*Mr. Sabin :* These artificial asphalts have some very remarkable commercial differences from the natural asphalts. For example, they resist the action of sodium hydroxide. Sodium hydroxide seems to combine with almost all natural asphalts, but not with pitches or tars. In the same way for the purpose for which I use it, it is impossible to use it as asphalt, or in the way in which you can use any natural asphalt. You can not melt it alone without decomposition. It can be melted with other substances, such as rosin or some mineral oils. But it does not mix with the vegetable oils, such as linseed by itself. It is used very successfully as an insulator, as many of the pitches are. It has many useful and valuble qualities, which none of the asphalts have, especially that of resisting caustic alkali, but for many purposes it differs as widely from natural asphalt as if it were entirely and absolutely a different substance.

REVIEWS.

THE VALENCY OF OXYGEN AND THE STRUCTURE OF COMPOUNDS CONTAINING IT.

Hydrogen Dioxide.—In a recent issue of the Berichte der deutschen chemischen Gesellschaft[1] J. W. Brühl calls attention to the significance of recent work of Moritz Traube upon the structural formula of hydrogen peroxide. Traube found that when, in the electrolysis of water, the electrodes are separated by a diaphragm, no hydrogen peroxide forms. If now air be blown through the solution in contact with the cathode, hydrogen peroxide forms in quantity, presumably by the oxidation of the nascent hydrogen by the molecular oxygen of the air. Traube has also shown that when silver oxide is reduced to metal with formation of water and free oxygen, the latter comes from the peroxide, the oxygen of the water coming from the silver oxide, thus :

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$
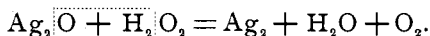
The constitutional symbol of hydrogen peroxide is usually written H.O.O.H. If this be correct we should expect it to unite with the olefines forming glycols by direct addition. Glycols seem not to be formed in this way, except in the case of

[1] **28**, 2847.

ethylene glycol, which, according to Carius,[1] is formed by add-
ing ethylene to hydrogen peroxide in "verhältnissmässig sehr
Kleine Mengen." But even if this reaction takes place it would
not prove the correctness of the above structural formula since
glycols are formed by acting on the olefines with potassium per-
manganate. The formation of hydroxides by the action of
hydrogen peroxide on the metals, such as zinc, is inconclusive
for the same reason.

Neither does the formation of salts, such as barium dioxide
from hydrogen peroxide prove anything, since we know many
acids which contain no hydroxyl.

Because of the fact that in all its decompositions, molecular
and not atomic oxygen, was liberated, and of its formation from
molecular oxygen and atomic hydrogen, Traube wrote the
symbol :

$$H.O:O.H.$$
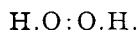
Additional interest attaches to this question since Wolffenstein
has shown[2] that hydrogen peroxide may be concentrated and
obtained by distillation in a vacuum as an explosive, nearly
anhydrous substance.

Spring has recently shown[3] that thick layers of hydrogen per-
oxide have a bluer color than water, and since ammonium
iodide is colorless, and NH_4II_2 and NH_4II_4 are green or violet,
this indicates the possible presence also of molecular oxygen in
the peroxide.

From his determination of its specific heat Spring concludes
that the elements H_2 and O_2 in combining have used only a part
of their potential energy, which is more nearly in harmony with
Traube's formula than with that commonly accepted.

Brühl has now[4] determined the index of refraction of the pure
nearly anhydrous substance and the specific gravity, and from
these he has calculated the specific refraction and dispersion and
the molecular refraction and dispersion. The molecular refrac-
tion and dispersion is found to be :

$$M_a = 5.791.$$
$$M_{Na} = 5.817.$$
$$M_\gamma - M_a = 0.136.$$

If we subtracted from the corresponding constants for water,
the constants for the hydrogen atom, the values for the latter
being nearly the same as in its compounds, we get the following :

[1] *Ann. Chem.* (Liebig), 126, 209.
[2] *Ber. d. chem. Ges.*, 27, 3307.
[3] *Ztschr. anorg. chem.*, 8, 424 ; 9, 205.
[4] *Loc. cit.*

	M_a.	M_{Na}.	$M_\gamma - M_a$.
HOH	3.69	3.71	0.09
H	1.10	1.05	0.04
HO	2.59	2.66	0.05

This would give, doubling these values for hydrogen peroxide :

	M_a.	M_{Na}.	$M_\gamma - M_a$.
H.O.O.H	5.18	5.32	0.10

These values are, however, much smaller than those observed for hydrogen peroxide, (see above). The easiest explanation of the fact that the spectrometer constants of hydrogen peroxide are considerably larger than would correspond to the symbol H.O.O.H, lies in the assumption of multiple union between the oxygen atoms. This would necessitate the assumption of multiple union in ordinary oxygen, and while this is not proven, it is indicated by the recent work of Olszewski and Witowski,[1] and especially by the work of Liveing and Dewar[2] on liquid oxygen. If we compare the optical equivalents of two atoms of oxygen in water with the constants of molecular oxygen, we get :

	M_a.	M_{Na}.	$M_a - M_\gamma$.
2O in water	2.968	3.212	0.036
O_2 as molecular oxygen { liquid	3.958	3.964	0.069
{ gaseous	....	4.09	....

This shows that the optical constants of the molecular oxygen are considerably greater and the dispersion double that of the oxygen in water. This is, however, the best criterion of multiple union of the atoms.

But if in hydrogen peroxide the oxygen atoms are united by multiple union, fewer valencies must be concerned than in molecular union.

If this conjecture be granted, we should find the oxygen constants from hydrogen peroxide somewhat smaller than the molecular oxygen, and this is the case, as is seen below :

	M_a.	M_{Na}.	$M_\gamma - M_a$.
Oxygen in water (2O)	2.968	3.212	0.036
Oxygen, O_2, in hydrogen peroxide	3.591	3.717	0.055
Oxygen, O_2, molecular { liquid	3.958	3.964	0.069
{ gaseous	....	4.09	....

If we assume Traube's symbol for hydrogen peroxide to be correct, we must call oxygen trivalent, for which we have no

[1] Bulletin Acad. Cracovie, Oct. *1891*, 341.
[2] Phil. Mag., **37**, 268.

warrant; neither is any member of the oxygen group of the periodic system known with a valence of three.

On the contrary, sulphur, selenium and tellurium are bivalent and quadrivalent, and several compounds indicate the quadrivalence of oxygen, such as Rose's quadrantoxides, (Ag_4O), but especially the compound of Friedel[1] $HCl(CH_3)_2O$.   If it be granted that oxygen may be quadrivalent, we may then write hydrogen peroxide :

$$H.O.O.H.$$

All the known properties of hydrogen peroxide; its formation from nascent hydrogen and molecular oxygen ; its decomposition by nascent oxygen; its endothermic decomposition are explained by this structural formula.

Constitution of Ozone.—On the assumption of the quadrivalence of oxygen, the symbol of ozone may be either

$$\text{O}\diagup\diagdown\text{O}=\text{O} \quad \text{or} \quad \text{O}\diagup\!\!\diagdown\text{O}=\text{O}$$
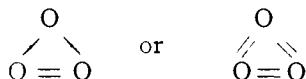
No data are yet at hand sufficient to decide this question.

Constitution of Carbon Monoxide.—For many years carbon monoxide has remained as the single illustration of the bivalence of carbon. If we assume that oxygen is quadrivalent, however, this difficulty at once disappears. The spectrometric behavior of carbon monoxide favors this view.   Brühl has shown[2] that carbon monoxide has the following molecular refraction :

$M_{Na}.$

Found 5.04
Calculated for C:O 4.79

This small difference is, however, many times greater than the possible experimental error.

The assumption of the structure C:O for carbon monoxide involves the assumption of unsaturated oxygen in numerous carbon compounds ; at least in those containing an uneven number of carbon atoms ; but we have also many sulphur and nitrogen compounds in which these atoms are bivalent and trivalent respectively.

The Constitution of Water.—In another paper Brühl considers[3] the result of this new view upon the constitution of water.   It is known that in aqueous solutions of salts of strong acids and bases, the observed alteration of the freezing and boiling points is nearly double the normal amount deduced from van't Hoff's

1 *Bull. soc. Chim.*, 24, 160, 241.
2 *Ber. d. chem. Ges.*, 24, 663.
3 *Ber. d. chem. Ges.*, 28, 2866.

equation. We know also that Arrhenius has accounted for this by supposing that in such solutions the salts are decomposed into their ions.

It is known, further, that many organic substances, such as the fatty acids, oximes, alcohols, etc., form double molecules or molecular complexes when dissolved in hydrocarbons, chloroform and carbon disulphide, and that these complexes are broken up when these substances are dissolved in water, and to a certain extent also when dissolved in alcohols, ethers, esters, ketones and phenols. The latter class of solvents are to a certain extent also ionizing, since when saturated with hydrochloric acid they act as conductors, while solutions of hydrochloric acid in benzene and other hydrocarbons are non-conductors.

Why water so far surpasses other solvents in its power to allow of this dissociation is not known, but the explanation is easily found if we write water as an unsaturated compound giving oxygen four bonds, thus:

$$H \cdot \overset{.}{\underset{.}{O}} \cdot H.$$
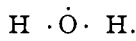
In fact the properties of water indicate almost with certainty that it is unsaturated, for nearly all substances have a tendency to unite with it—are hygroscopic. Numerous hydrates and compounds with water of crystallization exist, and, finally, water is the universal solvent. The supplementary valencies of the quadrivalent oxygen are evidently the cause of the formation of the ions, and the molecular aggregates the reason of the dissociating power of the water.

This notion receives further support when we remember that all those organic solvents which are known as good dissociation media contain oxygen—ethers, alcohols, esters, ketones, phenols, urethane, etc.—while those free from oxygen, such as the hydrocarbons, chloroform, carbon disulphide, carbon tetrachloride have little or no power to cause dissociation.

EDWARD HART.

THE HISTORY OF ELECTRIC HEATING APPLIED TO METALLURGY.[1]

Sir Humphry Davy is justly regarded as the father of dry electro-metallurgy. After making full allowance for the unusual facilities at his command, it still remains that his intelligent, faithful and extended use of his facilities is worthy of the utmost honor.

[1] Read before the Washington Section, Dec. 12, 1895.