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60. Yoshihiro Maekawa: Studies on the Higher Derivative Automatic Titration. I. Theoretical Considerations. (1).

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The 2nd derivative automatic titration is an entirely new automatic titration which was designed by Prof. Seishi Takagi and the author,[1] and in this titration, the electronically differentiated 2nd derivative voltage is used as the magnetic cock operating a signal and the titration is stopped automatically at the end point.

In the present paper, the higher derivative automatic titration is presented which is more general than the 2nd derivative automatic titration.

The electronic differentiation circuit, used in the 2nd derivative automatic titration, was a simple resistance-capacitance network (Fig. I-1). However, it is known that e_1, the output voltage of this circuit, is nearly equal to the 1st derivative of e_0, the input voltage, when the values of R and C are properly chosen. So, if several of the properly chosen R-C differentiation networks are selected, required output nearly equal to the higher derivative can be obtained.

In practice, however, we should insert a vacuum tube amplifier between the R-C differentiation networks to decrease the mutual actions and cover the loss of the network (Fig. I-2).

As we previously reported, the insertion of a vacuum tube amplifier (Fig. I-3) is simply equal to the change of the time constant of R-C differentiation network from $(R \times C)$ to $\{R_0^2C/(R_a + R_L)\}$, as far as only the wave form and not the magnitude of the output voltage is considered (where R_a = plate resistance of vacuum tube, R_L = load resistance, $R_0^2 = R_aR_L + R_aR + R_LR$). So, in the present paper, insertions of vacuum tube amplifiers and the mutual actions will be neglected, and it will be assumed that all the time constants $\tau(= R \times C)$ of R-C differentiation networks are identical, because we can get the best results when all the time constants are identical.[1]

Now, let $e_0(t)$ be the input voltage, with Laplace-transform $E_0(p)$. (In the remainder of this paper the Laplace-transform will be written $\mathfrak{L}$-transform.)

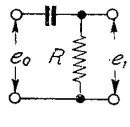

Fig. I-1.
C-R Differentiation Circuit

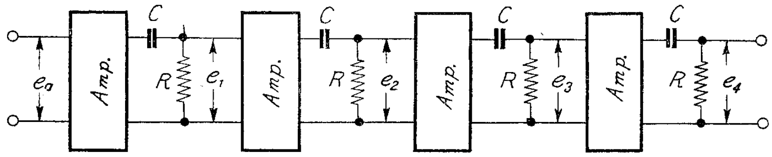

Fig. I-2.
C-R Higher-Differentiation Circuit (Amp. = Vacuum tube amplifier)

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1) S. Takagi, Y. Maekawa: Japan Analyst, **3**, 478(1954).

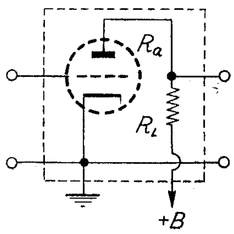

Fig. I-3.
Vacuum Tube
Amplifier

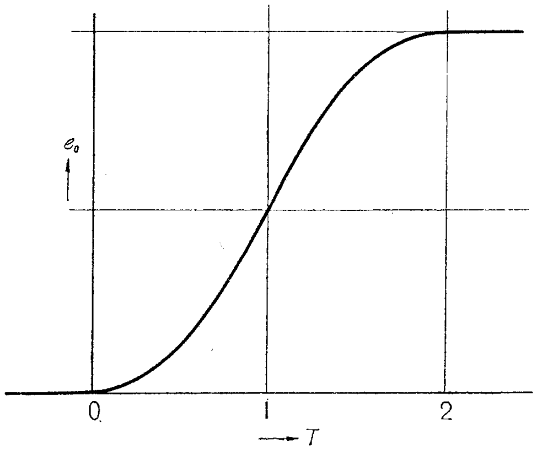

Fig. I-4.
Input Voltage
Curve (e_0)

$$E_0(p) = (1 - \varepsilon^{-hp})^2/h^2p^2 \quad \text{(I- 1)}$$

$e_0(t)$ has the wave form represented in Fig. I-4.

Let $e_n(t)$ be the output voltage of nth differentiation circuit, with $\mathfrak{L}$-transform $E_n(p)$.

From $E_n(p) = p\cdot E_{n-1}(p)/(p + 1/\tau)$[1] .... (I- 2)

$$(n = 1,\ 2, \ldots\ldots n)$$

By a simple process of elimination, one gets

$$E_n(p) = p^n E_0(p)/(p + 1/\tau)^n \quad \text{(I- 3)}$$

$$= (1 - \varepsilon^{-hp})^2/h^2p^{2-n}(p + 1/\tau)^n \quad \text{(I- 4)}$$

Thus, $e_n(t)$, the response function that equals $\mathfrak{L}^{-1}[E_n(p)]$ is given by

$$e_n(t) = \frac{1}{2\pi j}\int_{c-j\infty}^{c+j\infty} \frac{\varepsilon^{pt}(1 - \varepsilon^{-hp})^2}{h^2p^{3-n}(p + 1/\tau)^n}\,dp \quad \text{(I- 5)}$$

Let

$$f_n(t) = \frac{1}{2\pi j}\int_{c-j\infty}^{c+j\infty} \frac{\varepsilon^{pt}}{h^2p^{3-n}(p + 1/\tau)^n}\,dp \quad \text{(I- 6)}$$

Then

$$e_n(t) = f_n(t)\cdot H(t) - 2f_n(t - h)\cdot H(t - h) + f_n(t - 2h)\cdot H(t - 2h) \quad \text{(I- 7)}$$

$f_n(t)$ can be calculated by the next equation

$$f_n(t) = \sum \text{residue of pole of } \frac{\varepsilon^{pt}}{h^2p^{3-n}(p + 1/\tau)^n} \quad \text{(I- 8)}$$

The calculated results of $f_n(t)$ for n from 1 to 4 are as follows :

$$f_1(t) = \tau^2(\varepsilon^{-t/\tau} + t/\tau - 1)/h^2 \quad \text{(I- 9)}$$

$$f_2(t) = \tau^2\{1 - \varepsilon^{-t/\tau}(1 + t/\tau)\}/h^2 \quad \text{(I-10)}$$

$$f_3(t) = t^2\varepsilon^{-t/\tau}/2h^2 \quad \text{(I-11)}$$

$$f_4(t) = t^2\varepsilon^{-t/\tau}(3 - t/\tau)/6h^2 \quad \text{(I-12)}$$

simplifying by putting $T = t/h$, $\alpha = \tau/h$, one gets

$$e_n(T) = f_n(T)\cdot H(T) - 2f_n(T - 1)\cdot H(T - 1) + f_n(T - 2)\cdot H(T - 2) \quad \text{(I-13)}$$

$$f_1(T) = \alpha^2(\varepsilon^{-T/\alpha} + T/\alpha - 1) \quad \text{(I-14)}$$

$$f_2(T) = \alpha^2\{1 - \varepsilon^{-T/\alpha}(1 + T/\alpha)\} \quad \text{(I-15)}$$

$$f_3(T) = T^2\varepsilon^{-T/\alpha}/2 \quad \text{(I-16)}$$

$$f_4(T) = T^2\varepsilon^{-T/\alpha}(3 - T/\alpha)/6 \quad \text{(I-17)}$$

The equations (I-13) and (I-14), (I-13) and (I-15), (I-13) and (I-16), and (I-13) and (I-17), give the response of the 1st, 2nd, 3rd, and 4th differentiation circuits, which are plotted in Figs. I-5, -6, -7, and -8, respectively.

Some outstanding points of this higher derivative automatic titration are as follows :

1) The titration is stopped at the point which is indicated by the quick jump of the higher derivative voltage to somewhat positive from negative (the points are indicated by circles in Figs. I-6, -7, and -8).

2) The derivative voltage depends on the shape of the titration curve and not on the magnitude of the input voltage. Therefore, it is unnecessary to adjust the titrator for many different titrations.

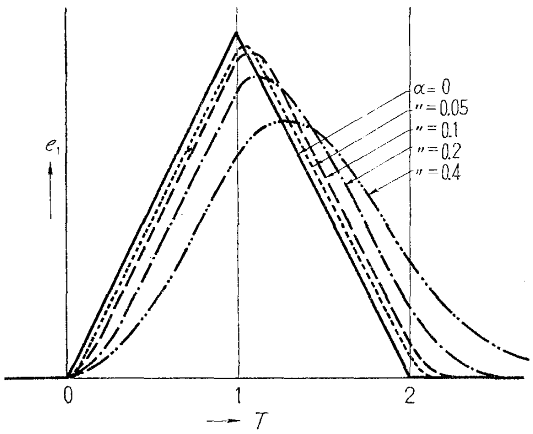

Fig. I-5.
1st Derivative Voltage Curve (e_1)

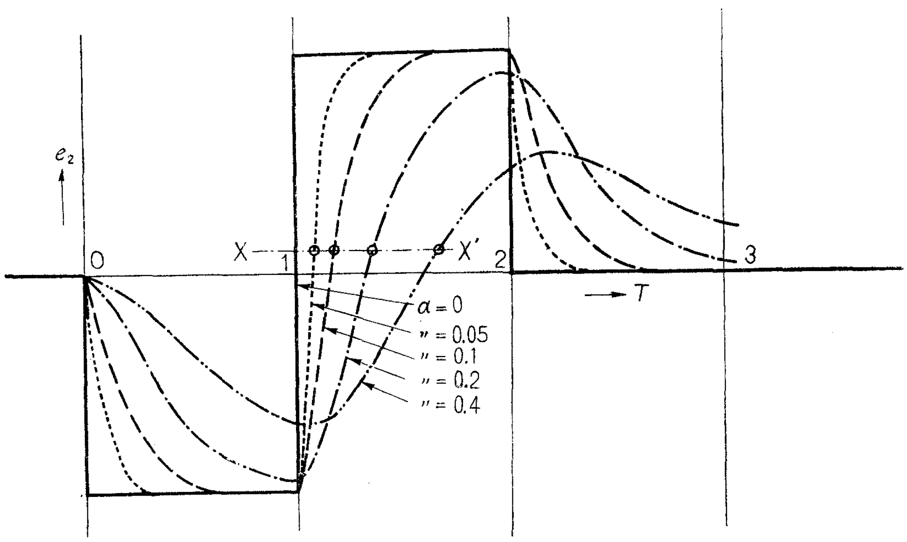

Fig. I-6. 2nd Derivative Voltage Curve (e_2)

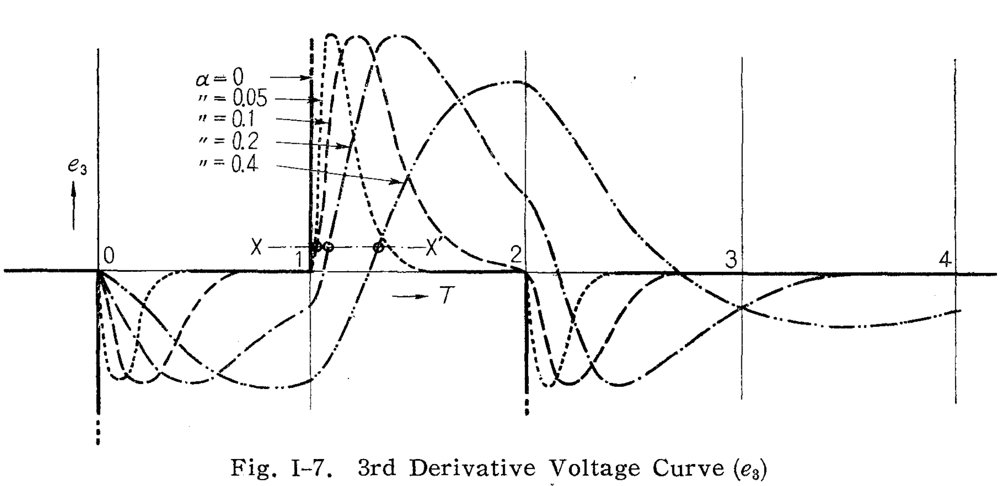

Fig. I-7. 3rd Derivative Voltage Curve (e_3)

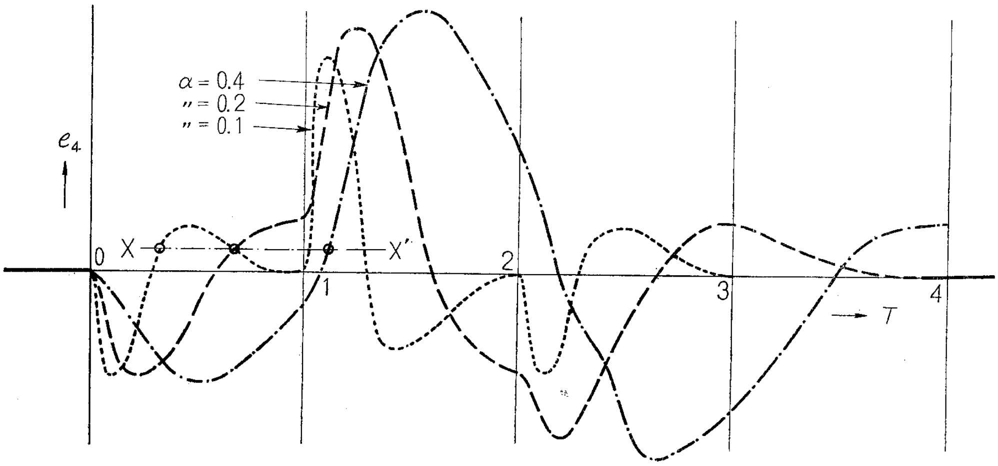

Fig. I-8. 4th Derivative Voltage Curve (e_4)

Comparison of Figs. I-5, -6, -7, and -8, from these view points reveal the following:

1) The 1st derivative voltage may not be used for this automatic titration, because it dose not change its polarity during titration.

2) The 2nd derivative voltage may be used, but, especially in the case of large α value, it changes gradualy from negative to positive, and the positions of the points, indicated by circles in Fig. I-6, differ from that of the theoretical end point, $T=1$.

3) The 3rd derivative voltage may be more properly used, because it changes very rapidly from negative to positive near the theoretical end point.

4) The 4th derivative voltage may not be used, because the points, indicated by circles in Fig. I-8, largely change their positions with α value, and do not coincide with the theoretical ent point, $T=1$.

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Summary

Under the assumption that each of the time constants of *R–C* differentiation networks is identical in all higher derivative automatic titrations, it will be concluded theoretically that it is the best to use the 3rd derivative voltage as triggering signal of the higher derivative automatic titration, in an ordinary potentiometric titration.

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