

Citation:

Johannes Diderik van der Waals, The cooling of a current of gas by sudden change of pressure, in: KNAW, Proceedings, 2, 1899-1900, Amsterdam, 1900, pp. 379-389

The conic Q_2 lying in the plane Φ of C_2 belongs six times to the section of Σ and Φ .

Moreover as each bisecant of R_5 lying in Φ determines a conic Q_2 of Σ , this surface is of order $4 \times 2 + 6 \times 2 + 10 = 30$.

Through the point S_k of R_5 lying in Φ ten conics Q_2 of Σ_{30} , pass, viz. the four conics determined by the chords $S_k S_l$ and the conic Q_2 to be counted six times containing all the points S_k . So R_5 is a tenfold curve.

If C_2 breaks up into two right lines l and m intersecting each other in P the locus consists of the cubic surface Π_3 belonging to P and the surface Ψ_{27} formed by the conics Q_2 resting on l and m . And now according to 12. the curve R_5 is a ninefold curve of Ψ_{27} and according to 7. a single curve on Π_3 ; so in accordance with what was mentioned above it is a tenfold curve of $\Sigma_{30} \equiv \Psi_{27} + \Pi_3$.

As C_2 and R_5 have α points in common, we find in a similar way that the conics Q_2 which meet C_2 in two points not situated on R_5 form a surface of order $\frac{3}{2}(4-\alpha)(5-\alpha)$, where R_5 is a curve of multiplicity $\frac{1}{2}(4-\alpha)(5-\alpha)$, C_2 being a $(4-\alpha)$ -fold line.

14. We shall still determine the number of conics Q_2 resting on the α -conic C_2 , the β -conic D_2 and the γ -conic E_2 .

The surface Γ_3 of the conics Q_2 , cutting R_5 in P and P' , and C_2 have $(6-\alpha)$ points in common. So R_5 is a $(6-\alpha)$ -fold curve of the locus of the conic Q_2 , passing through P and meeting C_2 ; so this surface is of order $3(6-\alpha)$.

Of its sections with D_2 a number of $(6-\alpha)(6-\beta)$ are not situated on R_5 , which proves that R_5 is a $(6-\alpha)(6-\beta)$ -fold curve of the surface of the conics Q_2 resting on C_2 and D_2 ; so this latter surface is of order $3(6-\alpha)(6-\beta)$.

Consequently there are $(6-\alpha)(6-\beta)(6-\gamma)$ conics Q_2 , having a point in common with each of the conics C_2, D_2, E_2 .

In particular any three conics Q_2 are cut by one conic Q_2 only.

Physics. — “The cooling of a current of gas by sudden change of pressure.” By Prof. J. D. VAN DER WAALS.

If a gas stream under a constant high pressure is conducted through a tube, so wide that we may neglect the internal friction, and this stream is suddenly brought under a smaller pressure, either by means of a tap with a fine aperture, or, as in the experiments of Lord KELVIN and JOULE by means of a porous plug, the

temperature of the gas falls. For a small difference in pressure of the gas before the tap and the gas behind the tap the amount has been determined by the experiments of KELVIN and JOULE. They represent the cooling $T_1 - T_2$ for air in the empiric formula:

$$T_1 - T_2 = k \frac{p_1 - p_2}{T_1^2}.$$

By means of the equation of state we calculate for this cooling ¹⁾, again on the supposition that p_1 and p_2 are small:

$$T_1 - T_2 = \frac{2}{m} \frac{273}{c_p} \left(\frac{2a}{1 + \alpha t_1} - b \right) (p_1 - p_2).$$

In this formula p_1 and p_2 are expressed in atmospheres, m is the molecular weight, c_p the specific heat at a constant pressure for the gas in a rarefied state.

If in the equation of state a is a function of the temperature, and is to be represented by $a \frac{273}{T}$, we should find, if T_1 and T_2 do not differ much, and p_1 and p_2 are small:

$$T_1 - T_2 = \frac{2}{m} \frac{273}{c_p} \left[3a \left(\frac{273}{T_1} \right)^2 - b \right] (p_2 - p_1).$$

It is still doubtful, which of those two formulae better represents the observations of KELVIN and JOULE. It is remarkable how different a value we find for this cooling, as for everything which relates to quantities of heat, if a is a function of the temperature. The accurate knowledge of this process has of late proved to be more necessary than before, as LINDE has applied this process for obtaining very low temperatures and as in LINDE's apparatus this way of expansion is made use of to obtain liquid air.

Let us represent the energy per unity of weight of the gas under the pressure p_1 by ϵ_1 . Let the specific volume be v_1 and the temperature T_1 . For the gas under the pressure p_2 we represent these quantities by ϵ_2 , v_2 , T_2 . Then the process is represented by the formula:

$$\epsilon_1 + p_1 v_1 - p_2 v_2 = \epsilon_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

¹⁾ Die Continuität etc., IIte Auflage Seite 123.

$$\varepsilon_1 + p_1 v_1 = \varepsilon_2 + p_2 v_2$$

With the symbol $\chi = \varepsilon + pv$ chosen by GIBBS, we may represent the process shortly by

$$\chi_1 = \chi_2 .$$

The vis viva of the progressive motion may be neglected, if the velocity of the motion is small. Moreover the section of the tube before- and after the tap may be chosen in such a way, that the velocity may be considered as invariable. We may therefore represent by ε the thermodynamic energy of a gas, being in equilibrium.

From the equation: $\left(\frac{\partial \varepsilon}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p$ we find, if we assume as equation of state: $p = \frac{RT}{v-b} - \frac{af(T)}{v^2}$:

$$\varepsilon = \varphi(T) - \frac{a}{v} [f(T) - Tf'(T)] .$$

The meaning of $\varphi(T)$ we find from $c_v = \left(\frac{\partial \varepsilon}{\partial T}\right)_v$, from which follows:

$$c_v = \varphi'(T) + \frac{a}{v} Tf''(T) .$$

The meaning of $\varphi'(T)$ is therefore the value of the specific heat at $v = \infty$, which we shall represent by $c_{v=\infty}$. If we think the substance in a very rarefied state to consist of molecules, which do not change with the temperature, we may put $c_{v=\infty} = \varphi'(T) =$ constant and so $\varphi(T) = Tc_{v=\infty}$. The quantity ε is:

$$\varepsilon = Tc_{v=\infty} - \frac{a}{v} [f(T) - Tf'(T)] .$$

If we write:

$$pv = RT + RT \frac{b}{v-b} - \frac{a}{v} f(T) ,$$

the value of χ becomes as follows:

$$\chi = (c_{v=\infty} + R)T - \frac{a}{v} \left[2f(T) - Tf'(T) \right] + RT \frac{b}{v-b}$$

or

$$\chi = c_{p=0} T - \frac{a}{v} \left[2f(T) - Tf'(T) \right] + RT \frac{b}{v-b}.$$

Making use of this value of χ , we deduce from $\chi_1 = \chi_2$ the following formula:

$$c_p (T_1 - T_2) = \left\{ \frac{a}{v_1} \left[2f(T_1) - T_1 f'(T_1) \right] - \frac{RT_1 b}{v_1 - b} \right\} - \left\{ \frac{a}{v_2} \left[2f(T_2) - T_2 f'(T_2) \right] - \frac{RT_2 b}{v_2 - b} \right\}.$$

If we want to keep a and b at the value which they have in the equation of state, in which the pressure of one atmosphere is chosen as the unity of pressure and the volume which the unity of weight of the gas occupies under that pressure and at 0° as unity of volume, this last formula assumes the following form:

$$c_p (T_1 - T_2) = \frac{2}{m} 273 \left\{ \frac{a}{v_1} \left[2f(T_1) - T_1 f'(T_1) \right] - \frac{RT_1 b}{v_1 - b} \right\} - \frac{2}{m} 273 \left\{ \frac{a}{v_2} \left[2f(T_2) - T_2 f'(T_2) \right] - \frac{RT_2 b}{v_2 - b} \right\}.$$

Let us think v_2 so great that the quantities $\frac{a}{v_2}$ and $\frac{RT_2 b}{v_2 - b}$ or $\frac{(1+a)(1-b)(1+\alpha t_2)b}{v_2 - b}$ may be neglected, then the cooling is determined by the value which $\frac{a}{v_1} \left[2f(T_1) - T_1 f'(T_1) \right] - \frac{RT_1 b}{v_1 - b}$ possesses. If at given T_1 we make the value of v_1 pass through all the values from $v_1 = \infty$ to $v_1 = b$, and if we think T_1 chosen in such a way that:

$$a \left[2f(T_1) - T_1 f'(T_1) \right] > (1+a)(1-b)(1+\alpha t_1)b,$$

the value of the expression:

$$\frac{a}{v_1} \left[2f(T_1) - T_1 f'(T_1) \right] - \frac{RT_1 b}{v_1 - b}$$

will begin with zero; then this expression will obtain a positive value, which rises to a maximum; after which it will diminish again and after having passed through zero, it may even become negative.

It appears from this remark, that at a given value of T_1 we may give to v_1 , and so also to p_1 such a value that the cooling has its maximum value; or in other words there is a most advantageous value for p_1 in LINDE's apparatus. The existence of such a most advantageous value follows of course by no means from the approximated empiric formula of Lord KELVIN and JOULE, which is generally used to explain the LINDE-process. Yet the existence of a most advantageous way of working has been observed, but it is ascribed to a quite different cause. So we read in „La liquéfaction des gaz. J. CAURO, pag. 33” about this what follows: „Comme „la production frigorifique de l'appareil dépend de la différence de „pression $p_1 - p_2$ avant et après l'écoulement et que, d'un autre „côté, le travail de compression est fonction du quotient de ces „mêmes pressions $\left(\frac{p_1}{p_2}\right)$, il est clair, que l'avantage est d'avoir une „grande différence de pression, mais en même temps un rapport „aussi faible que possible entre ces mêmes pressions.”

In this phrase very great importance is attached to the quantity of heat, which is developed when the gas, returning under the pressure p_2 , is again compressed to its original pressure p_1 — and this heat is in fact, considerable, and the more considerable the smaller p_2 is at given p_1 . It is even greater than the heat which is annihilated when the pressure is lowered to p_2 . But in the apparatus of LINDE the arrangement is such, that the developed heat is given out in quite a different part of the apparatus, from that where the cold is produced; and the gas heated by compression loses this heat before it reaches the cooling-spiral, so for instance by passing through the cooling mixture, which serves to dry the gas. And if this were not sufficient for taking away the heat which is produced by compression, it would not be difficult to find more efficacious means.

But in the quoted phrase the usual mistake has been made, against which I will warn here, viz. to put the cooling proportional to $(p_1 - p_2)$ — or to expect at any rate that the cooling will always increase with the increase of $p_1 - p_2$.

In order to find the condition which must be fulfilled that the cooling be maximum, we may consider χ_1 as function of T_1 and p_1 and χ_2 as function of T_2 and p_2 . The value of T_1 we think as

being given; also the value of p_2 . We get from:

$$\chi_1 = \chi_2$$

$$\left(\frac{\partial \chi_1}{\partial p_1}\right)_{T_1} dp_1 = \left(\frac{\partial \chi_2}{\partial T_2}\right)_{p_2} dT_2.$$

If T_2 is to be a minimum and therefore the cooling a maximum, then $\left(\frac{\partial \chi_1}{\partial p_1}\right)_{T_1}$ and therefore also $\left(\frac{\partial \chi_1}{\partial v_1}\right)_{T_1}$ must be 0.

Therefore:

$$\left(\frac{\partial \varepsilon_1}{\partial v_1}\right)_{T_1} + \left[\frac{\partial (\nu_1 v_1)}{\partial v_1}\right]_{T_1} = 0$$

or

$$\frac{a}{v_1^2} \left\{ 2f(T_1) - T_1 f'(T_1) \right\} = \frac{RT_1}{(v_1 - b)^2}.$$

If a is thought to be constant, this equation becomes:

$$\frac{2a}{v_1^2} = \frac{(1+a)(1-b)(1+\alpha t_1)}{(v_1 - b)^2}.$$

If, however, a is taken as $a \frac{273}{T}$, as CLAUSIUS does for CO_2 we find:

$$\frac{3a}{v_1^2} = \frac{(1+a)(1-b)(1+\alpha t_1)^2}{(v_1 - b)^2}.$$

In order to avoid needless calculations, I shall in what follows only examine the consequences if a is put constant.

Then we find:

$$\left(\frac{v_1}{v_1 - b}\right)^2 = \frac{2a}{(1+a)(1-b)(1+\alpha t_1)} = \frac{27}{4} \frac{T_2}{T_1}.$$

If we had sought the value of v , for which the value of pv is a minimum, we had obtained:

$$\left(\frac{v'}{v' - b}\right)^2 = \frac{27}{8} \frac{T_2}{T_1}.$$

From this appears that the value v_1 , for which a maximum value is obtained, is the same as that for which pv has a minimum value at a temperature equal to half T_1 .

If we had calculated the value of v_1 for which the cooling is 0, always on the supposition that $\frac{a}{v_2}$ and $\frac{b}{v_2 - b}$ may be neglected, we should have found:

$$\frac{v_1}{v_1 - b} = \frac{2a}{(1+a)(1-b)b(1+at_1)} = \frac{27}{4} \frac{T_x}{T_1},$$

while we obtain for the value v_1 , for which pv_1 has again the limiting value kT_1 :

$$\frac{v'}{v' - b} = \frac{a}{(1+a)(1-b)b(1+at_1)} = \frac{27}{4} \frac{T_x}{T_1}.$$

Here again we arrive at the result, that the value of v_1 , for which the cooling = 0, is the same as that for which pv has again the limiting value at a temperature of $\frac{T_1}{2}$.

Through this remark we are able to conclude also to the circumstances of the discussed cooling, if we know the course of pv .

Thus we find both the minimum product of pv and the value of $pv = RT$ at $v = \infty$ if $T = \frac{27}{8} T_x$ — and we find the maximum cooling and the cooling = 0 also if $v = \infty$ at a temperature which has twice this value. This means for the product pv that it is found greater than RT for every finite value of v — and for the cooling that it is negative for every value of v . At $T > \frac{27}{4} T_x$ the consequence of the process, in which $\chi_1 = \chi_2$, will be that the gas is heated when it flows out. As for hydrogen we may put $T = 40^\circ$, the gas will be heated at $T > 270^\circ$, so this must have been the case in the experiment of Lord KELVIN and JOULE¹⁾. As the experiment was made at $t = 17^\circ$ or $T = 290^\circ$, only a slight increase of temperature may have been observed, if we have determined the limits of the temperature correctly. If a is considered as a function of the temperature, these limits are rendered by other ratios. But the existence of such a limit of the temperature is beyond doubt.

When T is lowered, the value of v becomes smaller, as well for the maximum cooling, as for the limit between cooling and heating.

¹⁾ See also KAMERLINGH ONNES, Verslag Kon. Akad. Febr. 1895.

If we put e.g. $T = 2 T_*$, which is the case for air that is cooled somewhat below 0° centigrade, we find for the value of v for the maximum cooling $2,2 b$, and for the value of v for a cooling $= 0$ an amount $= \frac{27}{19} b$. For $T = T_*$ these values have decreased to $\frac{5}{3} b$ and $\frac{27}{23} b$.

By elimination of T we find for the locus of the points of maximum cooling in the p, v diagram:

$$p = \frac{a}{b} \frac{2v - 3b}{v^2}.$$

If we put $\frac{1}{v} = \varrho$ (density), we find the parabola:

$$p = \frac{a}{b} (2\varrho - 3b\varrho^2),$$

which yields $p = 0$ for $\varrho = 0$ and for $\varrho = \frac{2}{3} \frac{1}{b}$. The maximum value of p , which is found for $\varrho = \frac{1}{3b}$, is equal to $\frac{a}{3b^2}$ or to $9p_*$. For air (which we treat here for simplicity's sake as a single substance) this minimum pressure amounts to $9 \times 39 = 351$ atmospheres.

To the existence of such a parabola for the points, where pv has a minimum value, has been concluded by BELTRAMI from the observations concerning pv of AMAGAT.

For the points, for which the cooling $= 0$, we find:

$$p = \frac{a}{b} \frac{2v - b}{v^2}$$

or

$$p = \frac{a}{b} (2\varrho - b\varrho^2).$$

So also a parabola in the p, ϱ diagram.

By elimination of v_1 we get a relation between p_1 and T_1 , which has the following form:

$$p_1 = 27 p_* \left[1 - \sqrt{\frac{4}{27} \frac{T_1}{T_*}} \right] \left[3 \sqrt{\frac{4}{27} \frac{T_1}{T_*}} - 1 \right].$$

We find the maximum value of p_1 at $T = 3 T_\kappa$, and as has been mentioned before, it is equal to $9 p_\kappa$. So for air $9 \times 39 = 351$.

For $T = 2 T_\kappa$ we find $p_1 = 304$ atmospheres, and for

$$T = T_\kappa \quad p_1 = 100$$

The constant value which has been chosen in the apparatus of LINDE, may be considered as an arithmetical mean of the most advantageous pressure at the beginning and that at the end of the process.

But at the same time we may conclude from the circumstance that p_1 is a function of T_1 , that an apparatus, which would work theoretically perfectly, should be able to regulate the pressure p_1 according to the temperature which reigns in the inner spiral.

The numeric values of the pressure, and the limits of the temperature which have been found, will be different according to the equation of state which is used. But though we cannot warrant the absolute accuracy of the numeric values in consequence of the inaccuracies of the equation of state, yet we may prove, that from every equation of state, which properly accounts for the course of the product $p v$, as found experimentally, the existence of a pressure, for which the cooling is equal to 0, follows, and so also the existence of a pressure, for which the cooling has a maximum value. For as long as $p_1 v_1 < p_2 v_2$, the resulting external work will promote cooling. This influence is greatest for a pressure, at which $p_1 v_1$ has a minimum value. If $p_1 v_1$ is again equal to $p_2 v_2$, the cooling has the same value as it has in case of perfectly free expansion. But if the pressure is still higher, $p_1 v_1$ rises above $p_2 v_2$, and approaches infinitely to a limiting value which is ∞ , so that every cooling which would be the immediate result of free expansion, may be neutralized by that of $p_1 v_1 - p_2 v_2$. Only if we should assume also an infinite value for the cooling caused by free expansion, the above reasoning would not be convincing. But then, nobody will assume this.

We may represent the maximum cooling in the following simple form:

$$T_1 - T_2 = \frac{2}{m} \frac{273}{c_p} \frac{2a}{b} \left(\frac{b}{v_1} \right)^2$$

or

$$T_1 - T_2 = \frac{2}{m} \frac{273}{c_p} \frac{2a}{b} \left\{ 1 - \sqrt{\frac{4}{27} \frac{T_1}{T_\kappa}} \right\}^2$$

or

$$T_1 - T_2 = \frac{27 T_\kappa}{2 m c_p} \left\{ 1 - \sqrt{\frac{4}{27} \frac{T_1}{T_\kappa}} \right\}^2$$

From this we find at $T_1 = 2 T_x$ the value 55° .

Properly speaking we ought to subtract a certain amount from this 55° , because the opposed p_2 may not be neglected. Let us put it at $0,265 \times 20$. Then we may at $T_1 = 2 T_x$ put the cooling at 50° , if the opposed pressure amounts to 20 atm. and p_1 has the most advantageous value. According to the approximating formula we should find somewhat more than 75° .

For decreasing values of T_1 the maximum value increases, as

$$\left\{ 1 - \sqrt{\frac{4}{27} \frac{T_1}{T_x}} \right\}^2 \text{ increases with } T_1.$$

If we write:

$$\frac{T_1 - T_2}{T_x} = \frac{27}{2 m c_p} \left\{ 1 - \sqrt{\frac{4}{27} \frac{T_1}{T_x}} \right\}$$

it appears that if $\frac{T_1}{T_x}$ has the same value, $\frac{T_1 - T_2}{T_x}$ has also the same value for all gases for which $m c_p$ has the same value, and this is the case for all those whose molecules contain two atoms.

If we write:

$$\frac{m c_p (T_1 - T_2)}{T_x} = \frac{27}{2} \left\{ 1 - \sqrt{\frac{4}{27} \frac{T_1}{T_x}} \right\}^2$$

we conclude, that at the same value of $\frac{T_1}{T_x}$ the heat annihilated by the expansion is for all substances an equal fraction of T_x of T_1 , and so of the vis viva of the progressive motion.

It need scarcely be observed that if the expansion could have taken place in an adiabatic way, the cooling would have been much more considerable.

From the equation of state:

$$\left(p + \frac{a}{v^2} \right) (v - b) = RT,$$

follows for the course of the isentropic line:

$$\left(p + \frac{a}{v^2} \right) (v - b)^x = C,$$

in which x represents the value of $\left(\frac{c_p}{c_v} \right)$ at infinite rarefaction.

By elimination of p we find $T(v - b)^{x-1} = C_1$.

If we take $T_1 = 2 T_k$ and for v_1 the value for the greatest cooling according to the process $\chi_1 = \chi_2$, so $v_1 = 2,2 b$, and for v_2 a value, which corresponds to $p_2 = 20$ atm., then even by this one expansion the air would have been cooled already far below the critical point. Lord RAYLEIGH has already pointed out, that the process of LINDE might be improved by causing the expanding gas to perform more work. It remains therefore desirable to find an arrangement, by which the expansion approaches more nearly an isentropic process than is the case in the apparatus of LINDE.

Physics. — Prof. J. D. VAN DER WAALS presents for the proceedings a communication of Mr. H. HULSHOF at Delft, on: *“The direct deduction of the capillary constant σ as a surface-tension.”*

The amount of the capillary tension and the capillary energy, as found by Prof. VAN DER WAALS in his *Théorie Thermodynamique de la capillarité*, may also be determined directly. The existence of capillary tension is undoubtedly the consequence of molecular attraction. Therefore we shall have to examine the influence of molecular attraction in the capillary layer, i.e. we shall have to determine the value of the molecular pressure for an arbitrary point of the capillary layer. The equation of state gives $a\rho^2$ for the value of the molecular pressure; the equation of state, however, comprises only those cases, in which the distribution of matter is homogeneous. As the molecular pressure is the direct consequence of the attraction, which the particles exercise on one another and is therefore determined in a point by the condition of the surroundings, it may be expected that for not homogeneous distribution of matter the molecular pressure in different directions will have different values. The existence of capillary tension is to be ascribed to the fact, that in the capillary layer the molecular pressure in the direction of the surface of the liquid is different from that in the direction normal to the surface.

When the matter is homogeneously distributed the molecular pressure per surface element do is equal to the force with which all the matter on one side of the plane in which do is situated, attracts in the direction towards this plane the material cylinder with do as base, situated on the other side of the plane. In the capillary layer we can also define the molecular pressure in the same way.