XVI.—*The State of Carbon Dioxide in Aqueous Solution.*

By JAMES WALKER.

WHEN carbon dioxide is dissolved in water, a portion is converted into carbonic acid, H_2CO_3 ; and from the conductivity data of Knox (*Ann. Phys. Chim.*, 1895, 54, 44) and Walker and Cormack (*Trans.*, 1900, 77, 8) it appears that the acid accurately obeys Ostwald's dilution law.

Reasoning on the assumption that the amount of carbonic acid, dissociated and undissociated, was proportional to the amount of unchanged carbon dioxide in the solution, I showed that Ostwald's dilution law would not hold good for the range of dilution investigated, unless the proportion of the carbonic acid to the carbon dioxide were greater than one-fourth, and assumed that the same result would follow, at least for moderate dilutions, on the more probable hypothesis that the amount of undissociated carbonic acid only was proportional to the unchanged carbon dioxide.

Professor Abegg, of Breslau, who has worked at the similar problem of the state of ammonia in aqueous solution, kindly drew my attention to the fact that, on the second assumption, the deduction is not valid. The true dilution law for such a case may be deduced simply from the law of mass action without neglect of terms as follows.

Consider 1 gram-mol. of carbon dioxide dissolved in water, so as to form v litres of solution. Let a = number of gram-mols. of

unchanged CO_2 ; b = number of gram-mols. of undissociated H_2CO_3 ; m = number of gram-mols. of dissociated H_2CO_3 ; then

$$a + b + m = 1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the equilibrium between CO_2 and undissociated H_2CO_3 , we have, according to Guldberg and Waage's law, $\frac{a}{v} = r \frac{b}{v}$, where r is a constant, or $b = \frac{a}{r}$.

Equation (1) therefore becomes

$$a + \frac{a}{r} + m = 1, \text{ or } \frac{a}{r} (1 + r) = 1 - m,$$

and

$$b = \frac{a}{r} = \frac{1 - m}{1 + r} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For the equilibrium between the undissociated and dissociated H_2CO_3 , we have, according to the same law,

$$\left(\frac{m}{v}\right)^2 = k' \frac{b}{v},$$

where k' is a constant. Substituting the value of b in (2), we obtain

$$\left(\frac{m}{v}\right)^2 = k' \frac{1 - m}{(1 + r)v},$$

or

$$\frac{m^2}{(1 - m)v} = \frac{1}{1 + r} k' \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since both r and k' are constant, equation (3) expresses Ostwald's dilution law,

$$\frac{m^2}{(1 - m)v} = k,$$

in which k is the apparent dissociation constant found from measurements of the conductivity (compare Walker and Cormack, *loc. cit.*, p. 10). The constant k' is the real dissociation constant of carbonic acid, and is related to k by the equation

$$k' = (1 + r)k,$$

$1 + r$ being the constant ratio of the total non-ionised substance to the non-ionised but hydrated acid. For dilutions at which the degree of dissociation is small, this relation is identical with that previously given (Walker and Cormack, *loc. cit.*, p. 13).

It is evident from this that no conclusion can be drawn as to the degree of hydration of carbon dioxide (or any similar substance) in

aqueous solution from the mere fact that Ostwald's dilution law is obeyed, for the law of mass action leads to this relation whatever may be the degree of hydration.

UNIVERSITY COLLEGE,
DUNDEE.