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CONTENTS.

Physics. — "*Contribution to the theory of binary mixtures.*" VIII. By Prof. J. D. VAN DER WAALS.

THE INTERSECTION OF THE CURVE $\frac{d^2p}{dv\,dx} = 0$ WITH $\frac{dp}{dv} = 0$.

By the aid of the approximate equation of state the course of the curve $\frac{d^2p}{dv\,dx} = 0$ is given by the equation:

$$\frac{MRT\frac{db}{dx}}{(v-b)^3} = \frac{\frac{da}{dx}}{v^3}.$$

As has been observed before, it has a course which is analogous to that of the curve $\frac{dp}{dx} = 0$. At given value of T it has an asymptote for that value of x, for which in rarefied gas state, the deviation from the law of Boyle is maximum, viz. for which $MRT\frac{db}{dx}=\frac{da}{dx}$.

It has minimum volume on the line $v-b=3\frac{db}{dx}\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}}$, whereas the line $\frac{dp}{dx}=0$ has such a minimum volume on the line $v-b=2\frac{db}{dx}\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}}$.

The points of intersection of $\frac{d^2p}{dv\,dx}=0$ and $\frac{dp}{dx}=0$ indicate the points in which $\frac{dp}{dv}=0$ has a tangent parallel to the X-axis, as follows from $\frac{d^2p}{dv^2}\frac{dv}{dx}+\frac{d^2p}{dx\,dv}=0$. For such a point of intersection we have at the same time $\frac{MRT}{(v-b)^2}=\frac{2a}{v^3}$ and $\frac{MRT\frac{db}{dx}}{(v-b)^3}=\frac{\frac{da}{dx}}{v^3}$; and so $\frac{\frac{db}{dx}}{v-b}=\frac{\frac{da}{dx}}{2a}$, which last equation represents the locus of these points of intersection. Differentiating this locus "$v-b=2\frac{db}{dx}\frac{a}{\frac{da}{dx}}$" we find·

$$\frac{dv}{dx}=\frac{db}{dx}\frac{3\left(\frac{da}{dx}\right)^2-2a\frac{d^2a}{dx^2}}{\left(\frac{da}{dx}\right)^2}.$$

If in the diagram we think all the values of x present, e.g. ascending from the value of x for which $\frac{da}{dx}=0$, this locus is a curve with an asymptote for the value of x, for which $\frac{da}{dx}=0$, and it has a minimum volume for the value of x, for which $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$. For greater values of x the volume increases.

If in $\frac{\frac{db}{dx}}{v-b}=\frac{\frac{da}{dx}}{2a}$ the value $3b$ is put for v, we find $\frac{1}{b}\frac{db}{dx}=\frac{1}{a}\frac{da}{dx}$.

But then not only $\frac{d^2p}{dv\,dx}=0$ in the equation $\frac{d^3p}{dv^2}\frac{dv}{dx}+\frac{d^2p}{dv\,dx}=0$, but also $\frac{d^2p}{dv^2}$. The value of $\frac{dv}{dx}$ is then indefinite, and at the temperature at which this takes place, and which is the minimum temperature represented by $\frac{8}{27}\frac{a_x}{b_x}$, the curve $\frac{dp}{dv}$ has two branches, which intersect in the point given by $v=3b$ and x, belonging to $\frac{1}{b}\frac{db}{dx}=\frac{1}{a}\frac{da}{dx}$. For higher values of v, e.g. $v=4b$, the point of intersection of the two curves lies on the vapour branch of $\frac{dp}{dv}=0$, and vice versa. If we write $v=nb$, the form $\frac{2}{n-1}=\frac{\frac{1}{a}\frac{da}{dx}}{\frac{1}{b}\frac{db}{dx}}$ follows from $\frac{\frac{db}{dx}}{v-b}=\frac{\frac{da}{dx}}{2a}$. For those values of x for which the numerator is smaller than the denominator $n>3$, and vice versa. Only if also $\frac{da}{dx}=0$ should occur in the diagram, the value of n, and so also of v, is infinite.

If we determine the point in which the two curves touch, we shall find the same point in which $\frac{d^2p}{dv\,dx}$ has the minimum volume; for as the curve $\frac{dp}{dv}=0$ has a tangent parallel to the X-axis in every point of intersection, also the curve $\frac{d^2p}{dv\,dx}=0$ must have such a tangent in case of contact.

The condition that for a point of the last-mentioned curve $\frac{dv}{dx}=0$ is $\frac{d^3p}{dv\,dx^2}=0$. So we have

$$\frac{dp}{dv}=0 \quad \text{or} \quad \frac{MRT}{(v-b)^2}=\frac{2a}{v^3}$$

$$\frac{d^2p}{dv\,dx}=0 \quad \text{or} \quad \frac{MRT\frac{db}{dx}}{(v-b)^3}=\frac{\frac{da}{dx}}{v^3}$$

and

$$\frac{d^3p}{dv\,dx^2}=0 \quad \text{or} \quad 3\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^4}=\frac{\frac{d^2a}{dx^2}}{v^3}$$

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By comparing the square of the second of these equations with the product of the two others, we find back the condition:

$$\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}.$$

If we put $a = A + 2Bx + Cx^2$, in which $A = a_1$, $B = a_{12} - a_1$ and $C = a_1 + a_2 - 2a_{12}$, this equation leads to:

$$(B + Cx)^2 + \frac{B^2 - AC}{2} = 0$$

or

$$B + Cx = +\sqrt{\frac{a_1 a_2 - a_{12}^2}{2}}.$$

The positive sign before the radical sign is required by the condition that $\frac{da}{dx}$ must be positive. If x is to be real, $a_1 a_2$ must be $> a_{12}^2$, and the condition that x lies between 0 and 1 is indicated by the construction of fig. 33. Let OO' be the x-axis, and let PQ be

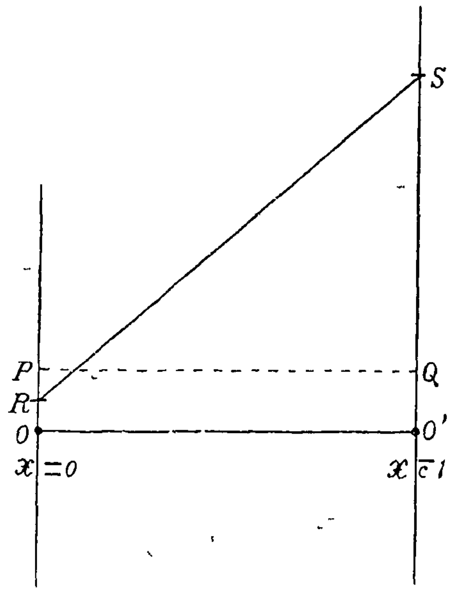

Fig. 33.

drawn at the height of $\sqrt{\frac{a_1 a_2 - a_{12}^2}{2}}$. Let us then take $OR = a_{12} - a_1$ and $O'S = a_2 - a_{12}$, then the point of intersection of RS and

PQ will have to lie between $x=0$ and $x=1$ for the condition $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$ to be fulfilled in the diagram.

According to the result arrived at in Contribution VII with regard to the point in which $\left(\frac{dp}{dx}\right)_v=0$ touches the line $\left(\frac{dp}{dv}\right)_x=0$, the value of x in which $\left(\frac{da}{dx}\right)^3=\frac{2}{3}a\frac{d^2a}{dx^2}$ must lie not very far from this point of contact.

But whether it might not even lie to the right of that value of x, for which $\frac{a_x}{b_x}$ has a minimum value, can only appear from a direct investigation. Then it may appear at the same time whether in case of contact of the two curves $\frac{dp}{dv}=0$ and $\frac{d^2p}{dvdx}=0$ the temperature has maximum value or minimum value.

Let us eliminate the value of v from the equations of the two curves. Among others we may do this by substituting the value of v from $\frac{2\frac{db}{dx}}{v-b}=\frac{1}{a}\frac{da}{dx}$ in $\frac{d^2p}{dv\,dx}=0$. Let us write:

$$\frac{v-b}{b}=2\frac{\frac{1}{b}\frac{db}{dx}}{\frac{1}{a}\frac{da}{dx}}=2z,$$

or

$$\frac{v}{b}=1+2z,$$

and

$$\frac{b}{v}\,\frac{1}{1+2z},$$

and

$$1-\frac{b}{v}=\frac{2z}{1+2z}.$$

From $\frac{d^2p}{dvdx}=0$ follows:

$$1-\frac{b}{v}=\sqrt[3]{\frac{MRT\frac{db}{dx}}{\frac{da}{dx}}}.$$

Hence:

$$\frac{\sqrt[3]{MRT\frac{db}{dx}}}{\frac{da}{dx}}=\frac{2z}{1+2z}.$$

Differentiating logarithmically, we get:

$$\frac{1}{3T}\frac{dT}{dx}-\frac{1}{3}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}=\frac{1}{z}\frac{da}{dx}\frac{1}{1+2z}$$

Now

$$\frac{1}{z}\frac{dz}{dx}=\frac{1}{a}\frac{da}{dx}-\frac{1}{b}\frac{db}{dx}-\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$$

or

$$\frac{1+2z}{3T}\frac{dT}{dx}-\frac{1}{3}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}(1+2z)=\frac{1}{a}\frac{da}{dx}-\frac{1}{b}\frac{db}{dx}-\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$$

or

$$\frac{1+2z}{3T}\frac{dT}{dx}+\frac{2}{3}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}(1-z)=\frac{1}{a}\frac{da}{dx}-\frac{1}{b}\frac{db}{dx}$$

or

$$\frac{1+2z}{3T}\frac{dT}{dx}=\left[\frac{1}{a}\frac{da}{dx}-\frac{1}{b}\frac{db}{dx}\right]\left[1-\frac{2}{3}\frac{a\frac{d^2a}{dx^2}}{\left(\frac{da}{dx}\right)^2}\right]$$

So the value $\frac{dT}{dx}$ is equal to 0, first if $\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dx}$, and secondly if $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$. If, when drawing T as function of x, we begin with small values of x, and if we should admit also negative values of x into our consideration, then both factors in the expression for $\frac{dT}{dx}$ are negative e. g. for $\frac{da}{dx}=0$, and so $\frac{dT}{dx}$ is positive. If x increases a value of x is reached for which one of these factors becomes equal to 0. For still higher value of x the second factor becomes equal to 0. Between these two special values of x, $\frac{dT}{dx}$ is negative — and for values of x which are larger than that for which also the second factor is zero, $\frac{dT}{dx}$ is again positive. So the value of T presents a maximum and a minimum.

In general we must now put two cases as possible according as the value of x for which $\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dv}$, is smaller or larger than that for which $\left(\frac{da}{dx}\right)=\frac{2}{3}a\frac{d^2a}{dx^2}$. The intermediate case in which these two values would coincide, might be considered as a third possibility. Let us call the maximum value of the temperature T_M, and the minimum value T_m. For a value of T below T_m there is only one point of intersection of $\frac{dp}{dv}=0$ and $\frac{d^2p}{dvdx}=0$, namely at small value of x. For values of T above T_M there is also only one point of intersection for large value of x. But for values of T between T_m and T_M there are three points of intersection. Of these three points of intersection there is always one, the middle one, which lies at a value of x lying between that which makes the first factor equal to zero, and that which makes the second factor equal to zero.

To give a survey of the course of the points of intersection of $\frac{dp}{dv}=0$ and $\frac{d^2p}{dvdx}=0$ at different temperatures, and so of the circumstances for which $\frac{dp}{dv}=0$ has a maximum or minimum volume, we shall have to separately treat the cases for the different situation of the two values of x, for which $\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dx}$, and $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$.

Let us first take the case for which the value of x for minimum value of $\frac{a_x}{b_x}$ is the smallest. This case is the simplest, and was discussed by me already before. Then a curve $\frac{d^2p}{dvdx}=0$ indicated in fig. 34 by α, passes through the double point of $\frac{dp}{dv}=0$. For lower T, α has assumed the position β, and $\frac{dp}{dv}=0$ the position γ, so that there are then two points of intersection (1 and 2) to be found.

But at higher T these points of intersection exist no longer; then the line $\frac{d^2p}{dvdx}=0$ runs between the two branches in which $\frac{dp}{dv}=0$ has split up, without intersecting them, at least at this place. There

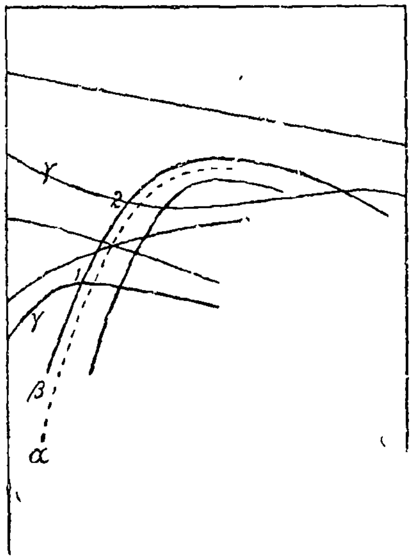

Fig. 34.

is, however, still a point of intersection, but at much greater value of x, namely a point of intersection formed by the branch of $\frac{d^2p}{dvdx}=0$ which runs again to larger volumes. In this point of intersection the righthand branch of $\frac{dp}{dv}=0$ has again minimum volume. So for values of T below that of the double point of $\frac{dp}{dv}=0$, the branch of the liquid volumes of $\frac{dp}{dv}=0$ has two points of intersection with $\frac{d^2p}{dvdx}=0$, so a maximum and a minimum volume, and for much smaller value of x there is then a minimum volume on the vapour branch. If we lower T still further, maximum and minimum volume of the liquid branch draw nearer to each other, and they coincide at the value of x for which $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$. Then the vapour branch has two coinciding values of x, for which $\frac{dv}{dx} = 0$, and so also a point of inflection, namely for the volume that is the smallest volume for which a point of intersection of the two curves exists. At still lower temperature the liquid branch has no longer a point of intersection; but the point of intersection of the vapour branch continues to exist, and proceeds continually to smaller value of x. I need hardly point out that in this description negative values of x are again not considered as unreal. The condition for a point occurring on the curve $\frac{dp}{dv} = 0$ in which $\frac{dv}{dx} = 0$ and $\frac{d^2v}{dx^2} = 0$ is found from:

$$\frac{d^2p}{dv^2}\frac{dv}{dx} + \frac{d^2p}{dvdx} = 0$$

and

$$\frac{d^2p}{dv^2}\frac{d^2v}{dx^2} + \frac{d^3p}{dv^3}\left(\frac{dv}{dv}\right)^2 + 2\frac{d^3p}{dvdx}\left(\frac{dv}{dx}\right) + \frac{d^3p}{dvdx^2} = 0.$$

Hence besides $\frac{dp}{dv} = 0$, also $\frac{d^2p}{dvdx} = 0$ and $\frac{d^3p}{dvdx^2} = 0$.

Let us now consider the second case, for which the value of x corresponding to $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$, is the smallest. For this value of x the value of T is then maximum, and the temperature for the double point of $\frac{dp}{dv} = 0$ will be a minimum. This means that with decrease of T two points of intersection *vanish*, whereas in the preceding case two new points of intersection *appear* with decrease of T.

Let us first consider this minimum temperature; then a curve $\frac{d^2p}{dvdx} = 0$ passes through the double point, which, in this point, may be considered to have two points in common with the line $\frac{dp}{dv} = 0$, and which has a third point of intersection for smaller value of x. This third point of intersection is to be found on the vapour branch of the lefthand branch of $\frac{dp}{dv} = 0$, because it has smaller x. Fig. 35 indicates the places of the three points of intersection for this value of T. With decrease of T two of the points of intersection lie on the vapour branch of the lefthand branch of the line $\frac{dp}{dv} = 0$, and a third point of intersection on the liquid branch of the other branch. With increase of T the two points of intersection on the left-hand branch coincide in the point for which x is found from $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$. Everything shows that at the temperature of the double point that part of the line $\frac{d^2p}{dvdx} = 0$ runs through the double

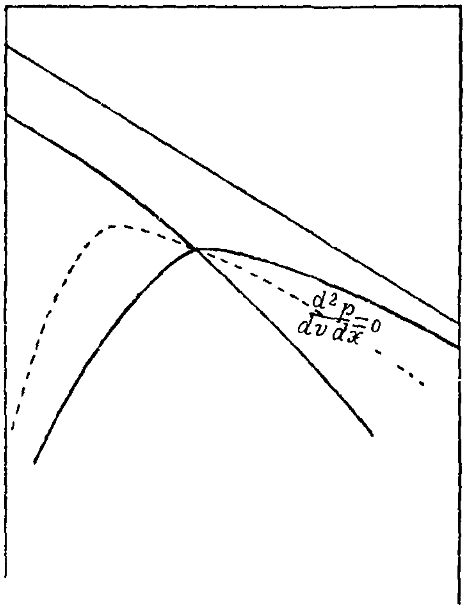

Fig. 35.

point that lies beyond the minimum volume. With T lower than that of the double point this part of the curve remains entirely in the unstable region.

If we try to ascertain on what it depends whether the value of x which corresponds to $\frac{1}{a}\frac{da}{dx} = \frac{1}{b}\frac{db}{dx}$ is smaller or larger than that for which $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$ we may, to decide this, substitute the value of x which follows from the second of these equations, in:

$$b\frac{da}{dx} - a\frac{db}{dx}.$$

If we then find a positive value for this form, the first case holds; then the point where $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$ lies in the region where the value of $\frac{a}{b}$ again increases.

Eliminating a we may also write for $b \frac{da}{dx} - a \frac{db}{dx}$

$$\frac{da}{dx} \left\{ b - \frac{3}{2} \frac{db}{dx} \frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}} \right\}$$

and as $\frac{da}{dx}$ must be positive, just as $\frac{d^2a}{dx^2}$, the sign depends on:

$$\frac{2}{3} b \frac{d^2a}{dx^2} - \frac{3}{2} \frac{db}{dx} \frac{da}{dx}.$$

And if we put $b_2 = nb_1$, $a = A + 2Bx + Cx^2$, this form becomes:

$$\frac{2}{3} C [1 + (n-1) x] - (n-1) [B + Cx]$$

or

$$\frac{2}{3} C + \frac{2}{3} (n-1) Cx - (n-1) (B + Cx)$$

or

$$\frac{2}{3} \frac{C}{n-1} - \frac{2}{3} B - \frac{B+Cx}{3}$$

Now we have found above $B + Cx = + \sqrt{\frac{a_1a_2 - a^2_{12}}{2}}$, and as $B = a_{12} - a_1$ and $C = a_1 + a_2 - 2a_{12}$, the sign depends on:

$$\frac{a_1 + a_2 - 2a_{12}}{n-1} - (a_{12} - a_1) - \frac{1}{2} \sqrt{\frac{a_1a_2 - a^2_{12}}{2}}.$$

If this sign is positive we have the case treated first. So for this case

$$\frac{(a_2 - a_{12}) - (a_{12} - a_1)}{a_{12} - a_1} > n - 1$$

or

$$\frac{a_2 - a_{12}}{a_{12} - a_1} > n.$$

is certainly necessary, but not sufficient.

With the following numerical values the conditions necessary for the first case, and the condition that the two values of x occur in the diagram, are satisfied.

Let $n=5$, $a_1=1$, $a_2=30$ and $a_{12}=2$. The value of x satisfying $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$, is found from:

$$(a_{12}-a_1)+(a_1+a_2-2a_{12})x=\sqrt{\frac{a_1a_1-a_{12}^2}{2}}$$

or

$$1+27x=\sqrt{13}=3{,}6$$

or

$$x_1=\frac{2{,}6}{27}.$$

The value of x satisfying $\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dx}$, is found from the equation:

$$B-\frac{n-1}{2}A+Cx+\frac{n-1}{2}Cx^2$$

or

$$-1+27x+54x^2=0$$

or

$$x_2=0{,}035.$$

If we had put $a_2=10$, leaving the other values unchanged, so that $\frac{a_2-a_{12}}{a_{12}-a_1}>n$ still remains larger than x, we find x_1 from the equation:

$$1+7x_1=\sqrt{3} \text{ and } x_1=0{,}1045$$

and x_2 from the equation:

$$-1+7x_2+14x_2^2=0$$

or

$$x_2=-\frac{1}{4}+\sqrt{+\frac{1}{14}}$$

$$4x_2=-1+\sqrt{\frac{15}{7}} \text{ and } x_2=0{,}116$$

And finally, let us take a numerical example, more in agreement with those which occur in the cases of minimum plaitpoint temperature studied experimentally. Let $n=1{,}5$, $a_1=1$, $a_2=1{,}45$, so that $T_{k_2}<T_{k_1}$. Let further $a_{12}=1{,}1$. Then x_1 is found from the equation:

$$0{,}1+0{,}25\,x=\sqrt{0{,}12}=0{,}3435\ldots.$$

$$x_1=0{,}974$$

and x_2 from the equation:

$$-0{,}15 + 0{,}25x + \frac{1}{4}\, 0{,}25\, x^2 = 0$$

or x_1 nearly equal to 0,5.

Here we very clearly get back the first case.

The intermediate case would require that x_1 should be equal to x_2. If we wish to direct our attention to other particularities of the intermediate case, we observe: 1. that then there is only one point of intersection for $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dvdx} = 0$ at every temperature; 2. that then at the double point of $\frac{dp}{dv} = 0$ one of the branches must have a tangent parallel to the X-axis; and so, the two values of $\frac{dv}{dx}$ for that double point being given by the equation:

$$\frac{d^3p}{dv^3}\left(\frac{dv}{dx}\right)^2 + 2\,\frac{d^3p}{dv^2dx}\left(\frac{dv}{dx}\right) + \frac{d^3p}{dvdx^2} = 0$$

$\frac{d^3p}{dvdx^2}$ is again equal to zero (see page 195). The curve $\frac{d^2p}{dvdx} = 0$ now does not pass through the double point either with its descending, nor with its ascending branch, but has there minimum volume. At lower temperature the vapour branch of $\frac{dp}{dv} = 0$ is cut in a point with somewhat lower value of x, and at higher temperature the liquid branch of the righthand branch is intersected with slightly higher value of x. Just at the temperature of the double point $\frac{d^2p}{dvdx} = 0$ touches with a tangent parallel to the X-axis.

If more in general, we wish to determine what the ratio of $\frac{\left(\frac{da}{dx}\right)^2}{a\frac{d^2a}{dx^2}} = m$ is at that value of x for which $\frac{a_x}{b_x}$ has minimum value, we may take the following course. From:

$$b\frac{da}{dx} = a\frac{db}{dx}$$

we derive:

$$[1 + (n-1)\,x]\,[B + Cx] = \frac{n-1}{2}\,(A + 2Bx + Cx^2)$$

or

$$x^2+\frac{2}{n-1}x+\frac{\frac{2}{n-1}B-A}{C}=0$$

and so

$$x=-\frac{1}{n-1}+\sqrt{\left[\frac{1}{(n-1)}-\frac{B}{C}\right]^2+\frac{AC-B^2}{C^2}}$$

From $\left(\frac{da}{dx}\right)^2=ma\frac{d^2a}{dx^2}$ we derive:

$$(2-m)(B+Cx)^2=m(AC-C^2)$$

or

$$x+\frac{B}{C}=\sqrt{\frac{m}{2-m}\frac{AC-B^2}{C^2}}$$

By equating the two values of x thus obtained, we find the equation:

$$\frac{B}{C}-\frac{1}{n-1}+\sqrt{\left[\frac{1}{(n-1)^2}-\frac{B}{C}\right]^2+\frac{AC-B^2}{C^2}}=+\sqrt{\frac{m}{2-m}\frac{AC-B^2}{C^2}}$$

from which follows:

$$\frac{AC-B^2}{C^2}=+2\left[\frac{1}{n-1}-\frac{B}{C}\right]\sqrt{\frac{m}{2-m}\frac{AC-B^3}{C^2}}+\frac{m}{2-m}\frac{AC-B^2}{C^2}$$

or

$$\frac{1-m}{2-m}\sqrt{\frac{AC-B^2}{C^2}}=\left[\frac{1}{n-1}-\frac{B}{C}\right]\sqrt{\frac{m}{2-m}}$$

or

$$\frac{1-m}{\sqrt{m(2-m)}}\sqrt{\frac{AC-B^2}{C^2}}=\frac{1}{n-1}-\frac{1}{\frac{a_2-a_{12}}{a_{12}-a_1}-1}=\frac{\frac{a_2-a_{12}}{a_{12}-a_1}-n}{(n-1)\left(\frac{a_2-a_{12}}{a_{12}-a_2}-1\right)}$$

or

$$\frac{1-m}{\sqrt{m(2-m)}}\frac{\sqrt{(a_1a_2-a_{12}^2)}}{a_{12}-a_1}=\frac{\frac{a_2-a_{12}}{a_{12}-a_1}-n}{n-1}$$

In particular it appears that $m=1$, if $\frac{a_2-a_{12}}{a_{12}-a_1}=n$; and if $\frac{a_2-a_{12}}{a_{12}-a_1}$ should be $\gtrless n$, then $m\lessgtr 1$, at least if $a_{12}>a_1$

If m is known for certain value of x, the decrease or increase of m may be derived from the equation:

$$(2-m)\,a=\text{constant},$$

which constant is equal to zero, if $a_1a_2=a_{12}^2$, and has else the sign of $a_1a_2-a_{12}^2$.