

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Multiple Rotatory Powers. By E. MULDER (Deut. Chem. Ges. Ber., vii, 1329—1332).

THE author distinguishes between stable and temporary (labile) rotatory powers, and considers that the phenomena of the conversion of dextroracemic acid into lævo-acid, &c., afford proof of the existence of more than one rotatory power; he gives no new facts on the subject, however.

C. R. A. W.

Function of Peroxides in the Galvanic Battery. By W. BEETZ (Pogg. Ann. Chem., 535—551).

THIS is an examination of Leclanché's battery, with a view to ascertain what is the best condition for the materials used in charging it, and what is the special part played by the manganic peroxide. In a cell formerly devised by the author, a massive piece of pyrolusite was surrounded with an acidified solution of potassium permanganate; the positive metal consisted of potassium-amalgam immersed in caustic potash. The electromotive force of this element was 3.02 (Daniell's = 1), which is the highest known for a single cell. In this combination the pyrolusite acted as the negative metal, and in the earlier forms of Leclanché's cell, a *plate* of pyrolusite was also employed, combining the functions of negative metal and depolariser. The use of the powdered peroxide is obviously more desirable; but the comminution seriously increases its resistance. This, indeed, is the case even with good conductors like platinum and gas-carbon, as is shown by some experiments in which copper was deposited on a platinum plate covered with the powder to be examined. Using platinum sponge, the copper was all deposited on the exterior, but with platinum black the deposition took place throughout the mass. Gas carbon behaved like the sponge when coarsely crushed, but like the black (misprinted *sponge* in the original) when finely powdered. The difference between coarsely and finely powdered pyrolusite was in the same direction. It would seem, therefore, *a priori*, that a mixture of coarsely crushed carbon with finely ground manganic peroxide, would possess all the advantages arising from the extended surface of the depolariser, and the high conducting power of the carbon. This was corroborated by experiments in which fine and coarse materials were variously mixed. The mixture mentioned above was superior to all others, both in a comparatively slight diminution of the current-strength when the

poles were connected, and in a rapid recovery when they were insulated again. The internal resistance was also scarcely higher than that of a cell containing powdered carbon only, and was hardly affected by working the cell; whereas in an element containing fine manganic peroxide alone, the resistance, which at starting was three times as high, was increased to seven times by half an hour's work.

The good conductivity and great depolarising power of lead peroxide suggest its employment in the place of the pyrolusite, and indeed elements constructed with this substance, and excited with sulphuric acid, potassium nitrate, or sodium carbonate, showed high electromotive force, and great constancy under varied circumstances; but the last possesses a high internal resistance, and that of the others, though low at first, increases enormously by use.

M. J. S.

Thermo-Chemical Researches.—XIII. Further Researches on certain Processes of Oxidation and Reduction. By JULIUS THOMSEN (Pogg. Ann., cli, 194—225).

THE author found that an error had crept into his former experiments with hypochlorous acid, which rendered the results inaccurate; he has, therefore, gone through the whole work again.

A. *Formation and Decomposition of Hypochlorous Acid.*—The solution was prepared by the absorption of the gaseous acid by water, and was found to retain its stability unimpaired for several days when it contained 200 molecules of water to each molecule of ClOH. Solutions of the acid in sodium hydrate were also found to be stable when the latter was not perfectly saturated, while on the other hand solutions of sodium hypochlorite, with an excess of acid, quickly underwent decomposition.

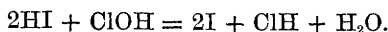
The affinity between the constituents of hypochlorous acid was estimated by two methods—its formation and its decomposition.

(a.) *Formation.*—From chlorine and sodium hydrate by the equation:— $2\text{NaOH} + 2\text{Cl} = \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$. The evolution of heat in this reaction corresponds with the formulæ:—

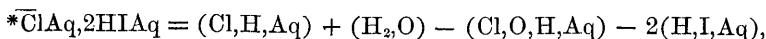
$$2\text{NaOHAq}, 2\text{Cl} = \left\{ \begin{array}{l} (\text{Cl}, \text{H}, \text{Aq}) + (\text{Cl}, \text{O}, \text{H}, \text{Aq}) - (\text{H}_2, \text{O}) \\ + (\text{NaOHAq}, \text{ClHAq}) \\ + (\text{NaOHAq}, \text{ClOAq}) \end{array} \right.$$

and the mean number found is $\text{Cl}, \text{O}, \text{H}, \text{Aq} = 29963$ heat-units.

(b.) *Decomposition.*—When more than two molecules of hydriodic acid react upon one molecule of hypochlorous acid in an aqueous solution, both acids undergo decomposition, thus:—



The formula of the reaction is therefore:—



* The bar over the symbols stands for HO, *e. gr.*, $\overline{\text{Na}} = \text{NaOH}$, &c.

and as—

$$\begin{array}{rcl} \overline{\text{ClAq}}, 2\text{HIAq} & = & 51537 \text{ heat-units,} \\ \text{H, I, Aq} & = & 13171 \quad , \end{array}$$

it follows that $\text{Cl, O, H, Aq} = 29793$ heat-units, which agrees very nearly with the number above given. The mean, therefore, of these two numbers (29878 heat-units) may be considered to approximate very closely to the true value.

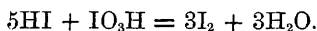
The evolution of heat in several reactions with hypochlorous acid may easily be found by means of this value. The acid may act as an oxidising agent by giving up oxygen:—

$$(\text{H, Cl, Aq}) - (\text{Cl, O, H, Aq}) = 9437 \text{ heat-units,}$$

or under the influence of hydrochloric acid it may be decomposed into chlorine and water, and thus act like chlorine itself:—

$$(\text{H}_2\text{O}) - (\text{Cl, H, Aq}) - (\text{Cl, O, Aq}) = - 836 \text{ heat-units.}$$

B. Formation and Decomposition of Iodic Acid. (a.) *Decomposition.*—Iodic acid in aqueous solution is completely decomposed when 1 molecule is acted on by 5 molecules of hydrochloric acid, thus:—

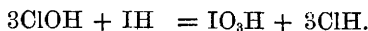


The evolution of heat is expressed by the reaction—

$$(5\text{IHAq}, \text{IO}_3\text{HAq}) = 3(\text{H}_2\text{O}) - 5(\text{I, H, Aq}) - (\text{I, O}_3, \text{H, Aq}),$$

and therefore $(\text{I, O}_3, \text{H, Aq}) = 55884$ heat-units.

(b.) *Formation.*—From hypochlorous acid and hydriodic acid, in proportion of more than 3 molecules of the former to 1 of the latter—



$$\text{Now as } (3\overline{\text{ClAq}}, \text{IHAq}) = 70682 \text{ heat-units,}$$

$$\text{and } \text{Cl, O, H, Aq} = 29878 \quad ,$$

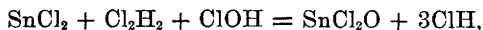
$$(\text{I, O}_3, \text{H, Aq}) = 55542 \quad ,$$

The mean of the two numbers (a) and (b) is therefore 55713 heat-units.

C. Oxidation of Stannous Chloride.—When chlorine is passed into a solution of stannous chloride, the liquid becomes yellow, and Berthelot explained this by supposing that a basic salt is formed together with hypochlorous acid. The author believes that it is due to the formation of metastannic acid.

The heat of oxidation of stannous chloride was estimated by three methods.

First. By the action of hypochlorous acid—

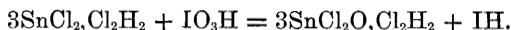


as $(\text{SnCl}_2\text{H}_2\text{Aq}, \text{ClOHAq}) = 75048$ heat-units and the evolution of heat is expressed by—

$$(\text{SnCl}_2\text{H}_2\text{Aq}, \text{O}) + \text{Cl, H, Aq} - (\text{Cl, O, H, Aq}),$$

therefore $75048 - 9437 = 65611$ heat-units is the heat of oxidation of stannous chloride in acid solution.

Second. From the reduction of iodic acid in presence of free hydrochloric acid—



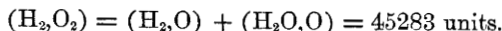
This method gave $(\text{SnCl}_4\text{H}_2\text{Aq}, \text{O}) = 66010$ heat-units.

Third. By what the author calls a "circular method," in which a molecule of an acid solution of stannous chloride is oxidised by potassium permanganate; next a molecule of the same tin-solution is oxidised by a solution of hydrogen peroxide containing free hydrochloric acid; and thirdly a molecule of the last solution is decomposed by potassium permanganate with evolution of oxygen. A peculiar relation is then found to exist between the heat-units in the three reactions, viz., that if the units of the first two reactions are added together and that of the third is subtracted from the sum, the result is double the heat of oxidation of stannous chloride. Omitting details, the results of the experiments were as follows:—

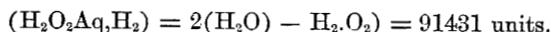
$(\text{SnCl}_6\text{H}_4\text{Aq}, \frac{1}{5}\text{Mn}_2\text{O}_8\text{K}_3\text{Aq})$	= 77345 heat-units.
$(\text{SnCl}_4\text{H}_2\text{Aq}, \text{H}_2\text{O}_2, \text{H}_2\text{Cl}_2\text{Aq})$	= 88820 ,,
$(\frac{1}{5}\text{Mn}_2\text{O}_8\text{K}_3\text{Aq}, \text{H}_2\text{O}_2, \text{H}_2\text{Cl}_2\text{Aq})$	= 34930 ,,
therefore $(\text{SnCl}_4\text{H}_2\text{Aq}, \text{O})$	= 65617 ,,

The mean number deduced from the three methods gives 65746 heat-units as the heat of oxidation of stannous chloride. From this value it may be seen that the evolution of heat which would take place if stannous chloride could be oxidised by gaseous chlorine, without formation of stannic oxide, would be 76019 heat-units, a value which the author has failed to obtain with sufficient accuracy by direct experiment.

D. Hydrogen Peroxide as an Oxidising Agent.—The evolution of heat in the reduction of hydrogen peroxide by stannous chloride amounts to 88820 heat-units, and the heat of oxidation of stannous chloride is 65746 units: therefore the evolution of heat in the decomposition of hydrogen peroxide into oxygen and water amounts to 23074 heat-units; and as the heat of formation of water is 68357 units, that of the peroxide is 45283 units, for



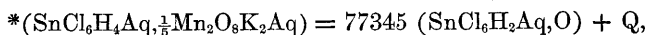
When hydrogen peroxide is reduced to water by the action of hydrogen, the evolution of heat is—



E. Potassium Permanganate as an Oxidising Agent.—If potassium permanganate is decomposed in a solution containing hydrochloric acid with evolution of 5 atoms of oxygen, the evolution of heat is—



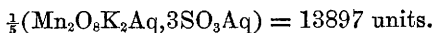
where Q is the value corresponding with one atom of oxygen. The decomposition of potassium permanganate by stannous chloride is—



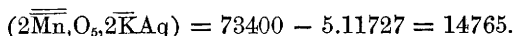
therefore $Q = 77345 - 65746 = 11599$ heat-units.

When the decomposition is effected by hydrogen peroxide, the value of Q is 11856 heat-units, therefore the mean value for each atom of oxygen when the permanganate is decomposed in a solution containing hydrochloric acid, with evolution of 5 atoms of oxygen, is 11727 heat-units.

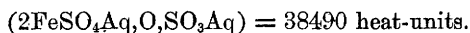
If sulphuric acid is employed in place of hydrochloric acid, the evolution of heat is greater—



The heat of formation of potassium permanganate from manganous oxide, potassium hydrate, and oxygen is—



If in the method described in a previous paper for estimating the evolution of heat in the decomposition of potassium permanganate with evolution of 3 atoms of oxygen and formation of manganese peroxide, we substitute the new value for $(2\overline{\text{Mn}}, \text{O}_5, 2\overline{\text{K}}\text{Aq})$, and also use the value given below—



we obtain for the mean value of $\overline{\text{Mn}}, \text{O}$ 21511 heat-units, and the equation $2(\overline{\text{Mn}}, \text{O}) + (2\overline{\text{Mn}}, \text{O}, \text{O}_3, 2\overline{\text{K}}\text{Aq}) = (2\overline{\text{Mn}}, \text{O}_5, 2\overline{\text{K}}\text{Aq})$ leads to the result $(2\overline{\text{Mn}}, \text{O}, \text{O}_3, 2\overline{\text{K}}\text{Aq}) = 28257$ heat-units, and hence the evolution of heat amounts to 9419 units for each atom of oxygen.

F. *Heat of Oxidation of Ferrous Chloride.*—This was determined by oxidation with (a) hypochlorous acid, (b) potassium permanganate, (c) gaseous chlorine. The values obtained were—

$$\text{Fe}_2\text{Cl}_6\text{H}_4\text{Aq}, \text{O} = \begin{cases} (a.) & 45556 \text{ heat-units.} \\ (b.) & 44988 \quad , \\ (c.) & 45207 \quad , \\ \hline \text{Mean} & 45250 \quad , \\ \text{and } (\text{Fe}_2\text{Cl}_6\text{H}_4\text{Aq}, \text{Cl}_2) & = 55523 \quad , \end{cases}$$

From these numbers the heat of oxidation of hydrated ferrous into hydrated ferric oxide may be calculated, and is found to be $(2\overline{\text{Fe}}, \text{O} = 54580$ heat-units.

The heat of oxidation of ferrous sulphate is also found to be 38490 heat-units for every atom of oxygen, when oxygen is employed, but if chlorine is used as the oxidising agent, the heat amounts to 48763

* The second half of this equation seems to contain some mistake.

units. This is the value only when the solution is neutral; for if an excess of sulphuric acid is present, the evolution of heat becomes greater, and is represented by $2(\text{FeSO}_4\text{Aq}, n\text{SO}_3\text{Aq})$, which when $n = 1$, *i.e.*, when 1 molecule of free acid is present for each molecule of ferrous sulphate, amounts to 1790 units, and increases with the value of n .

G. Chromic Acid as an Oxidising Agent.—This was estimated from the reduction of chromic acid to chromic oxide by means of stannous chloride, with the result, $(2\text{Cr}, \text{O}_3\text{Aq}) = 18868$ heat-units.

The tables given in a former paper (*see this Journal*, 1873, p. 1186) by the author must now be replaced by the following:—

TABLE II.—*Reducing Agents.*

Reaction.	Q.	
$(\text{SO}_2\text{Aq}, \text{Cl}_2)$	73907 heat-units	} for one molecule of chlorine.
$(\text{Fe}_2\text{Cl}_6\text{H}_4\text{Aq}, \text{Cl}_2)$	55523	
$(2\text{FeSO}_4\text{Aq}, \text{Cl}_2)$	48763	
$(\text{SnCl}_6\text{H}_4\text{Aq}, \text{Cl}_2)$	76019	
$(\text{SO}_2\text{Aq}, \text{O})$	63634	} for one atom of oxygen.
$(\text{Fe}_2\text{Cl}_6\text{H}_4\text{Aq}, \text{O})$	45250	
$(2\text{FeSO}_4\text{Aq}, \text{O}, \text{SO}_4\text{Aq})$	38490	
$(\text{SnCl}_6\text{H}_4\text{Aq}, \text{O})$	65746	

TABLE III.—*Oxidising Agents.*

Reaction.	Q.	Available oxygen-atoms.	Q for one atom of oxygen.
$(\text{Cl}_2, \text{H}_2\text{Aq}) - (\text{H}_2, \text{O})$	10273 heat-units	1	10273 heat-units.
$(\text{Br}_2, \text{H}_2\text{Aq}) - (\text{H}_2, \text{O})$	— 11605	1	— 11605
$(\text{Br}_2, \text{Aq}, \text{H}_2) - (\text{H}_2, \text{O})$	— 12683	1	— 12683
$(\text{Cl}_2, \text{H}_2\text{Aq}) - (\text{Cl}_2, \text{O}, \text{H}_2\text{Aq})$. .	9473	1	9437
$(\text{Mn}_2\text{O}_8\text{K}_2\text{Aq}, 6\text{HClAq})$	58635	5	11727
$(\text{Mn}_2\text{O}_8\text{K}_2\text{Aq}, 3\text{SO}_3\text{Aq})$	69485	5	13897
$(\text{Mn}_2\text{O}_8\text{K}_2\text{Aq}, 2\text{HClAq})$	55757	3	18586
$(\text{Mn}_2\text{O}_8\text{K}_2\text{Aq}, \text{SO}_3\text{Aq})$	59547	3	19849
$(\text{MnO}, \text{SO}_3\text{Aq})$	4969	1	4969
$(2\text{CrO}_3\text{Aq}, 3\text{SO}_3\text{Aq})$	30452	3	10151
$-(2\text{MnO}, \text{O}_3, 2\text{KAq})$	28257	3	9419
$-(2\text{Mn}, \text{O}_5, 2\text{KAq})$	— 14765	5	— 2953
$-(\text{Mn}, \text{O})$	— 21511	1	— 21511
$-(2\text{Cr}, \text{O}_3, \text{Aq})$	— 18868	3	— 6289
$-(\text{H}_2\text{O}, \text{O}, \text{Aq})$	+ 23074	1	+ 23074
$-(\text{HAq}, \text{O}_3)$	— 42542	3	— 14181

The paper concludes with full details of the experiments.

G. T. A.

Relations between Affinity and Dissected (Structural) Formulæ.

By C. R. ALDER WRIGHT (Phil. Mag. [4], xlviii, 401—430).

AFFINITY is defined as being measured by the number of absolute units of work gained during the coalescence of weights $w_1, w_2, w_3 \dots$, of various forms of matters so as to give a weight $w_1 + w_2 + w_3 + \dots = \Sigma(w)$ of a single homogeneous body, termed a *compound* of the other forms of matter which are said to be *constituents*. The unit of affinity would therefore be when one absolute unit of work (meter-gram-second system) is gained during the formation of a gram of product; for convenience, however, affinity may be expressed in heat-units, one absolute work unit being equal to 0.00024054 gram-heat-unit.

Knowing the affinity F between any given constituents under given conditions of pressure, temperature, &c., obtaining during coalescence, then, F' under any other conditions can be calculated by the formula—

$$F' = F + h_1 + h_2 + h_3 \dots - h_n,$$

where $h_1, h_2, h_3 \dots h_n$ are the amounts of heat requisite to alter the temperatures of the various constituents and the compound respectively from the old to the new conditions. The author institutes comparisons between the affinity-values obtained for various organic bodies indicated by the general formula $C_m H_n O_p$, by the aid of the equation

$$2\delta F_{100} = 12m(h_1 + h_3) + n(h_2 + h_4) + 16ph_5 - 2\delta(H_1 + H_2) - h_6,$$

where $2\delta F_{100}$ is the affinity per meter gram of the compound* examined, δ being the vapour-density, and F_{100} the affinity per gram.

h_1, h_2 , and H_1 are the "heats of combustion" (at 15°) of carbon, hydrogen, and the compound respectively.

h_3, h_4, h_5 , and H_2 are the amounts of heat required to raise one gram of carbon, hydrogen, oxygen, and compound respectively from 15° to 100° under constant pressure, and

h_6 is the heat equivalent to the work done in compressing the constituent hydrogen and oxygen (the volume occupied by the solid carbon being neglected) from the bulk actually occupied by them jointly at 760 mm. and 100° to the bulk occupied by the vapour of the compound under these conditions.

Substituting the proper numerical values, this equation becomes

$$2\delta F_{100} = m \times 95.813 + n \times 34.564 + p \times 0.296 - 2\delta(H_1 + H_2) - (n + p - 2) \times 0.372.$$

where $n + p - 2$ is the number of *metropneums** of contractions that

* The term *one metropneum* is used instead of the indefinite phrase "one volume," to indicate the bulk occupied by 1 gram of hydrogen under any given circumstances of pressure and temperature, *i.e.*, 1 metropneum = $11160 \times \frac{273 \times t}{273}$

$\times \frac{760}{p}$ cubic centimeters at temperature t and pressure p . The term *one metrogram* is used to indicate a quantity representing the weight in grams of two metropneums of vapour (*i.e.*, is used instead of the term "one molecule" in cases where no question arises as to theoretical views concerning the constitution of matter). Vide *Chem. News*, July 18th, 1873, p. 25.

take place during the coalescence of the constituents; the unit of heat employed is 1000 gram heat-units, or 1 kilogram heat-unit.

The affinity-values thus obtained are therefore reduced to the following uniform standard. Solid carbon and gaseous oxygen and hydrogen are supposed to coalesce forming a given compound in the gaseous state, the materials and products being all viewed as being examined at the uniform temperature 100° , the compound being under a pressure of 760 mm., and the materials under such a pressure as to render the bulk of the gaseous oxygen and hydrogen (neglecting the space occupied by the solid carbon) equal to that of the compound. This standard is only suggested as a provisional one, a somewhat different one being possibly more convenient for other analogous thermochemical calculations.

By the aid of the above formula the following values are calculated:—

Substance.	$2\delta F_{100}$.	Substance.	$2\delta F_{100}$.	Substance.	$2\delta F_{100}$.
Oxygen	0	Ethylic alcohol	63.7	Methyl butyrate	$\left\{ \begin{array}{l} 115.1 \\ 105.0 \text{ cor.} \end{array} \right.$
Hydrogen	0	Amylic „	86.2	„ valerate	$\left\{ \begin{array}{l} 115.2 \\ 110.0 \text{ cor.} \end{array} \right.$
Marsh-gas	+21.7	Cetylic „	106.7	Ethyl formate..	$\left\{ \begin{array}{l} 92.0 \\ 86.0 \text{ cor.} \end{array} \right.$
Acetylene	-50.6	Formic acid ..	97.2	„ acetate..	91.5
Carbon oxide.....	+27.5	Acetic „ ..	110.0	„ butyrate..	$\left\{ \begin{array}{l} 147.7 \\ 110.0 \text{ cor.} \end{array} \right.$
Carbon dioxide....	+95.6	Butyric „ ..	146.3	„ valerate..	114.4
Ethylene	- 5.5	Valeric „ ..	149.5	Amyl acetate ..	$\left\{ \begin{array}{l} 96.7 \\ 114.4 \text{ cor.} \end{array} \right.$
Amylene	+10.3	Palmitic	204.3	„ valerate..	151.3
Diamylene.....	46.3	Stearic.....	154.0	Cetyl palmitate.	242.7
Cetylene	129.1	Ethylic ether .	33.0	Acetone.....	59.9
Tetramylene.....	196.9	Amylic „ ..	83.5	Phenol.....	29.5
Water	57.9	Methyl formate	68.0		
Methylic alcohol ...	53.4	„ acetate	87.0		

The numerical data required for the calculations are taken from the results of Regnault, Kopp, Favre and Silbermann, Julius Thomsen, Dulong, Andrews, &c.; the values of $2\delta F_{100}$ marked "cor." are those regarded as near the truth in certain cases, in which, for reasons assigned in the paper, there is reason for suspecting the accuracy of the calculated value; from the nature of the above formulæ, a very small error in the determination of the value of H_1 makes a large error in the value of $2\delta F_{100}$.

From these "reduced affinity-values" the author deduces the following general rules, each of which is fully discussed and copiously illustrated by examples.

(1.) The formation of an olefine and water from an alcohol is accompanied by heat-absorption in the case of lower members of the series, and by heat-evolution in the case of cetylic alcohol. Similarly the formation of formic acid from carbon oxide and water is accompanied by heat-absorption.

(2.) The production of ethers and steam from alcohols is accompanied by heat-absorption.

(3.) The reaction of alcohols and acids together forming compound ethers and steam is accompanied by heat-absorption.

(4.) The oxidation of alcohols to acids and steam is accompanied by heat-evolution.

Some of these results are opposed to those calculated by Thomsen (*Deut. Chem. Ges. Ber.*, ii, 482) from Hermann's values for the heats of combustion reduced to a uniform standard, something like that adopted for affinity-values in this paper (*ibid.*, i, 18).

(5.) The differences between the affinity-value of any two substances represent the heat-disturbances that would ensue could an "operation" (Brodie, *Phil. Trans.*, 1866) be performed in the space filled by the vapour of the first body, such as to cause the space to be filled instead with the vapour of the second; and such "operations" are, to some extent, symbolised by the ordinary formulæ in use, e.g., the symbols CH_4 and $\text{CH}_3\cdot\text{CO}_2\text{H}$ represent the operation of conversion of two metropneums of marsh-gas into two of acetic acid: $\text{C}_2\text{H}_5\cdot\text{OH}$ and $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$ represent the operation of conversion of ethylic alcohol into ethylic ether, &c. When an operation is performed such as to be symbolised by the substitution of the radical or group of symbols CH_3 for an H symbol in the formula of a substance, this operation may be termed "methylation," the methylation being *hydrocarbonous* if the H symbol belongs to a constituent hydrocarbonous radical (CH_3 , CH_2 , or CH) in the formula, and *hydroxilic* if the H symbol belongs to an OH group. Then this rule holds. *In hydrocarbonous methylation heat is invariably evolved, and in hydroxylc methylation it is invariably absorbed.*

(6.) The operation indicated by the replacement of the symbol H_2 by an O symbol is always accompanied by *heat evolution*.

(7.) In all of these cases the following connection holds between boiling point and heat-disturbance. *If an operation be performed such that heat is evolved during its performance, the resulting product boils at a higher temperature than the original substance, and vice versâ.* This rule does not hold in some few cases, where a series of operations is performed, such that some of the operations would cause heat-evolution and some heat-absorption, the algebraic sum of the heat-disturbances during the several operations being occasionally of one sign, whilst that of the boiling-point alterations is of the other sign; usually, however, the rule holds even when a series of operations are successively performed.

(8.) Isomerides and polymerides are so related, that if a body be convertible into another of the same percentage composition by a process evolving heat, the boiling point is raised by the change; and *vice versâ*.

(9.) In most cases the addition of a C symbol to a formula causes heat-absorption; that of an O symbol, heat-evolution; and that of an H symbol also heat-evolution.

Finally the conclusion is drawn that the different positions with respect to one another of the constituent radicals in a dissected formula indicate not only differences in chemical reactions and physical pro-

perties, but also correlative differences in the amounts of work performed or gained in the formation under constant conditions of the substances thereby indicated from the forms of matter conventionally termed their constituent elements.

Admitting the atomic and molecular constitution of matter, the motions of the ultimate atoms, and the molecules made up of them, must be under the influence of definite laws of force; and the study of the energy-differences involved in chemical reactions affords a probable means of arriving at these laws. Should it be found possible to deduce from such experiments definite laws of force in harmony with all physical, chemical, and astronomical data, a great weight will be given to the fundamental hypothesis. But should it be found that the law of force between two given atoms, &c., calculated from one set of data is incompatible with that deduced from another set, or that the inter-atomic forces thus arrived at are irreconcilable with the physical intermolecular resultant forces, or that any other incompatibilities arise, it must follow that the primary hypothesis as to the atomic constitution of matter is untenable.

C. R. A. W.

On Siljeström's Experiments on the Changes of Elasticity in Rarefied Gases. By D. MENDELEJEFF (Deut. Chem. Ges. Ber., vii, 1339—1344).

THE relation, $PV = 1 - \alpha P$, inferred by Siljeström from his experiments on air at pressures between 7 and 770 mm. is considered to be erroneous by the author, who points out many sources of error in the experiments, and, moreover, shows that the very results which are the most trustworthy lead, if rightly interpreted, to the equation $PV = 1 + \alpha P$, which the author, in conjunction with Kirpitscheff, in a series of most carefully made experiments, had found to hold good for rarefied gases.

R. S.

On the Diffusion of Gases through the Walls of Soap-bubbles. (Preliminary Notice.) By F. C. G. MUELLER (Deut. Chem. Ges. Ber., vii, 1401).

WHEN a soap-bubble containing air is introduced into a bell-jar filled with hydrogen and left there for about 30 seconds, it will acquire the property of rising in the air and of exploding with a yellow flame on its approach to the flame of a Bunsen's burner. To ensure success the bubble must have a diameter of about 3 centimeters, and show bright colours. The experiment was devised to show the possibility of the diffusion of gases through liquid diaphragms.

R. S.

Relation between the Atomic Weight, Specific Gravity, and Hardness of the Metallic Elements. By S. BOTTONE (Pogg. Ann., cl, 644).

THE scale of hardness in the last column was obtained by observing the time required for a steel drill to penetrate to a determined depth.

	Sp. gr.	Atomic weight.	Sp. gr. Atom. wt.	Hardness.
Manganese	8·01	55·0	0·1457	0·1456
Cobalt	8·5	58·8	0·1446	0·1450
Nickel	8·28	58·8	0·1408	0·1410
Iron	7·7	56·0	0·1375	0·1375
Copper	8·66	63·4	0·1364	0·1360
Palladium.....	11·8	106·6	0·1107	0·1200
Platinum	21·5	197·4	0·1090	0·1107
Zinc	7·0	65·2	0·1077	0·1077
Indium	7·28	74·0	0·0983	0·0984
Gold	19·3	197·0	0·0980	0·0979
Silver.....	10·4	108·0	0·0963	0·0990
Aluminium	2·25	27·4	0·0821	0·0821
Cadmium	8·6	112·0	0·0768	0·0760
Magnesium	1·74	24·0	0·0726	0·0726
Zinc . . . 2.	7·2	118·0	0·0619	0·0651
Thallium	11·86	204·2	0·0574	0·0565
Lead	11·38	207·0	0·0550	0·0570
Sodium	0·93	23·3	0·0401	0·0400
Calcium	1·58	40·0	0·0394	0·0405
Potassium.....	0·86	39·1	0·0221	0·0230
Diamond	3·5	12·0	0·2917	0·3010

M. J. S.

Decomposition of Certain Salts by Water.

By A. DITTE (Compt. rend., cxxix, 915—918).

THE action of water upon mercuric sulphate, whereby *turpeth mineral* is produced, ceases when the sulphuric acid set at liberty attains a certain limited value. In proof of this the author has succeeded in preparing a solution of sulphuric acid of such strength that, according as the proportion of acid is increased or diminished, it either dissolves or decomposes the neutral sulphate. Such solution at 12° contains 67 grams of sulphuric anhydride per litre.

It was reasonable to suppose that the basic sulphate, though insoluble in water, might be soluble in solutions containing free sulphuric acid. If, then, some of the salt were mixed with a sulphuric solution of known strength, but containing less than 67 grams of anhydride per litre, the weight of mercuric oxide and excess of acid which passes into solution should satisfy the formula $\text{HgSO}_4 \cdot 2\text{HgO}$.

This was found to be the case: the solubility of the basic salt was also perfectly uniform. When, however, the proportion of sulphuric acid exceeded 67 grams per litre, the weight of mercury oxide which dis-

solved greatly exceeded the value represented by the ordinate corresponding with abscissæ of initial acid; in all probability therefore the excess of acid had reproduced and now held in solution neutral salt. For if the weight of mercuric oxide found be divided into two parts, one being fixed at 33·2 grams and the other variable, and if from the total sulphuric anhydride there be deducted, first 4·2 grams (which with 32·2 grams of oxide forms the basic sulphate and represents the solubility of this salt at 12°), and then a quantity such as, if combined with the remaining oxide, would form the *neutral* salt, in such case the excess acid remaining uncombined will be found to furnish invariably the number 67. In whatever manner the experiments were varied, uniform results were always obtained. The presence of foreign acids in no way modified the reaction, neither did the latter appear to depend in any way upon the proportions of neutral or basic salt contained in the solution. If the temperature were allowed to rise, further decomposition of neutral salt took place, showing that the minimum quantity of acid which a solution must contain in order to avoid decomposition increases with the temperature.

It would appear therefore that the quantity of sulphuric acid alone regulates the decomposition. If at 12° the solution contains less than 67 grams of acid per litre, whether another acid be present or not, the neutral sulphate is decomposed and sulphuric acid liberated, until the latter attains the above-mentioned limiting value. On the other hand, if the solution contains an excess of acid, some basic sulphate passes into solution as neutral salt, and the percentage immediately becomes reduced to the same figure as in the previous instance.

Bismuth nitrate and antimony trichloride were also examined (*ibid.*, cxxix, 956—960), and similar results were obtained.

A solution of nitric acid containing at 12° not less than 83 grams of anhydride per litre has no chemical action upon neutral bismuth nitrate, but dissolves both the latter and the oxynitrate up to its point of saturation, at the same time converting the basic into the neutral salt. But if an acid liquid containing *less* than 83 grams per litre be poured upon the oxynitrate, the latter dissolves as such, and it is not until the limiting quantity of free acid has been otherwise introduced into the solution, that the sense of the reaction is changed, or that the solution becomes capable of dissolving the neutral salt without decomposing it.

The quantity of free acid required increases with the temperature, so that when a solution of the neutral salt is heated a precipitate of sub-nitrate is produced.

The crystalline basic nitrate, $\text{BiO}(\text{NO}_3)$, is in its turn capable of being decomposed by a large quantity of water, and a still more basic salt produced, which is amorphous and opaque. This secondary action is exceedingly slight at ordinary temperatures, and does not in any way affect the preceding observations, but at 100° the limiting quantity of acid which was required to prevent decomposition appeared to be about 4·5 grams per litre. Protracted washing of the oxynitrate finally leaves a salt of fixed composition, $2[\text{BiO}(\text{NO}_3)] \cdot \text{Bi}_2\text{O}_3$.

The quantity of free hydrochloric acid which regulates the decomposition of antimony chloride is 159 grams per litre, the reactions

being strictly parallel with those of bismuth nitrate. The crystalline oxychloride is in like manner further decomposed by hot water and its octohedra converted into prisms of antimonious acid.

J. W.
