

"Conservation of Energy" and thus this latter law and the "Indestructibility of Matter" are closely akin.

From the above it follows that on the present basis any loss of energy must involve a decrease in mass. Thus when a chemical reaction which liberates heat has taken place, when a body is cooled or when by the process of radioactivity one substance loses energy and is transformed into another substance, there must be a decrease in the mass of the whole and hence also a decrease in weight. In the first two cases mentioned, however, the change is too small to be detected but in the last case the change should be appreciable, and we have a ready explanation of the irregularities which occur in the table of atomic weights.

Finally, it is pointed out that since gravity is proportional to mass it would appear that gravitation must be considered as acting between quantities of confined energy and not between "masses" in any other sense.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

## TWO NEW METHODS FOR THE DETERMINATION OF THE SECONDARY IONIZATION CONSTANTS OF DIBASIC ACIDS.

BY HERBERT N. MCCOY.

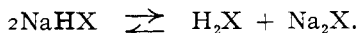
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The ionization of a dibasic acid,  $H_2X$ , takes place in two stages, represented by the following equations:



where  $k_1$  and  $k_2$  are the ionization constants, and where the formulae represent the molar or ionic concentrations of the corresponding substances. With the exception of a few moderately strong acids, like oxalic, all organic dibasic acids are found by conductivity measurements to dissociate essentially according to equation (1), in solutions more concentrated than milli-normal; they thus behave like monobasic acids.<sup>1</sup> The second constant,  $k_2$ , is always much smaller than the first. While the secondary ionization produces but a negligible effect in solutions of the free acid, in solutions of the acid salts its effect is of great importance.

When an acid salt, like  $NaHX$ , is dissolved in water it reacts, partially, forming the free acid and the neutral salt, according to the equation, thus:



The state of equilibrium reached is governed by equations (1) and (2), which, by combination, give

<sup>1</sup> Ostwald: *Z. physik. Chem.*, **3**, 281 (1889).

$$\frac{HX^2}{H_2X \cdot X} = \frac{k_1}{k_2} \quad (3)$$

Equation (3) applies to solutions containing all proportions of acid, acid salt and neutral salt, as well as to solutions resulting from the pure acid salt and water. I have found<sup>1</sup> that the equilibrium in solutions of the carbonates of sodium is accurately represented by the relationship

$$\frac{NaHCO_3^2}{H_2CO_3 \times Na_2CO_3} = \text{a constant.} \quad (3a)$$

Where the formulae now represent the total concentrations of the respective substances, Equation (3a) becomes identical with (3) for very dilute solutions, in which the salts are practically completely ionized. For a fixed concentration of total sodium, a good constant was found for all proportions of carbonate, bicarbonate and carbonic acid. The concentration of the later component was proportional to the concentration of the gaseous carbon dioxide, with which the solution was in equilibrium; the gaseous concentration, as determined by analysis, multiplied by the coefficient of solubility, gave the concentration of the free acid in solution.

The same principle may be applied also to the study of solutions of salts of all non-volatile acids, provided they are sufficiently soluble both in water and in some inert solvent, which is immiscible with water, the aqueous solution, containing the acid and neutral salts, is shaken, until equilibrium is reached, with a solvent in which the acid is soluble but the salts insoluble. The concentration of the un-ionized free acid in the aqueous layer is directly proportional to the concentration of the same substance in the immiscible solvent, the proportionality factor being the partition coefficient of the free acid alone, for the two solvents. A simple analysis of the aqueous solution gives the remaining data for the calculation of the concentrations  $HX$  and  $X$ .

The aqueous solution of the acid and neutral salts of a dibasic acid,  $H_2X$ , will, in general, contain the following seven<sup>2</sup> molecular and ionic substances:  $NaHX$ ,  $Na_2X$ ,  $H_2X$ ,  $Na$ ,  $H$ ,  $HX$  and  $X$ . If  $P$  is the partition coefficient, then  $H_2X$ , the molecular concentration of the un-ionized free acid, is equal to  $0.5 P$  times the equivalent concentration of the ether solution. The relations between the concentrations of the six remaining substances may be expressed by six equations, as follows:

$$H \cdot HX = k_1 H_2X. \quad (1)$$

If  $\alpha_1$  and  $\alpha_2$  are the degrees of ionization of the acid and neutral salts respectively, then, as close approximations,

<sup>1</sup> *Am. Chem. J.*, 29, 437 (1903).

<sup>2</sup> In moderately dilute solutions the amount of  $NaX$  ions is probably negligibly small.

$$HX = \alpha_1(NaHX + HX) \quad (4)$$

and

$$X = \alpha_2(Na_2X + X). \quad (5)$$

Since the solution is electrically neutral, we may write

$$Na + H = HX + 2X. \quad (6)$$

If the total concentration of the sodium is called  $m$ ,

$$NaHX + 2Na_2X + Na = m. \quad (7)$$

Finally, if the equivalent acid concentration of the aqueous solution (as shown by the titration with standard alkali) minus  $P$  times the equivalent concentration of the ether solution be called  $C$ , we may write

$$NaHX + HX + H = C. \quad (8)$$

(4) and (5) give

$$HX = \alpha_1(C - H). \quad (9)$$

(1) and (9) give

$$HX = \frac{\alpha_1 C}{2} + \sqrt{\left(\frac{\alpha_1 C}{2}\right)^2 - k_1 \alpha_1 H_2 X}. \quad (10)$$

If  $H$  is very small compared with  $C$ , equation (9) becomes

$$HX = \alpha_1 C, \text{ nearly.} \quad (11)$$

Equation (10) also reduces to (11) if  $k_1 \alpha_1 H_2 X$  is very small compared with  $\left(\frac{\alpha_1 C}{2}\right)^2$ .

(6) and (7) give

$$NaHX + 2Na_2X + HX + X - H = m. \quad (12)$$

(4), (5) and (12) give

$$\frac{HX}{\alpha_1} + \frac{2X}{\alpha_2} = m. \quad (13)$$

(9) and (13) give

$$X = \alpha_2 \left[ \frac{m + C}{2} - \frac{HX}{\alpha_1} \right]. \quad (14)$$

If  $HX = \alpha_1 C$ , equation (11),

$$X = \alpha_2 \left( \frac{m - C}{2} \right). \quad (15)$$

Equations (10) and (14) must be used for highly ionized acids, like oxalic and dibromsuccinic, but the simplified forms (11) and (15) may be used, without appreciable error for weaker acids like succinic.

The following pages give an account of a few preliminary experiments made with salts of succinic acid, at 20°, using ether as the auxiliary solvent. The partition coefficient of succinic acid for water and ether was found by shaking an aqueous solution of pure succinic acid with carefully purified ether at a temperature of 20°, for a period of five minutes, a separate experiment having shown that equilibrium was reached

in that length of time. Forty cc. of the aqueous solution required 27.96 cc. of decinormal barium hydroxide, phenolphthalein being used as indicator. Forty cc. of ethereal layer, after evaporation of the ether and re-solution of the acid in water, required 3.78 cc. of the same barium hydroxide solution. The apparent partition coefficient is  $27.96/3.78 = 7.40$ , but this must be corrected, since part of the acid in the aqueous solution is ionized, while that in the ethereal solution is not. The true partition coefficient is, as Nernst has shown<sup>1</sup> in all such cases, the ratio of the unionized portions of the acid in each solution. The aqueous solution was 4.28 per cent ionized, as calculated from its concentration, 0.0349 normal molecular, and the known ionization constant,<sup>2</sup>  $66.5 \times 10^{-6}$ . The true partition coefficient is, therefore,  $7.40 (1 - 0.0428) = 7.08$ . Another aqueous solution of 0.1362 normal and therefore 2.19 per cent. ionized, gave for the partition coefficient  $7.16 (1 - 0.0219) = 7.00$ . The mean of the two results, 7.04, is the true coefficient, which is independent of the concentrations of the solutions.

The details of a determination of the concentrations of the components of a solution containing both acid and neutral sodium succinate are illustrated by the following example: 20.00 cc. of exactly 0.2 molecular succinic acid and 20.00 cc. of exactly 0.25 normal sodium hydroxide were mixed with 50 cc. of purified ether and sufficient water so that after being shaken the volume of the aqueous solution would be approximately 50 cc. The mixture was then shaken vigorously for 5 or 6 minutes, at 20°, in a separatory funnel having three superimposed bulbs connected by short tubes, which were graduated. The two lower bulbs were each of 50 cc. capacity, while the upper bulb held about 150 cc. The two smaller bulbs and the connecting tubes were carefully calibrated. After being shaken, the solutions were allowed to settle. The volume of the ether was 50 cc.; that of the water solution was 50.42 cc.; therefore the sodium concentration,  $m$ , was  $\frac{20 \times 0.25}{50.42} = 0.09916$ . 20.00 cc. of the aqueous solution required 11.66 cc. of N/10 barium hydroxide; 40.00 cc. of the ethereal solution required 6.11 cc. of N/100 barium hydroxide. From these results it follows that the equivalent acid concentration of the aqueous solution was 0.05830, and that of the ethereal solution 0.001528. Therefore  $C = 0.0583 - (7.04 \times 0.001528) = 0.04754$ . If we take  $\alpha_1 = 0.80$  and  $\alpha_2 = 0.70$ ,<sup>3</sup> then  $HX = \alpha_1 C = 0.03803$  and  $X = 0.5 \alpha_2 (m - C) = 0.01807$ .  $H_2X = 0.5 \times 7.04 \times 0.001528 = 0.00538$ .

These values substituted in equation (3) give  $k_1/k_2 = 14.8$ .

<sup>1</sup> *Z. physik. Chem.*, 8, 110 (1891).

<sup>2</sup> Ostwald: *Ibid.*, 3, 282 (1889).

<sup>3</sup> See following paper.

The results of seven experiments, of which the above calculation represents the fifth, are given in the following table:

	Molecular conc. $H_2X$ .	Ionic conc. $HX$ .	Ionic conc. $X$ .	$k_1/k_2$ .
1	0.01487	0.0520	0.0120	15.2
2	0.01258	0.0504	0.0129	15.7
3	0.01060	0.0480	0.0140	15.5
4	0.00862	0.0448	0.0152	15.3
5	0.00538	0.0380	0.0181	14.8
6	0.00276	0.0301	0.0218	15.1
7	0.00105	0.0208	0.0258	16.0

Mean, 15.4

In all of the experiments represented by the above table the total sodium concentration was approximately  $N/10$ . For constant concentration of total base, the ratio  $k_1/k_2$  is seen to be practically constant;  $k_1 = 0.000,0665$ , therefore  $k_2 = 0.000,0043$ . Further extensive measurements, using the method here delineated, have been carried out by Mr. Chandler, as described in the article following.

The secondary ionization constant of a dibasic acid,  $k_2$ , may be calculated very readily by a second new method from the conductivities of dilute solutions of the acid and neutral sodium salts. A. A. Noyes has shown<sup>1</sup> that, for a dilute solution (say  $N/1024$ ) of the acid salt,

$$k_2 = \frac{(k_1 + m + H)H^2}{k_1(m - H)}. \quad (16)$$

(If the quantities on the right-hand side of equation (16),  $m$ , the total concentration of the sodium is known,  $k_1$  is also known;  $H$ , the concentration of free hydrogen ions, is the only unknown. This may also be found from relationships based upon the following considerations: For a very dilute solution of the pure acid-salt we may write

$$H\lambda_H + m\lambda_1 + HX\lambda_{HX} + X\lambda_X = mA_1 \quad (17)$$

where  $\lambda_1$  is the ionic conductivity of the univalent basic ion (sodium) and  $\lambda_H$ ,  $\lambda_{HX}$  and  $\lambda_X$  the ionic conductivities indicated by the subscripts;  $A_1$  is the observed molecular conductivity of the solution of the so-called acid salt;  $\lambda_1$  is known and  $\lambda_X$  may be obtained from a single determination of the conductivity of a very dilute solution of the neutral salt.

It is obvious that  $\lambda_{HX}$  can not be determined in the ordinary way, on account of the formation of H and X ions from the acid salt, but the value of  $\lambda_{HX}$  may be calculated, in most cases, from the observed conductivity of the acid salt solution, when the ionic concentrations of the various sorts of ions have been determined by the equilibrium method already described; this would not, however, lead to an independent determination of  $k_2$ . It has already been clearly shown by Ostwald<sup>2</sup>

<sup>1</sup> *Z. physik. Chem.*, **11**, 495 (1893).

<sup>2</sup> *Ibid.*, **2**, 840 (1888).

and by Bredig<sup>1</sup> that ionic conductivity depends upon the composition of an ion, and that the conductivity may be very closely estimated from the composition. The values of  $\lambda_{HX}$  found in the two ways agree well. It has been observed, further, by Mr. Chandler,<sup>2</sup> that  $\lambda_{HX}$  is, in all cases, very nearly equal to  $0.3\lambda_X$ . If we accept this as a fixed relationship, the result will be at least a very close approximation. Therefore

$$\lambda_{HX} = 0.3\lambda_X. \quad (18)$$

For a very dilute solution of an acid sodium salt of a dibasic acid, it is easily seen<sup>3</sup> that

$$H_2X = X - H, \quad (19)$$

and

$$H_2X + HX + X = m. \quad (20)$$

(1), (19) and (20) give

$$X = \frac{(k_1 + m + H)H}{k_1 + 2H}; \quad (21)$$

(19) and (20) give

$$HX = m + H - 2X; \quad (22)$$

(17), (18), (21) and (22) give

$$H_2 = \frac{m(2A_1 - 2\lambda_1 - \lambda_X) - k_1(\lambda_H + 0.7\lambda_X)H}{2\lambda_H + \lambda_X} = \frac{k_1m(A_1 - \lambda_1 - 0.3\lambda_X)}{2\lambda_H + \lambda_X}. \quad (23)$$

If

$$\frac{m(2A_1 - 2\lambda_1 - \lambda_X) - k_1(\lambda_H + 0.7\lambda_X)}{2(2\lambda_H + \lambda_X)} = a \quad (24)$$

and

$$\frac{k_1m(A_1 - \lambda_1 - 0.3\lambda_X)}{2\lambda_H + \lambda_X} = b, \quad (25)$$

$$H = a + \sqrt{a^2 + b}. \quad (26)$$

Equations (24) and (25) may be simplified for sodium salts at the definite temperature, 25°, as follows. Let the concentration,  $m$ , =  $\frac{1}{1024}$ , and let  $A_2$  be the equivalent conductivity of the salt  $\text{Na}_2\text{X}$  at this concentration, at which the equivalent conductivity due to the sodium ion is about 49.5. Therefore,  $\lambda_1 = 49.5$  and  $\lambda_X = 2(A_2 - 49.5)$ . The value of  $\lambda_H$  is 352, at 25°, according to Kohlrausch and Steinwehr.<sup>4</sup> Substitution of these values in (24) and (25) gives

$$a = \frac{m(A_1 - A_2) - k_1(0.7A_2 + 141)}{2A_2 + 605} \quad (27)$$

and

<sup>1</sup> *Z. physik. chem.*, 13, 191 (1894).

<sup>2</sup> Next article.

<sup>3</sup> Equations (19) and (20) have been used by Noyes, *Loc. cit.*

<sup>4</sup> *Berl. Akad. Sitzber.*, 26, 570 (1902).

$$b = \frac{k_1 m (A_1 - 0.6 A_2 - 20)}{2 A_2 + 605} \quad (28)$$

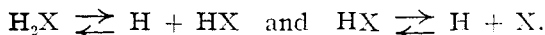
In equation (26) the value of  $H$  is expressed in terms of quantities which are either known or easily determined experimentally, and, therefore,  $k_2$  may now be obtained by substitution of the value of  $H$ , so found, in equation (16). The following application to the case of tartaric acid will serve as an illustration of the method, while numerous additional acids are similarly treated in Mr. Chandler's article. For tartaric acid,  $k_1 = 970 \times 10^{-6}$ ;<sup>1</sup> if  $m = \frac{1}{1024}$ ,  $A_1 = 141$  and  $A_2 = 108$ . Therefore,  $a = -2.167 \times 10^{-4}$ ,  $c = +6.480 \times 10^{-8}$ ,  $H = 117.6 \times 10^{-6}$  and  $k_2 = 34.3 \times 10^{-6}$ . The ratio  $k_1/k_2 = 28.3$ .

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]  
**THE IONIZATION CONSTANTS OF THE SECOND HYDROGEN ION  
 OF DIBASIC ACIDS.**

BY E. E. CHANDLER.

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It is generally believed that dibasic acids ionize in two stages, thus:



From a study of the conductivities of dibasic acids, Ostwald<sup>2</sup> concluded that, excepting strong acids like oxalic, the second stage of the ionization did not take place to an appreciable extent at concentrations greater than milli-normal, since the primary ionization constant,  $k_1$ , as calculated from the relation,

$$H \cdot HX = k_1 \cdot H_2X, \quad (1)$$

where the formulae  $H, HX$ , etc., represent molecular or ionic concentrations, was really a constant for all concentrations greater than 1/1024 normal. For smaller concentrations the apparent value of  $k_1$  as calculated on the basis of equation (1) usually increased appreciably. This increase is the result of the ionization of the second hydrogen ion.

If the secondary ionization constant, *i. e.*, the ionization constant of the second hydrogen ion of a dibasic acid, is called  $k_2$ , then

$$H \cdot HX = k_2 \cdot HX. \quad (2)$$

The magnitude of this constant has been determined previously for a considerable number of acids by four entirely different methods.

Trevor<sup>3</sup> determined the rate at which dilute solutions of acid salts of dibasic acids invert cane sugar, and from the results calculated the concentrations of the hydrogen ions in the solutions used. It was assumed

<sup>1</sup> Walden, *Z. physik. Chem.*, 8, 445 (1891).

<sup>2</sup> *Ibid.*, 3, 281 (1889).

<sup>3</sup> *Ibid.*, 10, 321 (1892).