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small irregular vibrations occurring in most electrocardiograms, where they sometimes reach a height of 0,1 to 0.5 mm. and more, but are sometimes entirely absent, as e.g. in N°. 6 of Mr. AD.

These vibrations are not caused by tremors of the floor or other irregularities which should be ascribed to an insufficient technique as is easily shown by the vibrationless normal curves at the end of almost every series of electrocardiograms. Hence they must be caused by electromotive agents in the human body itself and the question arises whether they find their origin in the action of the heart or of other organs. We may expect that an investigation undertaken with this object will give a definite answer to this question.

Physics. — Dr. J. E. VERSCHAFFELT. *"Contributions to the knowledge of* VAN DER WAALS' *ψ-surface.* VII. *The equation of state and the ψ-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components."* (part 4). Supplement N°. 6 (continued) to the Communications from the Physical Laboratory at Leyden by Prof KAMERLINGH ONNES.

(Communicated in the meeting of May 30, 1903).

17. *The α, β-diagram.*

In the previous communications the different phenomena in the neighbourhood of the critical point in substances with small proportions of one component have, according to our plan set forth at the beginning, entirely been expressed by means of the a and β and the co-efficients that can be derived from the general empirical reduced equation of state. For shortness, and to avoid the constant repetition of the same factors (comp. § 1) I have used till now, instead of the differential quotients of the general empirical reduced equation of state, the co-efficients k, where the m's (comp. form. 19) have been expressed by means of a and β, but henceforth, as the numerical values are more important I shall make use again of the differential quotients of the reduced equation of state itself, used in equation (1). It seemed important to me to completely determine by means of the numerical values of a and β the different cases which, according to the formulae found by KEESOM (Comm. N°. 75) and by me (loc. cit.), may present themselves in the relative situation of the different critical points. To illustrate this I intend to divide an a, β-diagram into fields in which there is a definite relative situation, by means

of lines, as Korteweg has done in another diagram (the x, γ-diagram)[1]).

This investigation showed that the last of the eight cases distinguished by Korteweg of which the inconsistency was demonstrated by him for one special case only, did not exist in general, at least for all the equations of state which satisfy the law of corresponding states. Not to make the investigation too elaborate I have compared the situation of the plaitpoint only with that of the critical state of the pure substance, that is to say I have considered the fields within which $T_{xpl} >$ or $< T_k$, $p_{xpl} >$ or $< p_k$ and $v_{xpl} >$ or $< v_k$. I have also determined in which area the retrograde condensation is of the first or the second kind; and lastly I have indicated in the diagram what had been observed experimentally.

The plaitpoint temperature. According to form. (59) the plaitpoint temperature of the mixture is higher or lower than the critical temperature of the pure substance as the expression

$$\frac{m^2_{01} + RT_k m_{11}}{RT_k m_{11}} \alpha = - \frac{m^2_{01} + RT_k m_{11}}{RT_k k_{11}}$$

is positive or negative; and, k_{11} being negative, $T_{xpl} - T_k$ has the same sign as the numerator.

If for shortness we put

$$\mathfrak{p}_{01} = \frac{\partial p}{\partial t}, \ \mathfrak{p}_{11} = \frac{\partial^2 p}{\partial v \partial t}, \ \mathfrak{p}_{21} = \frac{\partial^3 p}{\partial v^2 \partial t}, \cdots \mathfrak{p}_{30} = \frac{\partial^3 p}{\partial v^3}, \ \mathfrak{p}_{40} = \frac{\partial^4 p}{\partial v^4}, \ \text{etc.}$$

and for convenience we leave out an index which refers to the critical state, because only those values are used which refer to the critical state,

$$m^2_{01} + RT_k m_{11} = p^2_k [(\beta - \mathfrak{p}_{01} \alpha)^2 - C_4 \mathfrak{p}_{11} \alpha], \ [2])$$

so that the area, where $T_{xpl} > T_k$ is separated from that where $T_{xpl} < T_k$ by a line of which the equation is:

$$(\beta - \mathfrak{p}_{01} \alpha)^2 - C_4 \mathfrak{p}_{11} \alpha = 0.$$

This line, a parabola, represented on the annexed plate [3]) by

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[1]) Proc. Royal Acad., Jan 31, 1903. The x and γ are connected in a simple linear way with α and β (comp. the previous communication p. 666).

[2]) For we have (comp. form. (19):

$$m_{01} = p_k (\beta - \mathfrak{p}_{01} \alpha), \ m_{11} = - \frac{p_k}{v_k} \mathfrak{p}_{11} \alpha, \ m_{21} = - \frac{1}{2} \frac{p_k}{v_k^2} [\mathfrak{p}_{21} \alpha + \mathfrak{p}_{30} (\alpha - \beta)], \cdots$$

$$m_{30} = \frac{1}{6} \frac{p_k}{v_k^3} \mathfrak{p}_{30}, \ m_{40} = \frac{1}{24} \frac{p_k}{v_k^4} \mathfrak{p}_{40}, \ \text{etc.};$$

For the definition of C_4 comp. Kamerlingh Onnes (Arch. Néerl. (2), 5, 670, 1901; Comm. no. 66).

[3]) The figure is drawn by using the values of $\mathfrak{p}_{11}$, $\mathfrak{p}_{11}$ etc. which will be calculated in the next section. For clearness I have represented the x's in a 5 times larger scale than the β's.

$bAOb'$ corresponds to Korteweg's first boundary [1]). Outside the parabola $T_{xpl} > T_k$, inside $T_{xpl} < T_k$.

The plaitpointpressure. From form. (60) we derive that $p_{xpl} >$ or $< p_k$ as $\mathfrak{p}_{01} (\beta - \mathfrak{p}_{01} \alpha)^2 >$ or $< C_4 \mathfrak{p}_{11} \beta$. The equation of the boundary

$$\mathfrak{p}_{01} (\beta - \mathfrak{p}_{01} \alpha)^2 - C_4 \mathfrak{p}_{11} \beta = 0,$$

is that of a parabola represented in the figure by $cOBc'$. Outside the parabola $p_{xpl} > p_k$, inside $< p_k$.

The plaitpointvolume. The manner in which v_{xpl} depends on α and β may be derived from form. (61); it is expressed by Keesom's formula (2c), which I borrow from him in my notations:

$$v_{xpl} = v_k + v_k(\alpha-\beta)x - \frac{(\beta-\mathfrak{p}_{01}\alpha)v_k x}{C^2{}_4 \mathfrak{p}_{21}\mathfrak{p}_{30}} [\mathfrak{p}_{11}(\beta-\mathfrak{p}_{01}\alpha)^2 - C_4\mathfrak{p}_{21}(\beta-\mathfrak{p}_{01}\alpha) - 3C_4\mathfrak{p}^2{}_{11}\alpha].$$

Hence the boundary is here:

$$0 = -\mathfrak{p}_{11}(\beta-\mathfrak{p}_{01}\alpha)^2 + C_4\mathfrak{p}_{21}(\beta-\mathfrak{p}_{01}\alpha)^2 + 3C_4\mathfrak{p}^2{}_{11}\alpha(\beta-\mathfrak{p}_{01}\alpha) + C^2{}_4\mathfrak{p}_{11}\mathfrak{p}_{30}(\alpha-\beta).$$

This is a curve of the third degree, like Korteweg's third boundary, with which it corresponds in this diagram.

In order to investigate this curve I introduce, following the example of Korteweg, a parameter z, by putting

$$z = \beta - \mathfrak{p}_{01} \alpha.$$

and I find that α and β, by means of that parameter are expressed thus:

$$\alpha = \frac{z}{N} [- \mathfrak{p}_{11} z^2 + C_4 \mathfrak{p}_{21} z - C^2{}_4 \mathfrak{p}_{11} \mathfrak{p}_{30}]$$

$$\beta = \frac{z}{N} [- \mathfrak{p}_{01} \mathfrak{p}_{11} z^2 + C_4 \{\mathfrak{p}_{01} \mathfrak{p}_{21} - 3 \mathfrak{p}^2{}_{11}\} z - C^2{}_4 \mathfrak{p}_{11} {}_{30}],$$

where

$$N = C^2{}_4 \mathfrak{p}_{11} \mathfrak{p}_{30} (\mathfrak{p}_{01} - 1) - 3 C_4 \mathfrak{p}^2{}_{11} z.$$

As α and β are single valued functions of z, all lines which are parallel to the straight line $\beta = \mathfrak{p}_{01} \alpha$ (Oa of the figure) intersect the curve at one single point at a finite distance.

If we put:

$$z_1 = \frac{C_4\mathfrak{p}_{30}(\mathfrak{p}_{01}-1)}{3\mathfrak{p}_{11}}, {}^2)$$

the straight line $\beta = \mathfrak{p}_{01} \alpha + z_1$, being a dotted line in the figure (CD),

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[1]) To avoid mistakes I use here the word boundary, instead of the expression border curve used by Korteweg; for in our demonstrations the word border curve has a very special meaning, viz. that of a boundary between stable and unstable states.

[2]) As $\mathfrak{p}_1$ is also equal to the direction-cosine $\left(\dfrac{d\mathfrak{p}}{d\mathfrak{r}}\right)_k$ of the tangent to the reduced vapour tension curve at the critical point, and as it follows from the form of that line that $\left(\dfrac{d\mathfrak{p}}{dt}\right)_k > 1$, z_1 must necessarily be positive.

is an asymptote of the cubic curve. It has two branches, of which the one ($dGEd'$) situated above the asymptote, is given by values of z, which are larger than z_1, the other ($d''OHFd'''$),- below the asymptote for $z < z_1$.

α becomes equal to zero not only for $z = 0$, but also for two other real values of z, of which the one is positive, the other negative; I shall call the positive root z_2, the negative one z_3. In the same manner β vanishes for $z = 0$ and also for two other real values of z, of which again one (z_4) is positive, the other (z_5) negative.- We can prove that always $z_5 > z_3$; for z_2 and z_4, three cases are possible: both are larger than z_1, and then $z_4 > z_2$, or both are equal to z_1, or both are smaller than z_1 and then $z_4 < z_2$. With the values of the derivatives, to be introduced presently, the order of the roots is:
$$z_4 > z_2 > z_1 > 0 > z_5 > z_3,$$
and hence follows the form of the cubic curve as it is drawn in the figure [1]).

One can easily see that $v_{xpl} > v_k$ above the branch $z > z_1$, and within the branch $z < z_1$, while $v_{xpl} < v_k$ in the area which lies partly between those two branches and which extends further to the right of both.

Retrograde condensation is of the first kind when $v_{Tpl} < v_{Tr}$, and of the second when $v_{Tpl} > v_{Tr}$. According to form. (41) and (26) $v_{Tpl} > v_{Tr}$ when m_{01} and $m^2_{01} + RT_k m_{11}$ have the same sign; $m^2_{01} + RT_k m_{11}$ is positive outside the parabola $bAOb'$ and negative inside, while m_{01} is positive above the straight line Oa and negative below it. Hence we have $v_{Tpl} > v_{Tr}$ and retrograde condensation of the second kind: 1st. inside the parabola $bAOb'$ and below the straight line Oa, 2nd. outside the parabola and above the straight line; at all other points $v_{Tpl} < v_{Tr}$ and the retrograde condensation is of the first kind.

Here follow the physical characteristics of the fields into which the figure is divided by the boundaries under consideration:

Field 1 : $T_{xpl} > T_k$, $p_{xpl} > p_k$, $v_{xpl} > v_k$, $v_{Tpl} > v_{Tr}$, r. c. II

2 : $T_{xpl} > T_k$, $p_{xpl} > p_k$, $v_{xpl} < v_k$, $v_{Tpl} > v_{Tr}$, r. c. II

3 : $T_{xpl} > T_k$, $p_{xpl} > p_k$, $v_{xpl} < v_k$, $v_{Tpl} < v_{Tr}$, r. c. I

4 : $T_{xpl} > T_k$, $p_{xpl} > p_k$, $v_{xpl} > v_k$, $v_{Tpl} < v_{Tr}$, r. c. I

5 : $T_{xpl} > T_k$, $p_{xpl} < p_k$, $v_{xpl} > v_k$, $v_{Tpl} < v_{Tr}$, r. c. I

6 : $T_{xpl} < T_k$, $p_{xpl} < p_k$, $v_{xpl} > v_k$, $v_{Tpl} > v_{Tr}$, r. c. II

7 : $T_{xpl} < T_k$, $p_{xpl} < p_k$, $v_{xpl} > v_k$, $v_{Tpl} < v_{Tr}$, r. c. I

8 : $T_{xpl} < T_k$, $p_{xpl} < p_k$, $v_{xpl} < v_k$, $v_{Tpl} < v_{Tr}$, r. c. I

9 : $T_{xpl} < T_k$, $p_{xpl} > p_k$, $v_{xpl} < v_k$, $v_{Tpl} < v_{Tr}$, r. c. I.

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[1]) It will be seen that this form agrees entirely with that derived by KORTEWEG in the x, γ-diagram from a special equation of state.

It will be seen that the figures 1 and 2 of the plate belonging to the first paper (Comm. 81) refer to points situated in the part on the right of the β-axis of the fields 1 and 2; figs. 3 and 4 to the same fields on the left of the β-axis; figs. 5 and 6 to the fields 7, 8 and 9; figs. 7 and 8 to the part of the fields 3, 4 and 5 lying on the right of the β-axis; figs. 9 and 10 to the same fields on the left of the β-axis; and lastly figs. 11 and 12 to field 6.

In the figure I have marked three points P, Q and R, of which the first relates to carbon dioxide with a small quantity of hydrogen ($a = -1,17$, $\beta = -1.62$), the second to carbon dioxide with a small quantity of methyl chloride ($a = 0,378$, $\beta = 0,088$) and the third to methylchloride with a small quantity of carbon dioxide ($a = -0,221$, $\beta = 0,281$). From the situation of P, viz. in field 2, it should follow that $T_{xpl} > T_k$, whereas the observations showed that $T_{xpl} < T_k$; this deviation has been pointed out before. [1] Moreover the situation of P in field 2 points to a system of isothermals of the mixtures as represented in figs. 1 and 2 of the first paper, while in reality this system of isothermals corresponds to figs. 5 and 6, that is to say to one of the fields 7, 8 or 9. The point P lies very near the limit of field 9, and hence it is possible that a more accurate determination of a and β would remove the point P into field 9 where indeed it should lie according to the plaitpoint constants observed and the character of this field, if at least the law of corresponding states can be applied. The points Q and R, so far as we know with certainty, are situated in the right field. [2]

The straight line $\beta = \mathrm{P}_{01} a$ agrees with Korteweg's second boundary. It is determined by the circumstance that along the connodal line $\left(\dfrac{d\mathit{v}}{dv}\right)_{pl} = 0$; we find from the formulae (37), (41) and (26) that:

$$\left(\frac{d\mathit{v}}{dv}\right)_{pl} = -\frac{2m_{30}RT_k}{m^2_{01} + RT_k m_{11}}(v_{Tpl} - v_{Tr}) = \frac{m_{01}}{RT_k} x T_{pl},$$

so that $\left(\dfrac{d\mathit{v}}{dv}\right)_{pl}$ becomes zero with m_{01}. Thus above the straight line Oa $\left(\dfrac{d\mathit{v}}{dv}\right)_{pl}$ is positive, below it, negative, hence in connection with the

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[1] Comp. 2nd paper, p. 334.

[2] It must be remarked that the deviation of the point Q in consequence of our insufficient knowledge of a and β would be much less striking than in the case of point P; e. g. whether Q ought to be placed in the neighbouring field 4 or not, could be only concluded from the sign of $v_{xpl} - v_k$, but we do not know with certainty what this sign should be for mixtures of carbon dioxide and methylchloride.

preceding it follows that KORTEWEG's eighth case:

$$T'_{xpl} < T_k \ , \quad \bar{v}_{apl} < v_k \ \text{ en } \left(\frac{dx}{dv}\right)_{pl} < 0$$

is in general not possible.

A direct proof of this circumstance may easily be given. Because m_{01} must be negative, I put $\beta = \mathfrak{p}_{01} \, \alpha - r^2$; $T_{xpl} < T_k$ requires that

$(\beta - \mathfrak{p}_{01} \, \alpha)^2 = C \, \mathfrak{p}_{11} \, \alpha - s^2$. Hence we may put: $\alpha = \dfrac{r^4 + s^2}{C_4 \mathfrak{p}_{11}}$ and

$$v_{apl} = v_k \ -v_k \, (\mathfrak{p}_{01}-1)\frac{r^4 + s^2}{C_4 \, \mathfrak{p}_{11}} x + r^2 \, v_k \, x + \frac{r^2 \, v_k \, x}{C^2_4 \mathfrak{p}_{11}\mathfrak{p}_{30}}[C_4\mathfrak{p}_{21}r^2 - \mathfrak{p}_{11}(3s^2 + 2r^4)],$$

so that all the terms of v_{apl} are positive. Hence we see that, if $T_{xpl} < T_k$ and $\left(\dfrac{dx}{dv}\right)_{pl} < 0$, $v_{apl} < v_k$ is an impossibility.

18. *The numerical value of the reduced differential quotients.*

To find this numerical value I have first tried to derive it directly from the observations by means of graphical representations; but as I did not succeed in finding more or less reliable values for the higher differential quotients ($\mathfrak{p}_{21}$, $\mathfrak{p}_{30}$, $\mathfrak{p}_{40}$ etc.) I was obliged to use formulae which satisfactorily represented the observations. Undoubtedly KAMERLINGH ONNES'[1] developments in series are best fitted for this purpose, although just in the neighbourhood of the critical point, where in our case they have to be applied, they deviate rather much from the observations[2]. Therefore the values of the derivatives obtained in that way, especially those of the higher orders, can only be considered as approximate.

By means of the temperature co-efficients of reduced virial co-efficients marked by $V.s. 1$[3] derived from AMAGAT's observations, I find for those virial co-efficients ($\mathfrak{A}_1$, $\mathfrak{B}_1$, etc.) and their first derivatives according to the temperature ($\mathfrak{A}'_1$, $\mathfrak{B}'_1$ etc.) at the critical point ($t = 1$),

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[1] Proc. Royal Acad. 29 June 1901, Comm. N'. 71, and Arch. Néerl. (2). 6, 874, 1901, Comm. N'. 74.

[2] Comp. Arch. Néerl. loc. cit. p. 887. Previously I have given parabolic formulae (Proc. Royal Acad., 31 March 1900, Comm. N⁰. 55 and Arch. Néerl. (2), 6, 650, 1901) which very well represent the observations just in the neighbourhood of the critical point. These formulae, however, do not harmonize with our considerations, because they do not yield finite values for higher derivatives.

[3] Comm. N⁰. 74, p. 12.

$\mathfrak{A}_1 = + 366,25 \times 10^{-5}$ $\mathfrak{A}'_1 = + 366,25 \times 10^{-5}$

$\mathfrak{B}_1 = - 471,614 \times 10^{-8}$ $\mathfrak{B}'_1 = + 662,387 \times 10^{-8}$

$\mathfrak{C}_1 = + 233,300 \times 10^{-11}$ $\mathfrak{C}'_1 = - 355,774 \times 10^{-11}$

$\mathfrak{D}_1 = - 360,485 \times 10^{-18}$ $\mathfrak{D}'_1 = + 789,380 \times 10^{-18}$

$\mathfrak{E}_1 = + 683,07 \times 10^{-25}$ $\mathfrak{E}'_1 = + 346,72 \times 10^{-25}$

$\mathfrak{F}_1 = - 90,14 \times 10^{-32}$ $\mathfrak{F}'_1 = - 698,82 \times 10^{-32}$

If further we put $\lambda = 0,00102$ (calculated from $T_k = 304,45$, $p_k = 72,9$ and $v_k = 0,00424$, we find at the critical point:

$p_{00} = 0,98833$, $p_{10} = 0,10305$, $p_{20} = -0,16831$, $p_{30} = - 5,30648$,

$p_{40} = 75,79292$, $p_{01} = 7,34410$, $p_{11} = -9,99986$, $p_{21} = 27,76382$, etc.

The values of p_{00}, p_{10} and p_{20} ought to be equal to 1, 0 and 0 respectively; the tolerably large deviation of the two last derivatives proves that the series used do not represent the shape of the iso-thermals in the neighbourhood of the critical point so accurately as we might wish[1]. Hence it follows that the values of the other derivatives calculated here cannot be very precise, and probably this uncertainty increases with the order of the derivative.

I take as approximate values of the reduced differential quotients at the critical point:

$p_{30} = - 5,3$, $p_{40} = 76$, $p_{01} = 7,3$, $p_{11} = - 10$, $p_{21} = 28$, while $C_4 = 3,6$.[2]

According to VAN DER WAALS' original (reduced) equation of state:

$$ p = \frac{8:}{3v-1} - \frac{3}{v^2} , $$

we should have

$p_{30} = - 9$, $p_{40} = 126$, $p_{01} = 4$, $p_{11} = - 6$, $p_{21} = 18$, $C_4 = \frac{8}{3} = 2,7$;[3]

and according to this modified equation:

$$ p = \frac{8t}{3v-1} - \frac{3e^{1-t}}{v^2} : $$

$p_{30} = - 9$, $p_{40} = 126$, $p_{01} = 7$, $p_{11} = - 12$, $p_{21} = 36$, $C_4 = 2,7$.

Finally I substitute the numerical values of the derivatives obtained

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[1] On the cause of that inaccuracy and the possibility of improving upon it a new communication by KAMERLINGH ONNES is to be expected. (Comp. Comm. n⁰. 74, p. 15).

[2] KEESOM gives (Comm. n⁰. 75, p. 9 and 10) $C_4 = 3,45$, $p_1 = 7$, $p_{11} = - 9.3$.

[3] It will be seen that these values agree tolerably well with the former; it is thus not remarkable that so close a resemblance exists between the forms of the boundaries found by KORTEWEG and by me, which indeed is based on VAN DER WAALS' original equation.

above in formulae (9) and (10) and compare the result with the observations.

Equation (9) yields:

$$\frac{1}{2}(v_2 - v_1) = \sqrt{6\frac{p_{11}}{p_{30}}(1 - t)} = 3,37\sqrt{1 - t}$$

and equation (10):

$$\frac{1}{2}(v_2 + v_1) - 1 = -\frac{1}{p_{30}}\left[p_{21} - \frac{3}{5}\frac{p_{11}p_{40}}{p_{30}}\right](1 - t) = 10,9(1 - t).$$

In order to compare these results with the parabolic formulae of MATHIAS [1]), formulae must be derived for the reduced densities of the co-existing phases; representing these reduced densities by δ_1 and δ_2 I find, according to a transformation employed formerly: [2])

$$\frac{1}{2}(\delta_1 - \delta_2) = 3,37\sqrt{1 - t}$$

$$\frac{1}{2}(\delta_1 + \delta_2) - 1 = (\overline{3,37}^2 - 10,9)(1 - t) = 0,5(1 - t).$$

In the last formula, however, the co-efficient 0,5 is somewhat uncertain.

MATHIAS gives for the liquid branch, according to the observations of CAILLETET and MATHIAS [3]),

$$\delta_1 = 1 - 2,47(1 - t) + 4,09\sqrt{1 - t},$$

and for the vapour branch

$$\delta_2 = 1 + 2,91(1 - t) - 3,37\sqrt{1 - t}.$$

f From these formulae it would follow that the two branches of the border curve belong to different parabolae. The co-efficient of $\sqrt{1-t}$ or the vapour branch perfectly agrees with the one found, and the fact that MATHIAS has found a greater value for the same co-efficient in the liquid branch, may clearly be ascribed to the uncertainty of the then existing data on this subject. If we neglect this difference, the formulae of MATHIAS give:

$$\frac{1}{2}\delta_1 + \delta_2) - 1 = 0,25(1 - t),$$

a sufficient agreement with the co-efficient 0,858 later derived by him from AMAGAT's observations. The value 0,5 found above is in good harmony with this.

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[1]) Journ. d. Phys., (3), 1, 53, 1892. Ann. d. Toulouse, V.

[2]) Proc. Royal Acad., 27 June 1896; Comm. no. 28, p. 12. More acurately we have

$$\varrho = \frac{1}{v_k + \Phi \pm \varphi} = \frac{1}{v_k} \mp \frac{\varphi}{v_k^2} + \frac{1}{v_k^2}(\varphi^2 - \Phi)$$

[3]) Journ. d. Phys., (3), 2, 5, 1893. Ann. d. Toulouse. VI.