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LABOUR - BIOPHYSICAL EXTENSION OF HASSELBALCH - HENDERSON'S EQUATION.

Senseki TAKANO*

。 高 野 千 石:ハツセルバルハ・ヘンダースンの方程式の労働生物理学への拡張

1) Introduction.

I have already reported the fact¹⁾ that a remarkable linear correlation was found between the fatigue index which was measured by the cupriferrocyanide colloidal reaction ²⁻⁵⁾ and the similar index of the Zambrini's reaction. ⁶⁾ This fact shows that the mechanisms of both reactions are directly connected with the acidalkali equelibrium of blood system, and obviously with the acid formation in the working tissues by glycolysis on muscular contraction. Hence, we can easily conclude that these reactions will open up the possibilities of quantitative estimation of the constants of acidalkali equelibrium in the blood system, if we make an adequate unification to the various theories which were deduced by Hasselbalch⁷⁾ and Henderson,³⁾ Zambrini and Watanabe, and me myself. The question of acidalkali equelibrium of the blood system contains many important physiological functions of the maintenance of life, and especially of the fatigue induced by muscular contraction.

Thus, if we settle the theoretical relations in this unknown field, the substance of the cupriferrocyanide colloidal reaction will be thoroughly understood in the various cases of labour-physiology.

2) Theoretical treatment.

where $(pH)_S$ denotes the hydrogen-ion exponent of saliva, z is the fatigue index of the Zambrin's reaction and α,β are both constants.

The grounds of the formation of this formula are easy to be comprehended from the mechanism of that reaction. The general reagents of the reaction are 1.2-oxyanthraquinone and 1.2.6.-oxyanthraquinone, and these are mere indicators of saliva $(pH)_S$ and the fatigue index z is graded in proportion to the saliva pH.

On the other hand, according to the Watanabe's research, 10) the $(pH)_S$ correlates with the Van-Slyre's alkali reserve in volume percent (V) in blood by the next

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formula:

$$V = \varepsilon + \{ \gamma(pH)_S - \delta \}$$
(2)

where γ, δ and ε are constants. These numerical expressions are $\gamma = 12.5$, $\delta = 6.8$, $\varepsilon = 46.0$ respectively and these are already discussed in our previous paper. ¹¹⁾

According to the studies of Hasselbalch and Henderson, the hydrogen ion concentration of blood $(H^+)_b$ is expressed by the next formula:

$$(H^+)_b = k_1 \frac{[H_2CO_3]}{[BHCO_3]}$$
(3)

This is the original formula of Hasselbalch - Henderson's equation. Now we put the Van-Slyke's alkali reserve of blood in volume percent as follows:

$$V = \lambda [BHCO_3]$$
(4)

where λ is a proportional constant, and so we have:

or

$$\begin{array}{ll}
(pH)_b &= pk_1' + log \frac{V}{[H_2CO_3]} \\
pk_1' &= -log k_1 \lambda
\end{array}$$
(6)

The formula (6) is the special form of Hasselbalch-Henderson's equation represented by the Van-Slyke's alkali reserve (V) of blood.

From equation (2) and equation (6), we have:

$$(pH)_b = pk_1' + log \frac{\{\gamma (pH)_S - \delta_{\gamma} + \epsilon\}}{[H_2CO_3]} \qquad \dots (7)$$

by putting

$$\varepsilon - \gamma \delta = \varepsilon'$$

then

$$(pH)_b = pk_1' + log \{ \gamma (pH)_S + \varepsilon' \} - log[H_2CO_3] \cdots (8)$$

From equation (8) and equation (2) we have

$$(pH)_b = pk_1' + log\{\gamma(\alpha z + \beta) + \varepsilon'\} - log[H_2CO_3] \cdots (9)$$

or putting $\beta \gamma + \varepsilon' = \varepsilon''$, then

$$(pH)_b = pk_1' + log \left(1 + \frac{\alpha \gamma z}{\varepsilon''}\right) + log \frac{\varepsilon''}{[H_2CO_3]} \quad \cdots (10)$$

The value of $\alpha \gamma z/\varepsilon''$ culculated from the following values $\alpha = 0.2$, $\beta = 5.2$, $\gamma = 12.5$, $\delta = 6.8$ and $\varepsilon = 46.0$ respectively, is about 0.096153...z.

This value of z is ordinarily smaller than 10.0, excepting in the non-fatigued state. Thus,

$$\alpha \gamma z/\epsilon'' < 1$$
,

so we can expand the formula (10) with the approximation of the second term, on taking account of the accuaracy of the ordinary measurements of pH in blood. We have:

$$(pH)_b \doteq pk_1' + \frac{1}{2 \cdot 302} \left\{ \frac{\alpha \gamma z}{\varepsilon''} - \frac{\alpha^2 \gamma^2 z^2}{2\varepsilon''^2} \right\} + \log \frac{\varepsilon'}{[H \cdot CO_3]} \cdots (11)$$

This is the new form of Hasslbalch-Henderson's equation represented by the Zambrini's index.

Now, we have already reported by the experiments the relation of both indexes of cupriferrocyanide colloidal reaction and Zambrini's reaction.

These results are sumarized as follows:

$$z = \mu - \nu N$$
(12)

where μ and ν are some constants, and N, the fatigue index of cupriferrocyanide colloidal reaction, is culculated from the titrated volume of urine by the next formula¹⁸⁾:

$$N = \left(\frac{4}{x}\right)^{0.87} \quad \dots \tag{13}$$

By the substitution of z in the formula (12), we have:

$$(pH)_b = pk_1' + log \left\{ 1 + \frac{\alpha \gamma}{\varepsilon''} (\mu - \nu N) \right\} + log \frac{\varepsilon''}{[H_2CO_3]} \cdots (14)$$

or approximately

$$(pH)_b = pk_1' + \frac{\alpha\gamma(\mu - \nu N)}{2 \cdot 302 \ \varepsilon''} \left\{ 1 - \frac{\alpha\gamma}{2\varepsilon''} \ (\mu - \nu N) \right\} + \log \frac{\varepsilon''}{[H_2CO_3]} \quad \cdots (15)$$

Likely to the formula (11), this is also the new form of Hassetbalch - Henderson's equation represented by the fatigue index of the cupriferrocyanide colloidal reaction.

Although the numerical treatment of the various constants is omitted here, these equations of (11), (12) and (14) all contain in them the fatigue index z or N, so we can analyse the presumed relation of pH of blood and free carbonic acid activity in blood at any state of fatigue. By the substitution of the following constants which were already determined¹⁾ experimentally in the previous paper, we have:

$$\begin{split} \varepsilon' &= \varepsilon - \gamma \delta = -39.00, \quad \mu = 13.70, \quad \nu = 1.87, \quad \varepsilon'' = \beta \gamma + \varepsilon' = 26.00 \\ (pH)_b &= pk_1' + log(1 + 0.09615z) + log \frac{26}{[H_2CO_3]} \cdots (10') \\ (pH)_b &= pk_1' + 0.04174z + 0.00201z^2 + log \frac{26}{[H_2CO_3]} \cdots (11') \\ (pH)_b &= pk_1' + log (2.3165 - 0.1797N) + log \frac{26}{[H_2CO_3]} \cdots (14') \\ (pH)_b &= pk_1' + (0.57i9 - 0.07806N) \\ &\times (0.3417 + 0.08985N) + log \frac{26}{[H_2CO_3]} \cdots (15') \end{split}$$

If we take the secondary approximation, we have:

$$(pH)_b = pk_1' + 0.04174z + log \frac{26}{[H_2CO_3]} \cdots (16)$$

$$(pH)_b = pk_1' + 0.5719 - 0.07806N + log \frac{26}{[H_2CO_3]} \cdots (17)$$

The measurable and significant order of blood pH is about two or three terms below zero, so in practical treatments the culculation of the above formulas (16) and (17) is good for use. On the other hand, the value pk_1 is estimated about 6.1 by Henderson, hence by substituting this value in the formulas (16) and (17) we have:

$$(pH)_b = 6.10 + 0.04174z + log \frac{26}{[H_2CO_3]} \cdots (16')$$

 $(pH)_b = 6.6719 - 0.07806N + log \frac{26}{[H_2CO_3]} \cdots (17')$

3) Discussion and Culculation.

Culculating the free carbonic acid in blood in volume percent from the equation (17) on the various values of blood pH, we obtain the next table.

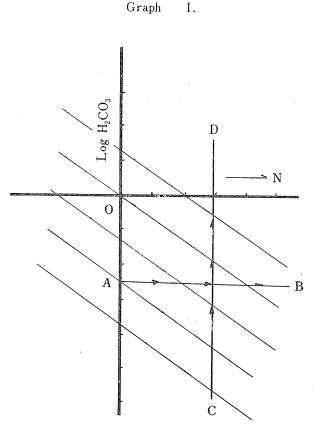
Table 2	
pH of blood,	"a" in eq. (19)
6.9	-0.22808
7.0	-0.32808
* 7.1	-0.42808
7. 2	-0.52808
7.3	-0.62808
7.4	-0.72808
7.5	-0.82808

where the parameter "a" denotes:

The graph (I) shows the relation between the free carbonic acid activity of blood and the fatigue index N which is defined by the formula (13). We can easily appreciate the condition of blood in the real muscular work. When work is done, and the final products of metabolite are increased in the blood, the $log \ \frac{[H_2CO_3]}{26}$ at constant $(pH)_b$ decreases along the paralleled lines in proportion to the increase of fatigue index N.

If the gas exchange in the lungs is kept constant, then the blood pH decreases along the line \overrightarrow{AB} , according as N increases. So we may conclude that the increase of fatigue index N means the generation of acidocis when the gas exchange is kept constant.

But in the real muscular work, the gas exchange rate is generally promoted, so the above mentioned consideration is only an ideal case. On the contrary, if the gas exchange of the lungs is extremely interrupted, even the slightly loaded muscular work would cause the considerable increase of fatigue index N. Such



cases were often observed experimentally in the case of tuberclosis patients ¹⁴⁾¹⁵. These results were also traced by Kudeo¹⁶⁾¹⁷ and his co-workers, and they recognized the presence of the above mentioned cases.

Generally speaking, it is all right to think that the tension of free carbonic acid in the artery blood is equal to the tension of the gas in the lungs. But this assumption is not correct when the gas exchange of the lungs is interrupted, and, in such a case, the abnormality of the increasing of the index of cupriferrocyanide colloidal reaction will have something of clinical importance.

The various experiments on the reaction in the field of tuberclosis may have been

undertaken according to the above mentioned category. Such an abnormality of increasing fatigue index of the reaction due to the above mentioned gas exchange interruption in the lungs is not only seen in tuberclosis, but also will be observed in cardioic dyspnea.

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