

*Citation:*

Kohnstamm, Ph., The shape of an empiric isothermal of a binary mixture, in:  
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By the three figures 16, 18 and 19, the fact is made intelligible, that sensation is lost towards the mid-ventral, not towards the mid-dorsal line. For this fact again the contrast between central and marginal areas of the dermatoma is necessary. Only by a quite separate series of experiments however, concerning sensibility in the middle of the dermatomata, (on the spot where the central area possesses a minimum of innervation) can it be made clear where the top of the insensible area must be situated, and in what manner is caused the interruption in the analgetic zone when two roots are sectioned.

**Physics.** — Dr. PH. A. KOHNSTAMM on: "*The shape of an empiric isothermal of a binary mixture*" (Communicated by Prof. J. D. VAN DER WAALS).

In § 8—§ 10 of my thesis for the doctorate I have discussed the shape of the empiric<sup>1)</sup> isothermal of a binary mixture. Without writing it down, I start there<sup>2)</sup> from the equation:

$$v = v_{vl} + v_d$$

where  $v_{vl}$  and  $v_d$  represent the actually measured volumes of liquid and vapour, and  $v$  the total volume. If we assume that we have to deal with a molecular quantity,  $v$  is at the same time the molecular volume of the mixture;  $v_{vl}$  and  $v_d$ , however, are no molecular volumes. Now I have shown, that the shape of the course of  $v$  as function of  $p$ , so also the shape of the empiric isothermal cannot differ sensibly

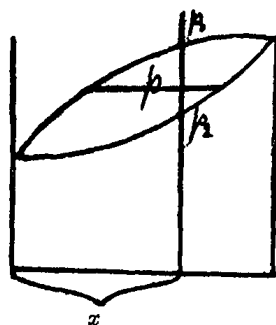


Fig 1.

from the shape of the course of  $v_d$  and after having drawn up a formula for  $v_d$ , I derive by differentiating this formula the shape of the empiric isothermal.

Perhaps we can arrive at this fundamental formula in a simpler way by not starting from the really measured vapour- and liquid volumes, but from the molecular volumes. We have then (see fig. 1):

$$v = \frac{x_2 - x'}{x_2 - x_1} v_{vl} + \frac{x' - x_1}{x_2 - x_1} v_d$$

<sup>1)</sup> I speak there of "derived" isothermal. The name chosen here is perhaps clearer.  
<sup>2)</sup> p. 141.

Here  $v$  is the same quantity as above;  $v_{vl}$  and  $v_d$ , however, are now the molecular liquid and vapour volumes;  $x'$ ,  $x_1$  and  $x_2$  are respectively the composition of mixture, liquid and vapour. We may write this equation:

$$v = v_{vl} + \frac{x' - x_1}{x_2 - x_1} (v_d - v_{vl}).$$

Here we must not neglect the second term with regard to the first, as the factor  $x' - x_1$  approaches 0, but in the second term we may neglect  $v_{vl}$  with respect to  $v_d$  and put for the latter  $\frac{MRT}{p}$ . By differentiation we get now:

$$dv = dv_{vl} + d \left( \frac{MRT}{p} \frac{x' - x_1}{x_2 - x_1} \right)$$

or, if we take the molecular liquid volume as invariable:

$$dv = d \left( \frac{MRT}{p} \frac{x' - x_1}{x_2 - x_1} \right)$$

and so proceeding in this way we arrive also at the general formula for the shape of the empiric isothermal given on p. 140 of my thesis.

Let us apply this formula in the case that the  $p_{x_1}$  line is a straight one, what comes to about the same thing as equal critical pressure for the two components.<sup>1)</sup>

In this case the  $p_{x_2}$  line is a hyperbola<sup>2)</sup>, so if  $p_A$  and  $p_B$ <sup>3)</sup> represent the vapour-tension of the components:

$$p = p_A(1 - x_1) + p_B x_1$$

and

$$p = \frac{p_A p_B}{p_B(1 - x_2) + p_A x_2}$$

If we now take  $p_1$  and  $p_2$  for the greatest and the smallest co-existing pressure which can occur with the composition  $x'$ , so

1) See Zeitschrift für phys. Chemie 36, p. 52.

2) VAN DER WAALS. Proc. IX p. 172.

3) We shall always assume  $p_B > p_A$ .

the pressure when the whole is vapour or the whole is liquid, we get also:

$$p_1 = p_A(1 - x') + p_B x'$$

$$p_2 = \frac{p_A p_B}{p_B(1 - x') + p_A x'}$$

If we substitute these values in our differential equation, we find:

$$(p_B - p)^2 (p - p_A)^2 \frac{dv}{dp} = -v_2 p_2 [(p_B - p)(p_1 - p_A) - (p_1 - p)(p - p_A)].$$

So we find that  $\frac{dv}{dp}$  is always  $< 0$ , as it ought to be, for

$$p_B - p > p_1 - p \text{ and } p_1 - p_A > p - p_A.$$

For the second differential coefficient we get

$$(p_B - p)^2 (p - p_A)^2 \frac{d^2v}{dp^2} = \frac{2v_2 p_2}{(p_B - p)(p - p_A)} \times \\ \times [(p_A + p_B - 2p)(p_B - p)(p_1 - p_A) + (p - p_A)^2 (p_1 - p)].$$

Now  $\frac{d^2p}{dv^2} = - \left(\frac{dp}{dv}\right)^3 \frac{d^2v}{dp^2}$  and as  $\frac{dp}{dv}$  is always negative  $\frac{d^2p}{dv^2}$  has the same sign as  $\frac{d^2v}{dp^2}$ .

Hence it is clear, that when  $2p < p_A + p_B$ , so  $x < 1/2$ , the convex side of the curve is always turned downward (fig. 2 I). If on the other hand  $x > 1/2$ , then the whole factor is negative for  $p = p_1$ ; it is therefore clear that on the side of the greatest pressure the empiric isothermal for those mixtures must begin with having its convex side turned upwards. But there can be but one inflection point, if any. For:

$$F(p) = (p_A + p_B - 2p)(p_B - p)(p_1 - p_A) + (p - p_A)^2 (p_1 - p)$$

$$F'(p) = -3[(p_1 - p)^2 + (p_1 - p_2)(p_A + p_B - p)]$$

$F'(p)$  is therefore always negative; the further we therefore get from  $p_1$ , in other words the smaller  $p$  becomes, the greater becomes  $F'(p)$ . So if the isothermal is first concave, it can become convex further on, but it cannot be convex at a certain value of  $p$  and become concave at a smaller value.

Let us now examine for which mixtures the inflection point, which has entered the isothermal at  $x = \frac{1}{2}$ , has reached the other end and we accordingly pass from the case of fig. 2 II to that of fig. 2 III.

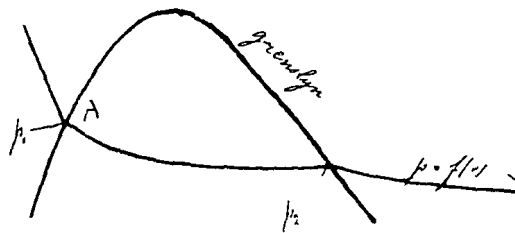


Fig. 2 I.

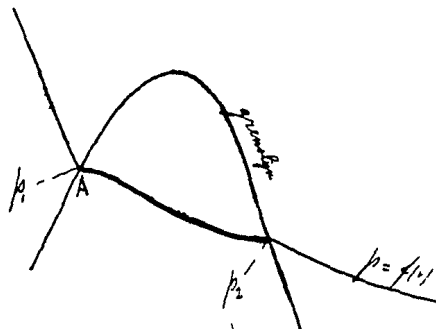


Fig. 2 II.



Fig. 2 III.

It is obvious that the  $p_2$  for this point must be greater than  $\frac{1}{2}(p_A + p_B)$ , for then the first term of  $F(p)$  is positive, so a fortiori the whole expression. In order to find the exact point where the inflection point makes its appearance we substitute in:

$$F(p) = 0 \text{ the value } p = p_2 = \frac{p_A p_B}{p_A + p_B - p_1}$$

and solve  $p_1$ .

This furnishes:

$$p_1 = p_B - \frac{1}{p_A^2 + p_B^2 + p_A p_B} [ \pm \sqrt{p_A^3 p_B^3 - p_A^3} ]$$

Now it is clear that only the positive sign is possible, else we could get a  $p_1 > p_B$ , and as  $p_1 = p_A + x'(p_B - p_A)$  we get for the composition of the mixture that separates case II from case III:

$${}_1x' = 1 - \frac{\sqrt{p_B^3 p_A^3 - p_A^3}}{p_B^3 - p_A^3}.$$

Therefore the inflection-point will appear for every mixture, for which  $1/2 < x' < {}_1x'$ . Hence we see that the region which remains for the entirely concave curve, depends only on  $p_A/p_B$ .

In order to examine this dependence more closely, I have inserted in my thesis a needlessly elaborate calculation, which I shall not repeat here, the more, because it contains an error of calculation which I could not correct anymore. In the formula for  $\varphi''(y)$  on pag. 153  $9y^6$  ought to be substituted for  $10y^6$ . In consequence of this fig. 16 is not quite accurate. Therefore I should like to substitute what follows for the passage of my thesis which applies to this.

If we introduce in the formula  ${}_1x'$ :

$$y = \frac{p_A}{p_B}$$

we get:

$${}_1x' = \frac{1 - \sqrt{y^3}}{1 - y^3} = \frac{1 - \sqrt{y^3}}{(1 - \sqrt{y^3})(1 + \sqrt{y^3})} = \frac{1}{1 + \sqrt{y^3}}$$

$$\frac{d{}_1x'}{dy} = - \frac{3}{2} \frac{\sqrt{y}}{(1 + \sqrt{y^3})^2}$$

From this formula follows that for  $y = 0$ , so  $p_A = 0$ ,  ${}_1x' = 1$ . So isothermals which are concave throughout their course do not exist. As

soon, however, as  $p_A$  gets a value, they appear and the region of the isothermals with an inflection-point decreases regularly, as appears from the differential coefficient which is always negative, till for  $y = 1$ , so  $p_A = p_B$ ,  $x' = 1/2$ . At this limit the region for isothermals with an inflection-point has quite disappeared, and only entirely concave or entirely convex isothermals exist, but it is clear that for  $p_A = p_B$  also all other pressures become equal in this case.

In order to solve the problem to its full extent, we have still to examine, at what pressure the inflection-point eventually appears in the derived isothermal. It is clear that in order to find that dependence between  $p$  and  $x'$ , we have simply to substitute in the equation  $F(p) = 0$ :

$$p_1 = p_A + x'(p_B - p_A).$$

In order to determine the pressure at the inflection-point belonging to the mixture  $x'$  we get therefore:

$$(p_A + p_B - 2p)(p_B - p)x'(p_B - p_A) + (p_1 - p_A)^3 [p_A - p + x'(p_B - p_A)] = 0$$

$$x' = \frac{(p - p_A)^3}{(p_B - p_A)[(p_A + p_B - 2p)(p_B - p) + (p - p_A)^2]}$$

The condition that  $x'$  must be positive, is fulfilled, for:

$$(p_A + p_B - p)(p_B - p) + (p - p_A)^2 = (p_B + p_A - 2p)^2 + (p - p_A)(p_B - p)$$

So we have for the locus of the inflection-points a cubic curve of which we saw before that in the heterogeneous region it cuts all the coordinates but once.

We get further:

$$(p_B - p_A) \frac{dx'}{dp} = \frac{3(p - p_A)^2 (p_B - p)^2}{[(p_A + p_B - 2p)(p_B - p) + (p - p_A)^2]^2}$$

so  $\frac{dp}{dx'}$  is always  $> 0$ , and has in the beginning at  $2p = p_A + p_B$

the value  $\frac{p_B - p_A}{3}$ , which disappears for  $p_A = p_B$ , as it ought to do.

And finally we get:

$$\frac{3}{(p_B - p_A)^3} \frac{d^2 p}{dx'^2} = \frac{dp}{dx'} \frac{2(2p - p_A - p_B)}{(p - p_A)^3 (p_B - p)^3} \times$$

$$\times [(p_B + p_A - 2p)^2 + (p - p_A)(p_B - p)]$$

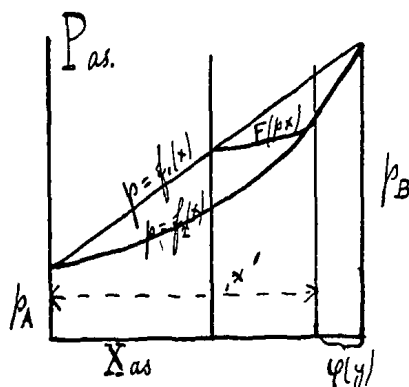


Fig. 3.

so that the locus is everywhere convex in the heterogeneous region with an inflection-point at the beginning, and we get a curve as drawn in fig. 3, which clearly indicates the different possibilities for the empiric isothermal. The point where the locus cuts the curve  $p = f(x_2)$  is of course determined by the formula for  $x'$ .

**Mathematics.** — “Factorisation of large numbers”, by Mr. F. J. VAES, Mechanical Engineer at Rotterdam. (Communicated by Prof. P. H. SCHOUTE).

#### Introduction.

The history of the research about the divisibility of large numbers is very simple.

ERATOSTHENES (275—194 b. C.) is said to have invented the method of the sieve (determination of the prime numbers under a given limit by removing from the series of odd numbers those divisible by 3, 5, 7, etc.).

In 1643 FERMAT decomposed a number proposed to him by MERSENNE. In a letter dated “Toulouse le 7 Avril 1643” we find: “Vous me demandez si le nombre 100895598169 est premier ou non, et une méthode pour découvrir, dans l’espace d’un jour, s’il est premier ou composé. A cette question, je réponds que le nombre est composé et se fait du produit de ces deux: 898423 et 112303, qui sont premiers.”

The method of FERMAT has never been published<sup>1)</sup>.

<sup>1)</sup> In 1640 FERMAT believed  $2^{2^n} + 1$  gives prime numbers for all values of  $n$ . Afterwards EULER found that  $2^{2^5} + 1$  (a number of ten figures) is the product of 641 and 6700417. The author is inclined to ask: If in 1643 FERMAT really could factorise