led to excellent constants: the theoretical treatment started from the assumption of a constant solubility product for calcium carbonate. In the address referred to, A. A. Noyes[1] mentions two or three other cases, such as the solubility of lead iodide in the presence of potassium iodide and of lead chloride in the presence of potassium chloride, and of calcium hydroxide in the presence of ammonium chloride, in which cases the theory is said to be sustained approximately.

In view of these facts and also in view of the results of the complete calculation of Arrhenius's data on the solubility of the silver salts, which removed the last *theoretical* foundation for the solubility product constant, we may well consider it for the present to be an approximate empirical principle, much in the same way as so many other important principles concerning electrolytes are still simply empirical, such as the isohydric principle itself, and the various rules—Rudolphi's, van't Hoff's, Kohlrausch's—expressing the equilibrium between strong electrolytes and their ions. A great deal more exact work on the extent of the reliability of the solubility principle will obviously be necessary to determine what the true relations are. If it should be confirmed still further and firmly established, the question of its theoretical bearing will become an interesting one—particularly in its relation to the other empirical principles of solutions of electrolytes.

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[CONTRIBUTION FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY OF THE HARVARD MEDICAL SCHOOL.]

A DIAGRAMMATIC REPRESENTATION OF EQUILIBRIA BETWEEN ACIDS AND BASES IN SOLUTION.

BY LAWRENCE J. HENDERSON.

Received March 27, 1908.

During a series of investigations concerning the adjustment of neutrality in the animal organism,[2] it has been found convenient to construct diagrams representing the equilibria between bases and acids of different ionization constants in solution of varying acidity and alkalinity. These diagrams, simple consequences of the concentration law, and of the principle of isohydric solutions, seem to possess certain advantages over other methods of presentation of the somewhat involved conditions. Especially are they useful to indicate immediately the adjustment of all possible equilibria of this sort, with at least a moderate degree of accuracy, and on account of such practical usefulness they are here presented.

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[1] *Loc. cit.*, p. 322.

[2] For general conclusions and the literature see Henderson, *American Journal of Physiology*, May, 1908.

Let it be required to find the extent to which any acid, HA, of any ionization constant, k, present in aqueous solution together with a varying amount of its salt of a strong base, for instance sodium hydroxide, exists uncombined as free acid in the solution, when the hydrogen ion concentration is equal to (H^+).

The ionization of the acid may be expressed by the reaction,

$$HA = H^+ + A^-$$

whence

$$(H^+) = k\frac{(HA)}{(A^-)}.$$

For all weak acids the concentration of undissociated molecules (HA), is almost precisely equal to the total concentration of free acid, and the concentration of the anions, (A^-), is equal to the total quantity of salt, NaA, multiplied by its degree of ionization, γ. Thus one obtains the equation

$$(H^+) = \frac{k}{\gamma} \times \frac{HA}{NaA}.$$

Let

$$\frac{k}{\gamma} = C$$

then

$$(H^+) = C \times \frac{HA}{NaA}. \qquad (1)$$

In this equation C is always greater than k. Under ordinary circumstances its value may be stated as follows:

$$2k > C > k.$$

In any particular case it is an easy matter to estimate the value of C, but for ordinary purposes very little error is involved in assuming equality between C and k, especially in very dilute solutions. The effect of concentration, however, is usually quite small.

From equation 1, there may be calculated the values of the ratio $\frac{HA}{NaA}$ corresponding to any values of (H^+) and C, and from the numbers thus obtained, the per cent. of free acid, $\frac{HA}{HA + NaA}$, may be deduced. On the accompanying diagram the results of such calculation are indicated.

Values of C are plotted logarithmically as abscissas; per cents. of acid uncombined, $\frac{HA}{HA+NaA}$, are plotted as ordinates. The several curves are drawn to connect points corresponding to equal hydrogen-ion concentrations, that is to say, to equal degrees of acidity and alkalinity, and these concentrations are indicated on the curves.

The use of the diagram may be illustrated as follows for the case of car-

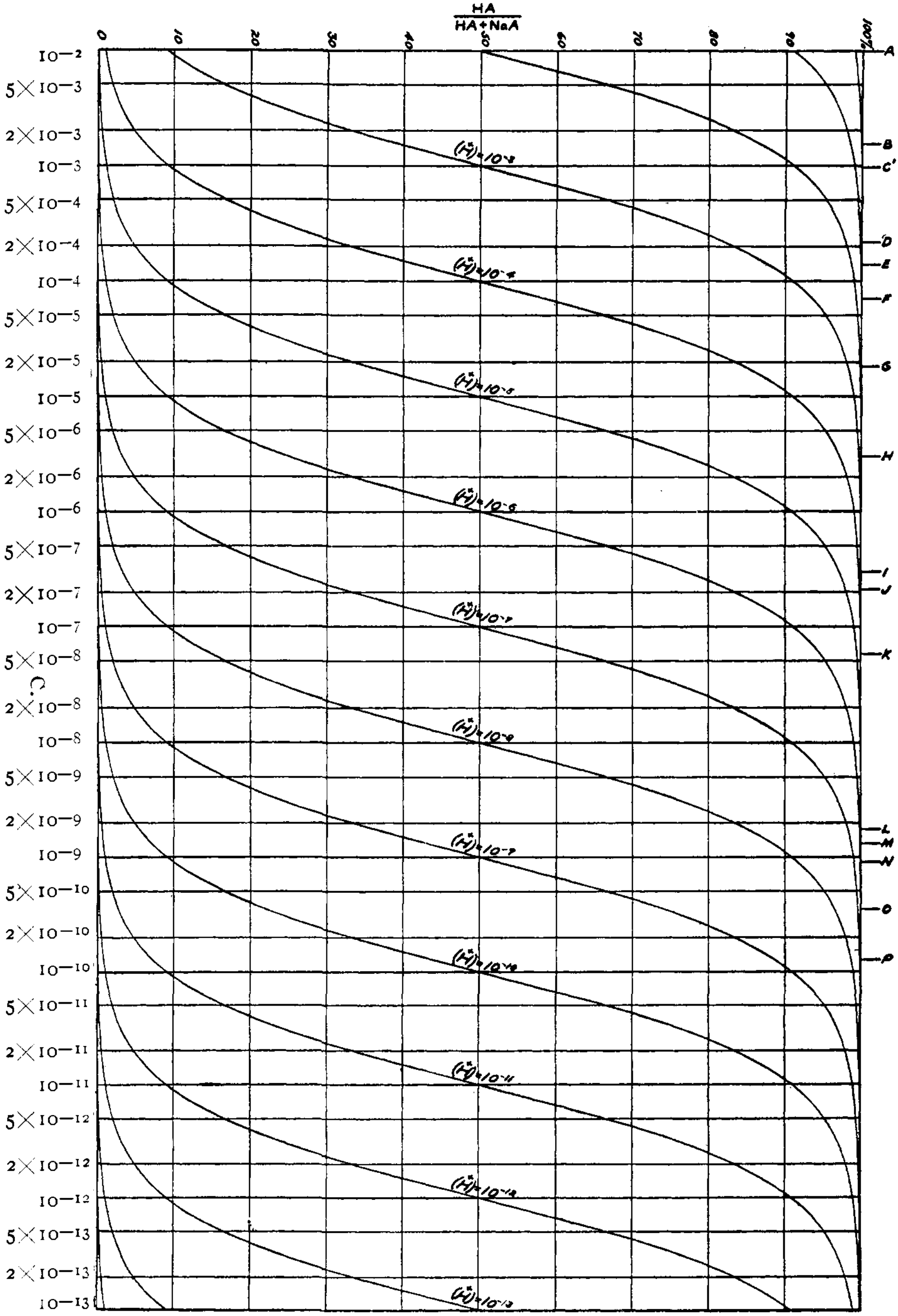
HA / HA+NaA
0
10
20
30
40
50
60
70
80
90
100%
10−2
5×10−3
2×10−3
10−3
5×10−4
2×10−4
10−4
5×10−5
2×10−5
10−5
5×10−6
2×10−6
10−6
5×10−7
2×10−7
10−7
5×10−8
C.
2×10−8
10−8
5×10−9
2×10−9
10−9
5×10−10
2×10−10
10−10
5×10−11
2×10−11
10−11
5×10−12
2×10−12
10−12
5×10−13
2×10−13
10−13
(H)=10−3
(H)=10−4
(H)=10−5
(H)=10−6
(H)=10−7
(H)=10−8
(H)=10−9
(H)=10−10
(H)=10−11
(H)=10−12
(H)=10−13
A
B
C'
D
E
F
G
H
I
J
K
L
M
N
O
P

Fig. 1.

bonic acid. The ionization constant of carbonic acid[1] is very nearly 3×10^{-7}. In a decinormal solution of sodium bicarbonate the degree of ionization is approximately 0.8. These numbers yield the equation

$$C = \frac{3.0 \times 10^{-7}}{0.8} = 3.8 \times 10^{-7}.$$

On examination it appears that the abiscissa corresponding to $C = 3.8 \times 10^{-7}$ is cut

At the ordinate. Per cent.	By the curve of hydrogen-ion concentration.
0.3	10^{-9}
2.7	10^{-8}
20.7	10^{-7}
72.3	10^{-6}
96.3	10^{-5}
99.6	10^{-4}

That is to say, at a hydrogen ion concentration $1 \times 10^{-9}\ N$, 0.3 per cent. of all the carbonic acid must be present as free acid, and as acidity increases this fraction increases, as defined by the above table, until when the acidity is greater than $1 \times 10^{-4}\ N$ hydrogen-ion concentration nearly all the carbonic acid must be free.

Disregarding the incompleteness of ionization, the following table is obtained from the diagram ($C = 3.0 \times 10^{-7}$).

Ordinate. Per cent.	Curve of hydrogen-ion concentration.
0.4	10^{-9}
3.2	10^{-8}
25.0	10^{-7}
77.0	10^{-6}
97.0	10^{-5}
99.6	10^{-4}

Evidently the differences between this table and the former one are unimportant for approximate estimations.

On the diagram, the letters above the lines of abscissas designate the ionization constant of these acids as follows:

Letter.	Acid.	k.	Letter.	Acid.	k.
A	Maleic[2]	1.17×10^{-2}	I	Carbonic[3]	3.04×10^{-7}
B	Monochloracetic[2]	1.55×10^{-3}	J	NaH_2PO_4[5]	2.0×10^{-7}
C[1]	Tartaric[2]	9.7×10^{-4}	K	Hydrogen sulphide[3]	5.7×10^{-8}
D	Formic[2]	2.14×10^{-4}	L	Boric[3]	1.7×10^{-9}
E	Lactic[2]	1.38×10^{-4}	M	Hydrocyanic[3]	1.3×10^{-9}
F	Aspartic[4]	6.9×10^{-5}	N	Alanine[4]	9.0×10^{-10}
G	Acetic[2]	1.80×10^{-5}	O	Glycocoll[4]	3.4×10^{-10}
H	Picolinic[2]	3.0×10^{-6}	P	Phenol[3]	1.3×10^{-10}

[1] Walker and Cormack, *J. Chem. Soc.*, 77, 20 (1900).

[2] Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

[3] Walker and Cormack, *J. Chem. Soc.* 77, 20 (1900).

[4] Winkelblech, *Z. physik. Chem.*, 36, 587 (1901).

[5] Private communication of Professor A. A. Noyes.

For convenience the ionization constants of certain acid substances are indicated as values of C on the diagram. In like manner, equilibria of these acids, and of all other acid substances, except very strong acids, whose case is obviously a special one, are defined by the diagram and may be read off from it directly, correcting for the ionization of the salt, if necessary.

By a somewhat different use of the diagram, equilibria in complicated mixtures are defined, and also isohydric solutions made up of any acids (with the exception noted) and strong bases.

In a solution made by neutralizing sodium hydroxide with phenol, boric acid, hydrogen sulphide, carbonic acid, picolinic acid, and acetic acid, let it be required to find the extent to which the base is combined with the several acids, the hydrogen ion concentration being 1×10^{-7}.

The curve of hydrogen ion concentration 1×10^{-7} cuts the abscissas

	Of	At the ordinate of per cent.
P	Phenol	99.9
L	Boric acid	98.5
K	Hydrogen sulphide	64.5
I	Carbonic acid	25.0
H	Picolinic acid	3.5
G	Acetic acid	0.4

Accordingly, in this solution, phenol is hardly at all combined with sodium, and acetic acid is almost completely combined with it. The other acids are partly free, approximately in the degrees indicated by the above percentages. The above numbers serve also to define one series of isohydric solutions made up of these acids and their sodium salts.

In like manner, all possible similar mixtures and all possible similar isohydric solutions are defined by the diagram.

The case of bases of varying strengths in equilibrium with strong acids, is strictly analogous. For the ionization reaction of a base

$$BOH = B^{+} + OH^{-}.$$

The following equation may be derived:

$$(OH^{-}) = C \times \frac{BOH}{BCl}.$$

This equation yields the diagram represented in Fig. 2, in form identical with the diagram of Fig. 1. The curves, however, represent hydroxyl ion concentrations; the abscissas are as before, values of C plotted logarithmically, and ordinates indicate per cent. of base which is uncombined with acid. The diagram is to be used in precisely the same way as Fig. 1, and for convenience the values of *k* for certain bases are indicated approximately upon it as values of C.

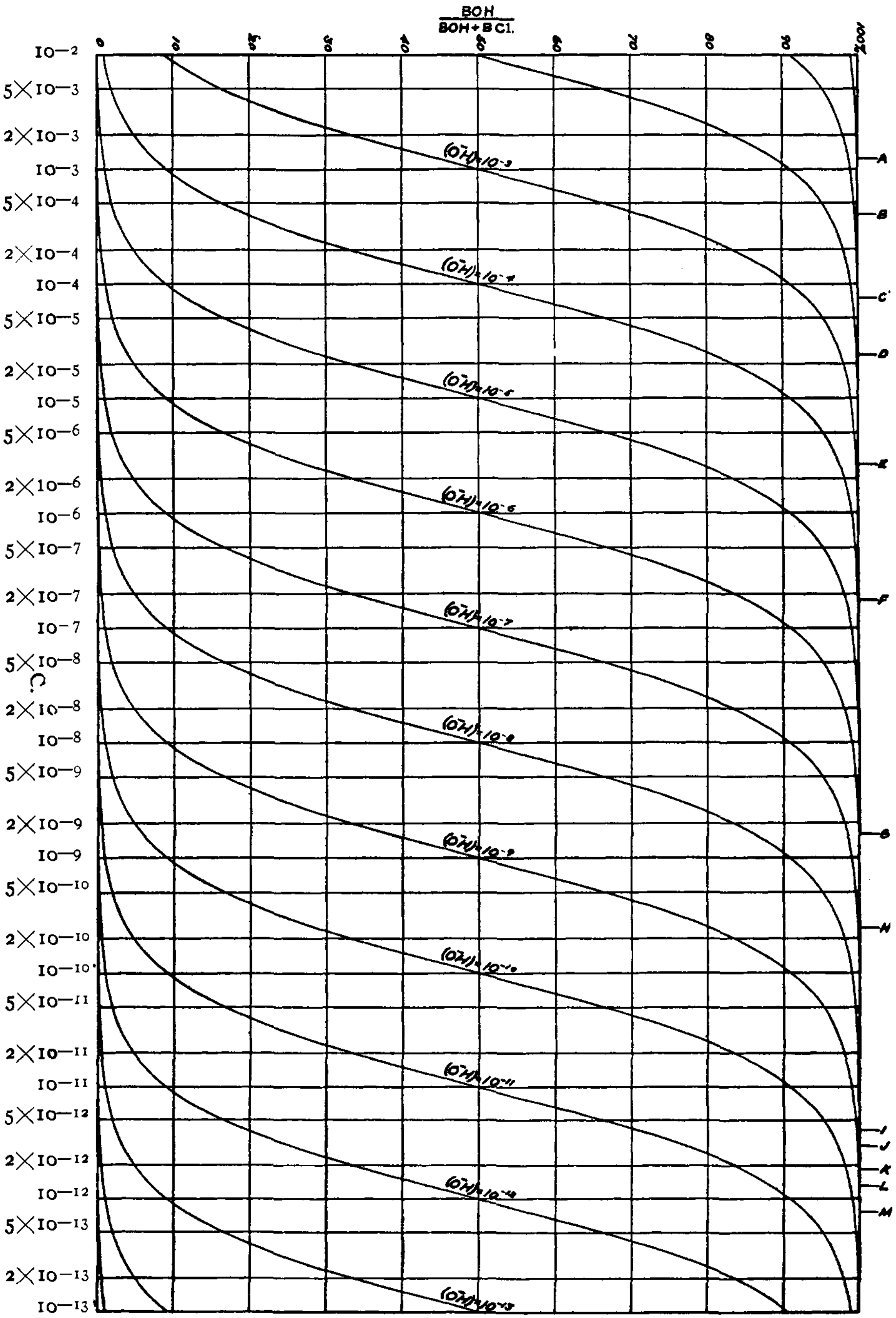
$\frac{BOH}{BOH + BCl}$
0
10
20
30
40
50
60
70
80
90
100%
10^{-2}
5×10^{-3}
2×10^{-3}
10^{-3}
5×10^{-4}
2×10^{-4}
10^{-4}
5×10^{-5}
2×10^{-5}
10^{-5}
5×10^{-6}
2×10^{-6}
10^{-6}
5×10^{-7}
2×10^{-7}
10^{-7}
5×10^{-8}
C.
2×10^{-8}
10^{-8}
5×10^{-9}
2×10^{-9}
10^{-9}
5×10^{-10}
2×10^{-10}
10^{-10}
5×10^{-11}
2×10^{-11}
10^{-11}
5×10^{-12}
2×10^{-12}
10^{-12}
5×10^{-13}
2×10^{-13}
10^{-13}
$(\bar{O}H)=10^{-3}$
$(\bar{O}H)=10^{-4}$
$(\bar{O}H)=10^{-5}$
$(\bar{O}H)=10^{-6}$
$(\bar{O}H)=10^{-7}$
$(\bar{O}H)=10^{-8}$
$(\bar{O}H)=10^{-9}$
$(\bar{O}H)=10^{-10}$
$(\bar{O}H)=10^{-11}$
$(\bar{O}H)=10^{-12}$
$(\bar{O}H)=10^{-13}$
A
B
C
D
E
F
G
H
I
J
K
L
M

Fig. 2.

These bases and their ionization constants are as follows:

Letter.	Base.	k.
A	Diethylamine[1]	1.26×10^{-3}
B	Methylamine[1]	5.0×10^{-4}
C[1]	Trimethylamine[1]	7.4×10^{-5}
D	Ammonia[1]	2.3×10^{-5}
E	Hydrazine[1]	2.7×10^{-6}
F	$(CH_3)_3SnOH$[1]	1.7×10^{-7}
G	*p*-Toluidine[2]	1.6×10^{-9}
H	Aniline[2]	4.9×10^{-10}
I	Alanine[3]	3.8×10^{-12}
J	Glycocoll[3]	2.9×10^{-12}
K	Sarcosine[3]	1.8×10^{-12}
L	Aspartic acid[3]	1.3×10^{-12}
M	Betaine[3]	7.6×10^{-13}

Summary.

A diagram is presented which expresses the requirements of the concentration law regarding the equilibrium in solution between strong bases and acids of all strengths. A precisely similar diagram indicates the equilibrium in solution between strong acids and bases of all strengths. (The diagrams are not useful for solutions containing both strong bases and strong acids in which the acidity or alkalinity is high.)

These diagrams define with considerable accuracy the conditions of equilibrium at all hydrogen- and hydroxyl-ion concentrations, between all bases and all acids with the above-mentioned exceptions, and in all mixtures of such substances. They also define all isohydric solutions of such substances in which this quality is dependent upon equality in concentration of hydrogen- and hydroxyl-ions alone.

THE HEATS OF SOLUTION OF THE THREE FORMS OF MILK-SUGAR.

BY C. S. HUDSON AND F. C. BROWN.

Received April 15, 1908.

Milk-sugar can be crystallized from solution in two forms, one of which is a monohydrate, $C_{12}H_{22}O_{11}.H_2O$, and the other an anhydrous modification, $C_{12}H_{22}O_{11}$, named β-anhydrous milk-sugar. When either of these crystalline milk-sugars is dissolved in water it changes partially to the other form until a condition of dynamic equilibrium is reached in which both forms are present in the solution. In distinction from the β-anhydride of milk-sugar there is an α-anhydride which is produced when hydrated milk-sugar is heated at 125° to constant weight. This α anhy-

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[1] Bredig, *Z. physik. Chem.*, 13, 289 (1894).

[2] Nernst, Theoretische Chemie, 3rd Edition, p. 497.

[3] Winkelblech, *loc. cit.*