zinc-carbon Couple. By BERTHELOT (*Compt. rend.*, **95**, 11—13).—The electromotive force of a zinc-carbon couple in dilute sulphuric acid varies greatly in consequence of polarisation, and the electrolytic effects which it can produce vary in exactly the same proportion. When the circuit is first closed, the electromotive force is greater than that of a Daniell cell in the ratio 1 : 1·29, but if the circuit remains closed, the electromotive force rapidly diminishes, and after 36 hours becomes less than half that of a Daniell. If the current is interrupted, the electromotive force gradually increases, but does not regain its original intensity. If, however, the carbons and porous cells are disconnected, well washed with water, and again set up, then on first closing the circuit the couple has exactly its original electromotive force. It is evident that a zinc-carbon couple cannot be used where a constant electromotive force is required. A zinc-carbon couple, when the circuit is first completed, will not decompose acidulated water, but if a zinc-cadmium couple is added, decomposition takes place. Two zinc-carbon couples will decompose potassium sulphate until polarisation has lowered the electromotive force below that of two Daniells. C. H. B.

Reply to Berthelot's Note "On the Electromotive Force of a Zinc-carbon Couple." By D. TOMMASI (*Compt. rend.*, **95**, 81—82).

External Work in a Closed Circuit. By R. COLLEY (*Ann. Phys. Chem.* [2], **16**, 39—56).—The constant performance of external work in the circuit always determines the production of a new electromotive force, the amount of which is proportional to the work done, and that no matter whether the resistance changes or not.

In a closed circuit, there can be no electromotive force which does not correspond with the constant work of chemical or other forces.

T. C.

Theory of the Equipotential Figures obtained by the Electrochemical Method. By A. GUEBHARD (*Compt. rend.*, **95**, 29—30).—The formation of Nobili's rings is not due to a *permanent* electrical condition between the electrodes, but to a very short period of variable condition. The thickness of the deposit does not increase with the

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time, but the extension of the rings ceases in a sharply defined manner. This metallic polarisation causes the production of a superficial inverse current. At the moment when the rings cease to increase, a permanent electrical condition is set up in the column of liquid of which the electrode forms the base, and each horizontal layer of this column separately obeys Lamé's equation. In order that any exchange may take place between the lowest layer of liquid and the electrode, it is necessary that the thickness of the polarising layer on the latter be proportional to the positive or negative values of ϕ given by the equation $\Delta_2\phi = 0$. This affords further proof of the simple law which the author has previously established. C. H. B.

Electrolysis of Hydrogen Peroxide. By BERTHELOT (*Compt. rend.*, **95**, 8—11).—A dilute solution (3 grams per litre) of hydrogen peroxide undergoes electrolysis in two different ways. With sufficiently high electromotive force, oxygen and hydrogen are given off at the two electrodes, but with low electromotive force, such as that of a zinc-cadmium couple, only oxygen is given off, and no hydrogen is evolved at the negative electrode. Under these circumstances electrolysis resembles the spontaneous decomposition of the peroxide, but is accelerated by the action of the current. Either the hydrogen peroxide splits up into oxygen and water, or, more probably, a secondary reaction takes place, and the electrolysed hydrogen combines with undecomposed hydrogen peroxide, forming 2 mols. water, thus: $H_2 + H_2O_2 = 2H_2O$. The final result $2H_2O_2 = 2H_2O + O_2$, is exothermic, and develops + 43·6 cal., for $H_2O_2 = H_2 + O_2$ absorbs — 47·4 cal., and $H_2 + H_2O_2 = 2H_2O$ develops + 90·6 cal. This form of electrolysis can consequently be effected by any electromotive force however feeble.

When the electromotive force is equal to that of a Daniell cell, hydrogen is given off as well as oxygen, and the simultaneous evolution increases as the electromotive force increases. The electromotive force of a Daniell cell is the result of a reaction which develops + 49 cal., a quantity slightly higher than that absorbed by the decomposition of the hydrogen peroxide into its elements. The peroxide may possibly first split up into oxygen and water, the latter then undergoing electrolysis, but in this, as in all cases of electrolysis, only the initial and final conditions enter in the calculation of the minimum electromotive force required. For the same reason, the presence of dilute acid does not interfere with the result.

That both modes of electrolysis may take place simultaneously, as the author has already found in the case of ferrous and manganous sulphates (*Compt. rend.*, **93**, 760), is shown by the variations in the relative proportions of the oxygen and hydrogen evolved. With higher electromotive force, sufficient to decompose water, the decomposition becomes complex, and the ratio of hydrogen to oxygen evolved is increased in consequence of the electrolysis of the water present. C. H. B.

Appearance of the Electric Arc in Vapour of Carbon Bisulphide. By JAMIN and MANEUVRIER (*Compt. rend.*, **95**, 6—7).—Two

Published on 01 January 1882. Downloaded on 27/01/2016 11:51:24.

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vertical parallel carbons are arranged in the receiver of an air-pump, and the latter is exhausted until the arc no longer forms, but is replaced by the ordinary vacuum discharge. Vapour of carbon bisulphide is then introduced in quantity sufficient to increase the pressure by 50—60 mm. Under these circumstances a brilliant arc is formed, 50—60 mm. in height, with the shape of a horse-shoe, and surmounted by a long vertical flame. The arc has a pale green colour, and as the tension of the bisulphide vapour increases, the light becomes unbearably brilliant, but at this point the resistance becomes so great that the arc is frequently extinguished. If the receiver contains air, a cloud of sulphur is formed and deposited on the sides. If, however, all air has been removed, this cloud does not form, but a brown substance which turns black is deposited on the sides of the receiver. This substance is volatile, and has an odour resembling that of sulphur; it is possibly either carbon monosulphide or an allotropic modification of sulphur.

The spectrum of the arc under these conditions is very discontinuous, and consists of four very similar groups of channelled bands in the red, yellow, green and violet respectively, that in the green having by far the greatest intensity. The peculiar colour of this arc may possibly render it useful for lighthouses and signalling.

C. H. B.

Heat of Formation of Thiocyanic Acid and of some Thiocyanates. By JOANNES (*Compt. rend.*, **94**, 797—800).—The reaction between potassium trisulphide and cyanide requires nearly half an hour for its completion, the final result being represented by the equation $K_2S_3 + 2KCN = 2KCNS + K_2S$; but from a comparison of the thermic changes with the amount of potassium cyanide formed during equal intervals, it would seem that some intermediate compound is first formed; this supposition is confirmed by the course of the reaction between potassium trisulphide and mercury cyanide, for although it takes about the same time as in the case of potassium cyanide before it is complete, the whole of the mercury is at once precipitated as sulphide, and the solution acquires an odour of hydrocyanic acid. The numbers obtained were as follows:—

Heat of solution of KCNS ..... = − 6·13 cal.
$K_2S_3 + 2KCN = K_2S + 2KCNS$ = + 30·86 ,,
$K + S + CN\,(gas) = KCNS\,(solid)$ = + 87·8 ,,

Heat of formation of thiocyanic acid—

$$H + S + CN\,(gas) = HCNS\,(solution) = 19{\cdot}9 \text{ cal.}$$

Heat of formation of sodium thiocyanate—

$$Na + S + CN = NaCNS = 77{\cdot}1 \text{ cal.}$$

Heat of formation of ammonium thiocyanate. Its

Heat of solution at 12° = − 5·67 cal.
$N + H_4 + S + CN = NH_4CNS$ = 59·12 ,,

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Heat of formation of silver thiocyanide—

$$Ag + S + CN = AgCNS = 16{\cdot}5 \text{ cal.}$$

Heat of formation of lead thiocyanide—

$$Pb + S_2 + 2CN = Pb(CNS)_2 = 43{\cdot}8 \text{ ,,}$$

Heat of formation of mercury thiocyanate—

$$Hg + S_2 + 2CN = Hg(CNS)_2 = 36{\cdot}0 \text{ ,,}$$

The heats of formation of the thiocyanates are intermediate between those of the corresponding iodides and bromides.

C. E. G.

Estimation of the Specific Gravity of Permanent Gases at High Temperatures. By V. MEYER and H. GOLDSCHMIDT (*Ber.*, **15**, 1161—1164).—To determine the sp. gr. of gases at a red or yellow heat, the authors employ the method lately described by them (*Ber.*, **15**, 137), but substitute for the glass bulb a straight glazed porcelain tube, 570 mm. long, and of a capacity of 100 c.c., terminating in capillary tubes, each 185 mm. long. The heating is effected by a Fletcher's tube furnace, giving with blast a temperature of about 1200°, and without the blast of about 800°. To avoid cracking the tube, the heating must be slow, some hours being taken to raise the tube to the required temperature. In making a determination, the heated tube is filled with dry air or nitrogen, this is then displaced into a measuring tube by means of a stream of the (absorbable) gas whose density is required, this is then in turn driven into a weighed absorption apparatus by a stream of dry air. The corrections are the same as in the former paper (*loc. cit.*) Determinations of the density of carbonic anhydride gave 1·55 at 802° (calculated 1·53) and 1·49 at 1180° (calculated 1·53). A series of determinations for cyanogen gave density at 100° = 1·82, at 182° = 1·83, at 250° = 1·79, at 310° = 1·76, at 446° = 1·81, and at about 800° = $\left\{\begin{matrix}1{\cdot}78\\1{\cdot}81\end{matrix}\right.$ (calculated 1·80). A determination could not be made at about 1200°, the cyanogen suffering decomposition at that temperature.

A. J. G.

Determination of Vapour-densities at the Boiling Point of Selenium. By L. TROOST (*Compt. rend.*, **95**, 30—33).—The author employed bulbs of about 300 c.c. capacity, constructed of very infusible glass. Two determinations of the vapour-density of iodine gave the numbers 8·57 and 8·53 respectively: hence it is evident that at 665° the coefficient of expansion of iodine vapour does not differ materially from that of air, although its coefficient of compressibility is very different. Two determinations of the vapour-density of sulphur gave the numbers 2·94 and 2·92, which show that the modification of sulphur having the vapour-density 6·6, splits up gradually into that having the vapour-density 2·2, just as ozone splits up gradually into oxygen.

C. H. B.

Experiments on the Diffusion of some Organic and Inorganic Compounds. By J. D. R. SCHEFFER (*Ber.*, **15**, 788—801).—The

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diffusion constants, as defined by Fick (*Pogg. Ann.*, **94**, 59), have been determined by a method described by Simmler and Wilde (*ibid.*, **100**, 217), which has been elaborated from Fick's formula (*loc. cit.*). The following tables contain the mean of the values obtained for the "diffusion constants" of the substances investigated :—

Substance employed.	Temperature of observation.	Diffusion constant.	Number of observations.
Hydrochloric acid	7·5°	2·17	6
,,	8	1·99	3
,,	8·5	2·21	4
,,	9	2·13	2
,,	15·5	2·56	2
,,	6·5	1·865	3
Oxalic acid	7·5	0·702	3
Acetic acid	8	0·66	3
,,	14·5	0·80	3
Tartaric acid	9	0·45	4
Succinic acid	15	0·546	3
Citric acid	9	0·41	3
Mannitol	10	0·58	3
Sodium acetate	14	0·70	4
,,	15	0·68	3
Chloralhydrate	9	0·53	4
Ammonium chloride	17·5	1·314	17·5

Graham's determinations give a diffusion constant for hydrochloric acid at 5° = 1·742. The author finds it to be 2·07 at 8°, and 2·57 at 15·5°. Supposing the rate of diffusion to vary according to the formula $K_t = K_o(1 + at)$, then from the equations $2{\cdot}07 = K_o\,(1+8a)$ and $2{\cdot}57 = K_o(1 + 15{\cdot}5a)$; the values for K_o and a can be calculated, and the value for K at 5° ; this latter was found to be 1·77, which agrees very well with Graham's result. P. P. B.

Influence of the Compressibility of the Elements on the Compressibility of their Compounds. By L. TROOST (*Compt. rend.*, **94**, 135—137).—The researches of V. Meyer, Crafts and Meier, and the author, have shown that the coefficient of expansion of iodine vapour increases with the temperature, and that its coefficient of compressibility diminishes with the pressure. The coefficient of compressibility of chlorine is practically the same as that of air. By determinations of vapour-density at low pressures, the author finds that the coefficients of compressibility of mercury vapour and mercuric chloride vapour at 440° are the same as that of air, whilst that of mercuric iodide vapour, at the same temperature, diminishes with the pressure. The vapour-density of the iodide vapour at 440° is 15·89 at 753·1 mm., 14·90 at 84·12 mm., and 14·82 at 46·3 m.m. It is evident therefore that the anomalous behaviour of iodine is also exhibited by its compound with mercury. C. H. B.