

Citation:

J.J. van Laar, The molecular rise of the lower critical temperature of a binary mixture of normal components, in:

KNAW, Proceedings, 8 I, 1905, Amsterdam, 1905, pp. 144-152

ordinary pressure, b.p. at 23 mm. 82° , m.p. $-19,5^\circ$, $n_D^{25} = 1,40526$.

Ethylmethylketonecyanohydrin, colourless liquid with a faint ketone-like odour. Sp. gr. at $18,5^\circ$ 0,9324. Boiling point at 20,5 m.m. 91° . Does not solidify in a paste of solid carbon dioxide and acetone. $n_D^{12,5} = 1,41775$.

Diethylketonecyanohydrin, colourless, a somewhat stronger odour than the former nitrile. Sp. gr. at $18,5^\circ$ 0,9300. Boiling point at 18,5 m.m. $97,5^\circ$, does not solidify in a paste of carbon dioxide and acetone. $n_D^{18} = 1,42585$.

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Chemistry. — “*The molecular rise of the lower critical temperature of a binary mixture of normal components.*” By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In the “*Chemisch Weekblad*” of April 8th 1905 (II, N^o. 14) I derived an expression for the so-called molecular rise of the lower critical temperature, viz:

$$\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = 2\sqrt{\theta\psi} - (1 + \psi),$$

in which θ represents the ratio of the two critical temperatures $\frac{T_2}{T_1}$ and ψ the ratio $\frac{b_2}{b_1}$.

In this I started from the approximate assumption, that the critical temperature of a binary mixture may be represented by the simple expression

$$fRT_x = \frac{a_x}{b_x}.$$

The formula found is at any rate more accurate than that of VAN 'T HOFF, according to which the molecular rise would be *constant* (Chem. Weekbl. of Nov. 21st 1903 (I, N^o. 8)), and I adduced a few examples to show that the expression found by me represents the experimental results of CENTNERSZWER¹⁾ very accurately — provided the molecular weight of the solvent SO_2 is *doubled*.

BÜCHNER in his thesis for the doctorate²⁾ came to pretty much the same result with regard to CO_2 as solvent. He, too, had to double the molecular weight of CO_2 in order to get sufficient concordance

¹⁾ Z. f. Ph. Ch. **46**, 427—501 (1903).

²⁾ June 1905, p. 125—130.

with my formula for the substances examined by him (except for naphthaline and chloro-nitrobenzol).

Now BÜCHNER thinks the assumption of a $(\text{CO}_2)_2$ bimolecular at the critical temperature very doubtful, and KUENEN too recently called my attention to the fact that according to *his* measurements ¹⁾ of the vapour pressures of liquid CO_2 at different temperatures, the vapour pressure factor f presents a perfectly *normal course*, in opposition to what the measurements of REGNAULT at 0° and 10° C., and those of CAILLETET at -50° to -80° give for it ²⁾.

Nor has the assumption of a bimolecular $(\text{SO}_2)_2$ really any foundation.

Now, just recently ³⁾ I have examined the accurate course of the plaitpoint curves for binary mixtures of normal substances, so that it is now possible to derive a more accurate expression than the above, in which the critical (plaitpoint) temperatures of the mixture were identified by approximation with the temperatures of the coincidence of the inflection points of the successive ψ -curves. That this was, of course, not true, was sufficiently known, and that the difference can be considerable has been more than once emphatically stated by VAN DER WAALS. One look at the plate adjoined to my paper mentioned above shows at once how perfectly different the course of the plaitpoint line — also at the beginning, at T_1 — can be.

It will appear from the following derivation that the values found from the above approximated formula should be *more than doubled* in many cases.

KESOM has already derived ⁴⁾ a general expression for the molecular rise $\frac{1}{T_1} \left(\frac{dT_x}{dv} \right)_0$, but as he used the law of the corresponding states, and as in his final expression, viz.

$$\frac{1}{T_1} \left(\frac{dT_x}{dv} \right)_0 = \alpha - \frac{\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau} \right) \right\}^2}{C_4 \frac{\partial^2 \pi}{\partial \omega \partial \tau}},$$

there occur all kinds of quantities, which have either to be determined experimentally, or have to be calculated from the equation of state, I preferred to derive the required expression directly from the relation found by me for the course of the plaitpoint line for mixtures of *normal* substances.

¹⁾ Phil. Mag. **61**, Vol. 2.

²⁾ See my paper in the Arch. Teyler (2) **9**, 3^e Partie, p. 54.

³⁾ These Proc. of June 1905, p. 33 et. seq.

⁴⁾ These Proc.; Comm. Leiden N^o. 75, p. 6.

2. This relation was the following: ¹⁾

$$x(1-x)\theta^3 \left[(1-2x)v - 3x(1-x)\beta \right] + \sqrt{a(v-b)^2} \left[3x(1-x)\theta(\theta - \beta\sqrt{a}) + \right. \\ \left. + a(v-b)(v-3b) \right] = 0 \dots \dots \dots (1)$$

In this $\theta = \alpha v - \beta\sqrt{a} = (b_1\sqrt{a_2} - b_2\sqrt{a_1}) + a(v-b)$; $\alpha = \sqrt{a_2} - \sqrt{a_1}$ and $\beta = b_2 - b_1$.

In the derivation it was only assumed that $\frac{a_{12}}{a} = \sqrt{a_1 a_2}$ might be put, so that the quantity a may be represented by $\left\{ (1-x)\sqrt{a_1} + x\sqrt{a_2} \right\}^2$. This is the *only* simplifying assumption.

We now proceed to make the above given expression homogeneous in the way of p. 35 et. seq. of my last paper. (These Proc. June 1905). By considering only the case $b_1 = b_2$ more closely (which was sufficient for our purpose), we simplified this expression considerably in the paper mentioned, but now we shall put the quantity β not $= 0$, so that a new variable quantity must be introduced.

Let us put as before:

$$\frac{\sqrt{a_1}}{\alpha} = \varphi \quad ; \quad \frac{b_1}{v} = \omega.$$

But now also:

$$\frac{b_2 - b_1}{v} = \frac{\beta}{v} = n\omega,$$

then we get:

$$\frac{\sqrt{a}}{\alpha} = \varphi + x \quad ; \quad \frac{b}{v} = \omega(1 + nx).$$

Hence after division by $x(1-x)\alpha^3 v^4$ (1) passes successively into:

$$\left(1 - \frac{\beta\sqrt{a}}{v\alpha} \right)^3 \left[(1-2x) - 3x(1-x)\frac{\beta}{v} \right] + \\ + \frac{\sqrt{a}}{\alpha} \left(1 - \frac{b}{v} \right)^2 \left[3 \left(1 - \frac{\beta\sqrt{a}}{v\alpha} \right) \left(1 - 2\frac{\beta\sqrt{a}}{v\alpha} \right) + \frac{a}{\alpha^2} \left(1 - \frac{b}{v} \right) \left(1 - 3\frac{b}{v} \right) \right] = 0,$$

and

$$\left(1 - n\omega(\varphi + x) \right)^3 \left[(1-2x) - 3x(1-x)n\omega \right] + \\ + (\varphi + x) \left(1 - \omega(1 + nx) \right)^2 \left[3 \left(1 - n\omega(\varphi + x) \right) \left(1 - 2n\omega(\varphi + x) \right) + \right. \\ \left. + \frac{(\varphi + x)^2 \left(1 - \omega(1 + nx) \right) \left(1 - 3\omega(1 + nx) \right)}{x(1-x)} \right] = 0.$$

¹⁾ l. c. p. 33, formula (2). Cf. for the derivation: These Proc. of April 1905.

For small values of x this becomes:

$$(1-n\omega\varphi)^3 + \varphi(1-\omega)^2 \left[3(1-n\omega\varphi)(1-2n\omega\varphi) + \frac{\varphi^2(1-\omega)(1-3\omega(1+n\varphi))}{x} \right] = 0.$$

As viz. ω approaches then to $1/3$, $1-\omega(1+n\varphi)$ is replaced by $1-\omega$, but $1-3\omega(1+n\varphi)$ has been retained. Further introduction of $\omega = 1/3$ yields:

$$(1-1/3 n\varphi)^3 + 1/3 \varphi \left[3(1-1/3 n\varphi)(1-2/3 n\varphi) + \frac{2/3 \varphi^2 (1-3\omega(1+n\varphi))}{x} \right] = 0,$$

from which follows:

$$\frac{2/3 \varphi^2 (1-3\omega(1+n\varphi))}{x} = - \frac{(1-1/3 n\varphi)^3}{1/3 \varphi} - 3(1-1/3 n\varphi)(1-2/3 n\varphi),$$

or, after division by $-2/3 \varphi^2$:

$$\frac{3\omega - 1}{x} + 3\omega n = \frac{(1-1/3 n\varphi)^3}{3/27 \varphi^3} + \frac{3}{2/3 \varphi^2} (1-1/3 n\varphi)(1-2/3 n\varphi).$$

If we now put $\omega = 1/3(1 + \sigma)$, we get:

$$\frac{\sigma}{x} = \frac{(1-1/3 n\varphi)^3}{3/27 \varphi^3} + \frac{9}{2\varphi^2} (1-1/3 n\varphi)(1-2/3 n\varphi) - n, \quad (1a)$$

as we may put $3\omega n = n$. Thus we have separated in the first member the only term in which numerator and denominator approach to 0, whereas: in the second member all infinitely small terms have been neglected by the side of those of finite value.

Formula (1a) indicates, in what way the volume v varies in the neighbourhood of $x=0$ with x , when we viz. vary the temperature in such a way that we remain in a plaitpoint.

3. Let us now introduce the temperature.

For this the relation holds: ¹⁾

$$RT = \frac{2}{v^3} \left[x(1-x)\theta^2 + a(v-b)^2 \right]. \quad \dots \quad (2)$$

Here θ is again $= \alpha v - \beta\sqrt{a}$. Reduction gives successively:

$$RT = \frac{2\alpha^2}{v} \left[x(1-x) \left(1 - \frac{\beta\sqrt{a}}{v} \right)^2 + \frac{a}{\alpha^2} \left(1 - \frac{b}{v} \right)^2 \right],$$

and

$$RT = \frac{2\alpha^2}{b_1} \omega \left[x(1-x) \left(1 - n\omega(\varphi+x) \right)^2 + (\varphi+x)^2 \left(1 - \omega(1+n\varphi) \right)^2 \right],$$

¹⁾ l. c. p. 33.

as $\frac{1}{v} = \frac{\omega}{b_1}$, while $\frac{\beta}{v}$ and $\frac{\sqrt{a}}{a}$ are replaced by their values (see § 2).

Now:

$$RT_1 = \frac{8 a_1}{27 b_1} = \frac{8 a^2 \varphi^2}{27 b_1},$$

hence:

$$T = {}^{27/4} T_1 \frac{\omega}{\varphi^2} \left[x(1-x) \left(1 - n\omega(\varphi+x) \right)^2 + (\varphi+x)^2 \left(1 - \omega(1+nx) \right)^2 \right].$$

If we now put $T = T_1(1+\tau)$, $\omega = 1/3(1+\sigma)$, this becomes for small values of x :

$$1 + \tau = {}^{9/4} \frac{1+\sigma}{\varphi^2} \left[x \left(1 - 1/3 n\varphi \right)^2 + \varphi^2 \left(1 + 2 \frac{x}{\varphi} \right) (1-\omega)^2 \left(1 - 2 \frac{\omega n x}{1-\omega} \right) \right],$$

in the second member of which only terms of finite value and those of the order x remain. We draw attention to the fact that according to (1a) σ is of the order x . Further substitution of $\omega = 1/3(1+\sigma)$ yields:

$$1 + \tau = {}^{9/4} \frac{1+\sigma}{\varphi^2} \left[x \left(1 - 1/3 n\varphi \right)^2 + {}^{4/9} \varphi^2 \left(1 + 2 \frac{x}{\varphi} \right) (1-\sigma)(1-nx) \right],$$

as $1 - \omega = 2/3 - 1/3 \sigma = 2/3(1 - 1/2 \sigma)$, so $(1-\omega)^2 = 4/9(1-\sigma)$

The last expression becomes now:

$$1 + \tau = (1 + \sigma) \left[x \frac{(1 - 1/3 n\varphi)^2}{4/9 \varphi^2} + \left(1 + 2 \frac{x}{\varphi} - \sigma - nx \right) \right],$$

or if we neglect terms of higher order than the first:

$$1 + \tau = \left(x \frac{(1 - 1/3 n\varphi)^2}{4/9 \varphi^2} + 1 + 2 \frac{x}{\varphi} - \sigma - nx \right) + \sigma.$$

And now it proves, that the terms with σ vanish, so that we *do not want* the value of $\frac{\sigma}{x}$ from (1a) for the calculation of the limiting

value of the relation $\frac{\tau}{x}$ ¹⁾. For the sake of completeness we have,

however, calculated this value, as it may be of importance for some problems to know in what way v varies with x in the neighbourhood of the lower critical temperature (remaining on the plaitpoint curve).

¹⁾ This is, of course, in connection with the fact that at the critical temperature of the first component the spinodal line *touches* the line $x=0$, and — as the spinodal curve is *vertical* at that place (i.e. // to the v -axis) for very small values of x — a change of v will therefore only bring about a change of temperature (and so also of the plaitpoint temperature) infinitely smaller than the change of temperature, brought about by a change of x .

So we find finally:

$$\frac{\tau}{x} = \frac{(1 - \frac{1}{3}\sqrt[3]{\varphi})^2}{\frac{1}{3}\varphi^2} + \frac{2}{\varphi} - n, \dots \dots \dots (2a)$$

which is the required expression, by means of which the limiting value of $\frac{\tau}{x}$ at $x=0$ may be calculated for every given value of φ and n .

4. Now it remains only to express the relations found in the ordinary variables.

These are viz. (see § 1):

$$\frac{T_2}{T_1} = \theta; \quad \frac{b_2}{b_1} = \psi.$$

Now the quantity φ introduced by us in § 2 and 3 is represented by :

$$\varphi = \frac{\sqrt{a_1}}{\alpha} = \frac{\sqrt{a_1}}{\sqrt{a_2} - \sqrt{a_1}} = \frac{\sqrt{b_1 T_1}}{\sqrt{b_2 T_2} - \sqrt{b_1 T_1}} = \frac{1}{\sqrt{\theta\psi} - 1},$$

while n is given by:

$$n = \frac{\beta}{v} : \omega = \frac{\beta}{b_1} = \frac{b_2 - b_1}{b_1} = \psi - 1.$$

Formula (2a) passes therefore into:

$$\frac{\tau}{x} = \frac{\left(1 - \frac{1}{3} \frac{\psi - 1}{\sqrt{\theta\psi} - 1}\right)^2}{\frac{1}{3}(\sqrt{\theta\psi} - 1)^{-2}} + 2(\sqrt{\theta\psi} - 1) - (\psi - 1),$$

or

$$\frac{\tau}{x} = \frac{1}{4} \left[(\sqrt{\theta\psi} - 1) - \frac{1}{3}(\psi - 1) \right]^2 + 2\sqrt{\theta\psi} - (1 + \psi),$$

or finally, as $\tau = \frac{T - T_1}{T_1}$:

$$\frac{T - T_1}{T_1 x} = \frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = 2\sqrt{\theta\psi} - (1 + \psi) + \frac{1}{4} \left\{ (\sqrt{\theta\psi} - 1) - \frac{1}{3}(\psi - 1) \right\}^2. \quad (3)$$

The original expression, derived on the assumption that fRT_x may be approximately represented by $\frac{a_x}{b_x}$, must therefore (see § 1) be completed by a term:

$$\frac{1}{4} \left\{ (\sqrt{\theta\psi} - 1) - \frac{1}{3}(\psi - 1) \right\}^2.$$

This is the correction which must be applied, and it is easy to see, that it can considerably modify the original approximated expression.

Let us now introduce the ratio of the *critical pressures* of the two components, viz.

$$\frac{p_2}{p_1} = \pi.$$

Evidently the relation $\psi = \frac{\theta}{\pi}$ exists, which changes (3) into:

$$\begin{aligned} \frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 &= 2\theta \sqrt{\frac{1}{\pi}} - \left(1 + \frac{\theta}{\pi} \right) + \frac{3}{4} \left\{ \left(\theta \sqrt{\frac{1}{\pi}} - 1 \right) - \frac{1}{3} \left(\frac{\theta}{\pi} - 1 \right) \right\}^2 \\ &= 2\theta \sqrt{\frac{1}{\pi}} - \left(1 + \frac{\theta}{\pi} \right) + \left\{ \frac{3}{2} \theta \sqrt{\frac{1}{\pi}} \left(1 - \frac{1}{3} \sqrt{\frac{1}{\pi}} \right) - 1 \right\}^2 \\ &= 2\theta \sqrt{\frac{1}{\pi}} - \frac{\theta}{\pi} + \frac{\theta^2}{\pi} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2 - 2\theta \sqrt{\frac{1}{\pi}} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right) \\ &= -\theta \sqrt{\frac{1}{\pi}} + \frac{\theta^2}{\pi} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2, \end{aligned}$$

or

$$\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = \Delta = \theta \sqrt{\frac{1}{\pi}} \left\{ \theta \sqrt{\frac{1}{\pi}} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2 - 1 \right\}, \quad \dots \quad (3a)$$

being the final expression for the molecular rise of the critical temperature on the side of the lower critical temperature.

Now a case of frequent occurrence is, that the *critical pressures* of the two components *differ little*. If these pressures are the same, $\pi = 1$, and (3a) becomes:

$$\Delta = \theta(\theta - 1), \quad \dots \quad (3b)$$

whereas the former, approximated expression (see § 1) for this case would yield: (ψ is then $= \theta$) $\Delta = \theta - 1 = \frac{T_2 - T_1}{T_1}$.

So for the case $\pi = 1$ the former expression must be multiplied by $\theta = \frac{T_2}{T_1}$, in order to yield the correct expression.

A few instances will prove that it is *no longer necessary* now to *double* the molecular formula of the solvent.

As π is near 1 in most cases, and the formula (3b) varies very little with changes in the value of π , we shall use the formula $\Delta = \theta(\theta - 1)$ for convenience, the sooner as the values of T_2 (the critical temperature of the dissolved substance) are all unknown, and can be given only by approximation.

Let us first take the four substances which CENTNERSZWER's experiments induced me to calculate in the "Chemisch Weekbl." (l.c. p. 227—228). We shall now calculate the values of T_2 from the values

of Δ found experimentally, and see if the values found in this way are about the double of those of the (absolute) melting temperatures ¹⁾.

	Δ found	θ calculated	T_2 calculated	Melting point	Quotient
Anthraquinone	3,58	2,46	1060°	560°	1,9
Resorcine	2,36	2,12	910°	480°	1,9
Campher	1,53	1,83	790°	450°	1,8
Naphtaline	1,45	1,80	770°	350°	2,2

1,95 average

The values of T_2 are calculated from $T_2 = \theta \times T_1$, where $T_1 = 430^\circ$, being the critical temperature of the solvent SO_2 .

So we find really a value in the neighbourhood of 2 for the ratio between critical temperature and melting temperature. We call attention to the fact that 2,0 is found as mean value for this ratio for bi- and tri-atomic substances; for multi-atomic-substances this mean value rises to 2,3. There are, however, substances, where the ratio mentioned falls to 1,4 or rises to 3,5. The values calculated by means of the formula $\Delta = \theta(\theta - 1)$ are therefore in any case not in contradiction with what experience teaches us.

In the second place we shall consider in the same way five substances, which have been examined by BÜCHNER only recently. (See Thesis for the doctorate, p. 128—129). The solvent was CO_2 , of which $T_1 = 304^\circ$.

	Δ found	θ calculated	T_2 calculated	Melting point	Quotient
Naphtaline	2,39	2,13	650°	350°	1,9 (in the preceding table 2,2)
$\text{C}_6\text{H}_4\text{Cl}_2$	2,65	2,20	670°	325°	2,1
$\text{C}_6\text{H}_4\text{Br}_2$	2,87	2,27	690°	360°	1,9
CHBr_3	2,32	2,10	640°	280°	2,3
$o\text{-C}_6\text{H}_4\text{ClNO}_2$	3,87	2,53	770°	305°	2,5

2,14 average

¹⁾ See my paper in the *BOLTZMANN-Festschrift* (1904), p. 322—324.

Here too, we find therefore values for the ratio in question, which are not in contradiction with its empirical value.

Doubling the molecular formula of the solvent is therefore no longer necessary, and we may, therefore, say that the formula found by us (3a) or approximated (3b) represents the molecular rise of the lower critical temperature very satisfactorily.

Finally I may point out, that the experiments — of CENTNERSZWER as well as those of BÜCHNER — are not so accurate that the difference between 1,9 and 2,2 for naphthaline is of much importance.

The reason of this is easy to see; it is exceedingly difficult to observe the critical *plaitpoint* temperature accurately. For it is required for this purpose, that the corresponding *volume* be accurately known beforehand, and that the volume of the tubes used be chosen accordingly. Else, of course, not the plaitpoint temperature sought, is found, but another temperature, situated more or less in its neighbourhood. And this too can be a source of inaccuracies¹⁾.

From all that precedes it sufficiently appears that VAN 'T HOFF's assertion that the value of Δ is constant, and equal to about 3, is altogether incorrect. For the value of Δ is quite determined by the ratio θ of the critical temperatures.

If θ should happen to be in the neighbourhood of 2,3, then $\Delta = \theta(\theta - 1)$ will lie in the neighbourhood of $2,3 \times 1,3 = 3$. And now it has been very misleading, that really for the examined substances the values of θ lie nearly all near 2,3. (For the five substances mentioned examined by BÜCHNER the mean value of θ is 2,25, for the substances investigated by CENTNERSZWER this is also the case). If $\theta = 3$, we should find about 6 for Δ , so this is twice as much! Hence there is no question of constancy.

¹⁾ Also CENTNERSZWER calls attention to this in his paper (Z. f. Ph. Ch. 46, p. 427—501 (1903). See specially p. 446, 459, 464—466, 469—470, 489—492 and 497—499. It appears from these passages, how much trouble he has taken to determine the exact "Füllungsgrad", and in this way to get as near as possible to the critical plaitpoint temperature. As the determination of the rise of the critical temperature was only of minor importance to BÜCHNER, the values given by him, cannot — as he himself states — lay claim to the accuracy reached by CENTNERSZWER.