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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

PART II.

### General and Physical Chemistry.

**Refractometric Observations.** By J. F. EYKMAN (*Ber.*, **25**, 3069—3079).—The author has determined the refraction and dispersion equivalents of a considerable number of isomerides with a view of drawing conclusions as to their constitution from the values of their molecular constants. The measurements were made for the lines  $H_\beta$  and  $H_\alpha$ . His results for the molecular refraction and dispersion calculated by means of Gladstone's and of Lorenz's formulæ are given in the following table:—

	Molecular refraction for A.		Molecular dispersion from $H_\beta$ and $H_\alpha$ .	
	Gladstone.	Lorenz.	Gladstone.	Lorenz.
Piperidine, $C_6H_{11}N$ .....	43·42	26·01	0·87	0·45
$C_6H_{13}N$ .				
1. Methylpiperidine .....	51·50	30·96	1·10	0·57
2. Methyl- $\alpha$ -methylpyrrolidine .....	51·24	30·89	1·09	0·56
3. $\alpha\alpha_1$ -(2, 5) Dimethylpyrrolidine (Tafel) .....	50·97	30·70	1·01	0·53
4. Butallylmethylcarbinamine .....	52·99	31·92	1·20	0·63

	Molecular refraction for A.		Molecular dispersion from $H_\beta$ and $H_\alpha$ .	
	Gladstone.	Lorenz.	Gladstone.	Lorenz.
$C_7H_{15}N$ .				
1. Methyl- $\alpha$ -pipecoline—				
(a.) From pentallylcarbini-				
methylamine .....	58.74	35.28	1.24	0.65
(b.) From Ladenburg's pipe-				
coline .....	58.62	35.18	1.24	0.64
2. Methyl- $\alpha\alpha_1$ -dimethylpyrrol-				
idine .....	58.63	35.30	1.21	0.63
3. Dimethylpiperidine .....	60.71	36.68	1.41	0.74
$C_8H_{17}N$ .				
1. Pentallylcarbini-dimethyl-				
amine .....	68.40	41.26	1.58	0.82
2. Butallylmethylcarbini-				
methylamine .....	68.01	40.99	1.51	0.80
$C_9H_{15}N$ .				
1. $\alpha$ -Methyltropidine .....	73.23	43.29	2.27	1.13
2. $\beta$ -Methyltropidine .....	75.79	44.39	2.54	1.23
$C_6H_{10}$ .				
(a.) Diallyl (b. p. 60—61°).	46.33	28.08	1.26	0.67
(b.) „ (b. p. 80—83°).	47.85	28.72	1.80	0.92
Tropilidene, $C_7H_8$ .....	51.50	30.32	2.06	1.00
Tropilen, $C_7H_{10}O$ .....	53.05	31.45	1.46	0.72
Tropidine, $C_8H_{13}N$ .....	61.73	36.59	1.41	0.71
Tropine, $C_8H_{15}NO$ .....	64.62	38.29	1.18	0.60
Ecgonine, $C_8H_{15}NO_3 \cdot H_2O$ ....	79.90	46.44	1.56	0.75
Pseudotropine (= Oscine) —				
(a.) Calc. for $C_8H_{15}NO$				
(Ladenburg) .....	58.49	34.91	1.05	0.46
(b.) Calc. for $C_8H_{13}NO_2$				
(Hesse, Schmidt) ....	64.30	38.38	1.16	0.50
Acetylacetone, $C_6H_{10}O_2$ ...	48.91	29.51	0.97	0.51

These results the author discusses in reference to the probable constitution of the substances, and finds that they agree in general with the views expressed by Merling (Abstr., 1891, 1506), from whom most of the specimens examined were obtained. J. W.

**Physical Character of the Lines in the Spark Spectra of the Elements.** By W. N. HARTLEY (*Proc. Roy. Soc.*, 49, 448—451).—Perrot has shown that the spark discharge is composed of two parts: the fiery track or central portion is a statical discharge, whilst the aureole or flame is dynamic and capable of electrolytic action.

From observations of the sparks and photographs of the spectra, the author considers that the principal lines lying between point and point of the electrodes are spectra of the fiery path of the spark; the extension of the principal lines above and below the points of the electrodes seem to be spectra of the aureole. Elements which are difficultly volatile, and those which are bad conductors, do not exhibit

spectra with extended lines, and, conversely, metals which are the best conductors, and the most volatile, give spectra with their principal lines largely extended. The metals magnesium, zinc, cadmium, aluminium, indium, copper, silver, and mercury are the best conductors, and consequently show considerable extension of their principal lines. With these metals, the continuous spectrum is very weak, and in the cases of thallium and mercury, the air spectra are suppressed by the dense vapours in the track of the spark. The extension of the lines is even observed with concentrated solutions of the metals.

The nimbus seems not to be wholly dependent on the volatility or readiness with which the metal is oxidised, although volatility certainly increases the nimbus. Amongst the photographed spectra, that of magnesium shows the largest nimbus, owing probably to the great actinic power of the rays emitted, and also to the large quantity of the metal in the track of the spark. After magnesium, cadmium and mercury exhibit the largest nimbus; those of platinum, gold, copper, and silver are small. There is a considerable nimbus about some of the lines of arsenic, antimony, bismuth, tin, and lead, and but very little about those of thallium and iridium. The nimbus is evidently an expression of the quantity of matter in the spark, and of the chemical activity of the rays emitted by the ignited vapour.

The continuous spectrum, which forms the background to the lines of certain spectra, must be due to the ignition of some solid substance or oxide. The spectra of gold, silver, platinum, mercury, iridium, zinc, and cadmium, metals which either are not oxidisable or form volatile oxides, do not have this background; the less metallic elements, tellurium, arsenic, antimony, and bismuth, however, show it very strongly. No sufficient explanation of this has yet been given.

The breadth of the principal lines in the photographed spectra is dependent on the actinic power, volatility, vapour density, and electrical conductivity of the metal. In accordance with this, the lines of cadmium are broader than those of zinc, which are in turn broader than those of magnesium.

W. J. P.

**The Planté Lead | Sulphuric Acid | Lead Peroxide Cell from a Chemical Standpoint. Part I.** By G. H. ROBERTSON (*Proc. Roy. Soc.*, **50**, 105—108).—The author was unable, either directly or indirectly, to obtain any evidence of the existence of an oxysulphate of lead corresponding with red lead; there is, therefore, no ground for supposing that the ordinary lead sulphate is not the only one concerned in the reactions occurring in the Planté cell. If the sudden lowering of the E.M.F. were caused by a change in the nature of the chemical compounds formed on the plates, it would be difficult to account for the very rapid recovery of the E.M.F. exhibited by an apparently discharged cell.

It would seem that the different behaviour of secondary cells containing sodium sulphate (1 per cent.) and cells containing none is due to the catalytic action of this salt on the hydrogen peroxide always found in the electrolysed acid of the strength used in such batteries, which is probably formed from persulphuric acid. Cells containing sodium sulphate show much less sulphating than do

ordinary cells, and the addition of this salt (1 per cent.) to the freshly electrolysed acid is always attended by a diminution in the amount of hydrogen peroxide. The acid taken from secondary cells reduces lead dioxide, and if hydrogen peroxide be added to the acid in the cells, an annulment or reversal of the E.M.F. occurs, whilst the introduction of hydrogen peroxide into the body of the dioxide paste produces an increase of E.M.F. in the case of a platinum | lead dioxide couple. The pink colour assumed by the acid in the Planté cell is due to the formation of permanganic acid from impurities in the lead.

W. J. P.

**The Planté Lead | Sulphuric Acid | Lead Peroxide Cell from a Chemical Standpoint. Part II. Discussion of the Chemical Changes occurring in the Cell.** By H. E. ARMSTRONG and G. H. ROBERTSON (*Proc. Roy. Soc.*, **50**, 108).—The authors arrive at the following conclusions:—(1.) That the cooling observed in the Planté cell can only be explained as resulting from the dissociation of the dilute sulphuric acid. (2.) That the observed loss in efficiency cannot be due to temperature changes, as these arise through actions occurring out of circuit. (3.) That if sulphating occurs at both plates in circuit and under the influence of sulphuric acid, the calculated E.M.F. is considerably higher than the observed value, whilst, if sulphating occur only at the lead plate, the calculated E.M.F. is far too low. This comparison, therefore, leads to no conclusion as to the exact nature of the changes which take place in the cell. (4.) That a counter E.M.F. of about 0.5 volt would account for the observed departure from the highest calculated value. Such a counter E.M.F. may exist, peroxides being always present in the electrolyte. (5.) That the observed loss of efficiency is due to the formation of peroxides in the electrolyte, and to the excessive sulphating occurring chiefly at the dioxide plate in the local circuit existing between the support and the paste.

W. J. P.

**Electrolysis of Silver Nitrate in a Vacuum.** By A. SCHUSTER and A. W. CROSSLEY (*Proc. Roy. Soc.*, **50**, 344—358).—The deposit of metallic silver obtained on electrolysis of silver nitrate solution in air, increases slightly in weight as the current density at the platinum cathode decreases. The authors find that this difference is persistent when the deposition occurs in a vacuum. The deposit is slightly increased in weight if electrolysis proceeds under diminished pressure; this is due to the withdrawal of oxygen, for if the solution be electrolysed in an atmosphere of this gas, a heavier deposit is obtained than in air.

The authors conclude that the true electrochemical equivalent of silver is probably not quite 0.1 per cent. greater than the value assigned to it by Rayleigh.

W. J. P.

**Electrolytic Dissociation and Ionisation.** By J. TRAUBE (*Ber.*, **25**, 2989—2993; compare *Abstr.*, 1891, 255, 390, 638).—The author now practically adopts the hypothesis of electrolytic dissociation to explain the behaviour of aqueous salt solutions, contending, however, that the dissociation into ions need not be complete dis-

sociation, but only a slackening of the bonds which hold the ions together. This modified dissociation he calls, after Fitzgerald, ionisation. J. W.

**Absorption of Radiant Heat by Alum.** By C. C. HUTCHINS (*Amer. J. Sci.* [3], **43**, 526).—It is a generally accepted opinion that a solution of alum acts as a particularly efficient absorber of rays of great wave-length; but the author shows by direct experiment that a solution of alum is really no better absorber than water, and that, furthermore, it would hardly pay to use plates of transparent alum, even if they were to be had. H. C.

**Specific Heat of Carbonic Anhydride.** By N. S. KURNAKOFF (*J. Russ. Chem. Soc.*, **22**, 493—495).—From the apparent specific heat of carbonic anhydride at high temperatures (above 2000°) the author calculates the true specific heat by means of the formula  $c = \frac{Ct - k(W + c_1t)}{(1 - k)t}$ , in which  $c$  is the true specific heat of carbonic anhydride,  $C$  the apparent specific heat,  $c_1$  the mean specific heat of its products of dissociation (carbonic oxide and oxygen),  $W$  the heat of formation of carbonic anhydride from its dissociation products at 0°,  $k$  the coefficient of dissociation, and  $t$  the temperature. The following table of results is given by the author. In it, the values of  $c_1$  are taken from Vielle's data, and the values of  $k$  are those given by Le Chatelier.  $W = 68,000$  cal.

$t$ .	$C$ .	$c_1$ .	$k$ .	$c$ .
2000°	19·1	9·0	0·035	18·3
2500	19·8	9·2	0·14	17·1
3000	20·6	9·4	0·3	15·7
3500	21·3	10·6	0·4	15·5
4000	22·1	11·5	0·45	17·0
4500	22·8	12·3	0·6 (?)	16·0

The true specific heat would thus seem to reach a minimum value at about 3500°. J. W.

**Heat of Combustion of Chlorine Compounds.** By BERTHELOT and MATIGNON (*Compt. rend.*, **115**, 347—350).—

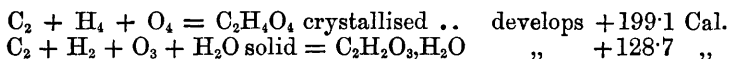
	Heat of combustion. Const. vol.	Molecular heat of combustion.		Heat of formation.
		Const. vol.	Const. press.	
Chloroacetic acid . . . . .	—	+ 174·2 cal.	+ 173·9 cal.	+ 123·0 cal.
Trichloroacetic acid . . . .	—	+ 106·3 „	+ 105·4 „	+ 132·1 „
Dichlorotrimethylene . . .	3900 cal.	+ 432·8 „	+ 433·1 „	— 2·6 „

The substitution of chlorine for hydrogen in acetic acid develops +25.3 Cal.; the substitution of 3 atoms of chlorine for 3 atoms of hydrogen in acetic acid develops  $+26.1 \times 3$  Cal. These numbers are somewhat lower than in the case of the substitution of chlorine for hydrogen in methane, the difference being probably due to the presence of oxygen.

The substitution of 2 atoms of chlorine for hydrogen in trimethylene develops  $+34 - x$  Cal.,  $x$  being the heat of formation of the hydrocarbon. C. H. B.

**Glyoxylic or Dihydroxyacetic Acid.** By BERTHELOT and MATIGNON (*Compt. rend.*, 115, 350—353).—The experiments were made with a crystallised specimen of glyoxylic acid which had lost 0.213 mol.  $\text{H}_2\text{O}$ , and the final values were calculated on the assumption that recombination with this quantity of water would cause no thermal disturbance.

Heat of combustion of glyoxylic acid at const. vol. = +128.1 Cal., at const. press. 127.5 Cal., and consequently



The conversion of ethane into gaseous alcohol by direct oxidation would develop +34.6 Cal.; the oxidation of alcohol to aldehyde develops +51.5 Cal., and of aldehyde into acetic acid +60.0 Cal. For the corresponding values in the cases of acetic, glycollic, and glyoxylic acids see following abstract.

As a rule, the substitution of HO for H in an acid, with production of an alcoholic function, develops from +35 to +45 Cal.

C. H. B.

**Heat of Combustion of Glycollic Acid.** By BERTHELOT (*Compt. rend.*, 115, 393).—Stohmann points out that the heat of combustion of glycollic acid as determined by Louguinine (*Ann. Chim. Phys.* [6], 23, 210—213) is +166.0 Cal., and not +186.0 Cal. It follows that the conversion of acetic acid into glycollic acid would develop +40.2 Cal., and the conversion of acetic acid into glyoxylic acid would develop +79.4 Cal. or  $+39.7 \times 2$ . C. H. B.

**Thermochemistry of Carbon Compounds of Mixed Function.** By L. VIGNON (*Compt. rend.*, 115, 354—356).—Experiments

	Heat of dissolution.	Heat developed by		
		1 mol. HCl.	2 mols. HCl.	3 mols. HCl.
$\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ .....	+0.06 Cal.	+3.50	+2.35	+0.61
$\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ .....	+0.26 „	+0.87	+0.00	+0.00
$\text{CS}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ .....	+0.22 „	+1.35	—	—

were made with tetramethyldiamidodiphenylmethane, tetramethyldiamidobenzophenone, and tetramethyldiamidothiobenzophenone.

The presence of the ketonic group CO destroys the basic function, but this effect is only partial in the case of the thioketonic group CS

C. H. B.

**Specific Gravity of Ice.** By J. V. ZAKRZEWSKI (*Ann. Phys. Chem.* [2], **47**, 155—162).—It is pointed out by the author that the determinations of the specific gravity of ice at the freezing point are not sufficiently accurate for the purposes of exact heat measurement by means of Bunsen's ice calorimeter. By using a modification of this instrument, he has made fresh determinations of the specific gravity of ice at temperatures very near 0°. The calorimeter was filled with mercury and boiled-out water, the exact weight of which was ascertained. This water was frozen very slowly at a temperature just below the freezing point, the crystallisation being started at a given point by means of the external application of solid carbonic anhydride and ether. The mercury expelled was then weighed. A check determination was made by melting the ice and ascertaining the weight of mercury sucked up by the apparatus. The two weights usually differed by a few milligrams on a total of 15—30 grams. The results of the measurements are as follows:—

Temperature.	Specific gravity.
—0.705°	0.916710
—0.700°	0.916713
—0.699°	0.916708
—4.720°	0.916995

From these values, the specific gravity of ice at 0° is 0.916660, and the coefficient of expansion 0.000077.

J. W.

**Relation between the Specific Gravity of Acid or Saline Solutions and the Molecular Weight of the Dissolved Substances.** By A. DE SAPORTA (*Bull. Soc. Chim.* [3], **7**, 184—190).—An acid or saline solution made by dissolving 52.63 grams of substance in a litre of distilled water is termed a *typical solution*, and is usually of greater sp. gr. than water. The excess of the sp. gr. above unity is termed the *typical density A* (*alourdissement type*), and if a gram-molecule *P* of the substance is substituted for the constant amount, a quantity  $AP/52.63$  is obtained which is termed the *theoretical molecular density*, and is held to be proportional to the *molecular excess* or difference between the molecular weight of the dissolved substance and that of water,  $AP/52.63 = K(P - 18)$ . From this it follows that  $A/K = 52.63 - 947.34/P$ , and the truth of the above supposition can be tested by comparing the values calculated from the right-hand side of the equation with those calculated from the left-hand side. The results are given for most of the commonly occurring inorganic acids and salts, and the agreement is fair, as a rule, when *K* is taken as unity, although more consistent results are obtained in some cases by giving it a higher value.

JN. W.

**Specific Volume of Sulphur.** By M. TOEPLER (*Ann. Phys. Chem.* [2], **47**, 169—174).—Monoclinic sulphur, plastic sulphur, obtained by rapid cooling from 140—170° to 20°, and liquid (syrupey) sulphur, obtained by very slow cooling through the same range of temperature, have been investigated by the author with respect to the volume they occupy at different temperatures.

His results are contained in the following table, the volume of liquid sulphur at 120° being taken as unity :—

	Monoclinic.	Liquid.	Plastic.
--20°	—	0·935	—
0	0·915	0·943	—
20	0·919	0·951	—
40	0·924	0·960	0·974
60	0·929	0·969	0·979
80	0·935	0·979	—
100	0·941	0·9889	—
120	—	1·0000	0·995
140	—	1·0117	1·001
160	—	—	1·007
180	—	—	1·014
200	—	—	1·021

J. W.

**Relations between the Surface Tensions of Liquids and their Chemical Constitution.** By C. E. LINEBARGER (*Amer. J. Sci.* [3], **44**, 83—92).—The author points out that up to the present little or nothing has been done towards establishing relations between the surface tensions of liquids and their chemical constitution. He proposes to investigate the subject, and the present paper is devoted mainly to a description of the method to be used in carrying out the experiments. This consists in determining the number of drops into which a certain volume of water divides in dropping down through liquids lighter than water, and in dropping up through liquids heavier than water, and the number of drops of a liquid dropping down, if heavier than water, and dropping up, if lighter, through that standard.

At the surface of two absolutely insoluble liquids, there would reign complete repulsion between the molecules; no molecule of one liquid would pass beyond a definite surface concentric with the surface of the liquids, and this surface would form an impenetrable barrier to molecules of each liquid. But in the case of liquids which dissolve one another a little, complete repulsion between the molecules prevails no longer, but, on the contrary, a slight attraction, so that now a molecule of one liquid may pass into the other. This would continue until the tension of solution of each liquid was reached. The question arises, whether the superficial tensions of liquids, saturated with each other, or pure, should be employed. In this preliminary investigation only the superficial tensions of liquids uncontaminated with one another were determined.

The experiments recorded with hydrocarbons and their derivatives indicate clearly that a connection exists between surface tension and



chemical constitution, but the data obtained are not yet sufficient to admit of generalisations being made. The author is continuing these investigations.  
H. C.

**Tensions of Vapours.** By C. ANTOINE (*Ann. Chim. Phys.* [6], **22**, 281—288).—In former papers (*Compt. rend.*, **107**, 681, 778, 836), the author has shown that the tensions of vapours could be calculated by the formula  $\log H = A - \frac{B}{t + c}$ ; the object of this communication is simply to modify some of the coefficients previously given, and to show how far the calculated values agree with those determined experimentally.  
F. S. K.

**Elasticity of Gases.** By C. PUSCHL (*Monatsh.*, **13**, 635—646).—Mendeléeff and others have shown that the product  $pv$ , which, in general, decreases on compression and increases on expansion, behaves in a precisely opposite manner at low pressures, and on expansion this product, therefore, reaches a maximum and then decreases. On the other hand, the fact that on compression the product reaches a minimum and then increases is well known. It follows from this that there are, ordinarily speaking, two points at which any gas will exactly obey Boyle's law. From experiments of Witkowski and others, it can be shown that the maximum of  $pv$  occurs with rising temperature at higher and higher pressures; the minimum, on the other hand, occurring at lower and lower pressures as the temperature rises. It, therefore, follows that at some particular temperature the above pressures for maximum and minimum  $pv$  will become the same, and the two points coincide. The point at which this occurs may be called the *symptotic point*. If the temperature be raised beyond this point,  $pv$  will no longer give on compression a maximum and a minimum, but only the one point in which both may be supposed to coincide, a thing which is noticed in the case of hydrogen at the ordinary temperature. The author discusses mathematically certain variations in the different properties of gases in the region of the symptotic point.  
H. C.

**Velocity of Etherification.** By V. KISTYAKOFFSKY (*J. Russ. Chem. Soc.*, **22**, 474—476).—The author has deduced the constant of velocity for the etherification of organic acids under the influence of inorganic acids, from experiments made in conformity with the following equations—

$$\frac{dx}{dt} = (a - x)k - xk_1,$$

and

$$0 = (a - \xi)k - \xi k_1,$$

in which  $a$  denotes the quantity of organic acid taken,  $x$  the quantity of ethereal salt formed,  $t$  the time,  $k$  and  $k_1$  the constants for the formation and decomposition of the ether:  $\xi$  is the value of  $x$  for which there is equilibrium between the opposing reactions. Large quantities of water and of alcohol were taken in proportion to the quantity of

organic acid, so that these might be assumed to remain constant during the reaction. On integration, the equations give  $k = \frac{\xi}{at} \log \frac{\xi}{\xi - x}$ ,  $k_1 = \frac{a - \xi}{at} \log \frac{\xi}{\xi - x}$ , from which  $k + k_1 = \frac{1}{t} \log \frac{\xi}{\xi - x}$ , the most useful form for calculation.

The quantity of inorganic acid used was less than that of the organic acid present. Under these circumstances it was found that the expression  $\frac{1}{t} \log \frac{\xi}{\xi - x}$  was, indeed, appreciably constant. The value of the constant thus obtained diminished as the quantity of water present was increased, and was proportional to the electrical conductivity of the solution when one inorganic acid was substituted for another.

The amount of organic acid converted into ethereal salt when equilibrium had taken place, was found to be proportional to the amount of it originally present in the solution. J. W.

**Attempt to found a Chemical Theory on a Basis of Physical Comparison.** By G. JAUMANN (*Monatsh.*, **13**, 523—566).—This paper contains an attempt to formulate a theory which might take the place of the atomic theory. It is purely inductive in all its parts, and does not start with preconceived ideas as to the constitution of matter or the nature of the change to be observed, but demands only for the explanation of stoichiometric phenomena the existence of a simple physical principle, such as holds for all other physical changes, and only such definite conceptions as are necessary for the application of this principle. If in physical structure all substances are alike, their chemical behaviour is determined by the numerical value of a single property on which all chemical properties depend, and which may be called the chemical condition or the *chemical*. Differences in the values of this property are, as the author shows, approximately measurable, and determine the changes which will take place in given substances under certain conditions. Application of the principle to a number of different cases is made in the paper. H. C.

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