

*Citation:*

Dalton, J.P., Researches on the Joule-Kelvin effect, especially at low temperatures. I. Calculations for hydrogen, in:

KNAW, Proceedings, 11, 1908-1909, Amsterdam, 1909, pp. 863-873

fluences from without, it stood to reason for me to try whether these data were to be used for the identification of blood-spots.

Now I have first dried some drops of blood from different animals (horse, cattle, rabbit) upon small pieces of linen, then extracted them by means of salt-solution and injected the extract subcutaneously into guineapigs in quantities equal to one drop of blood per animal. After the lapse of the usual incubation-stage of 12 or 14 days or longer the animals — as was indeed to be expected — had become hypersensitive to an intraperitoneal injection of 4 or 5 cM.<sup>3</sup> of the corresponding serum, and that in a quite specific sense. A guineapig e. g., which has been sensitized with the extract from a cowbloodspot, and does not in the least react upon an injection of 5 cM.<sup>3</sup> of horse-serum, is as sensitive to an injection of the same quantity of cow-serum the day after, as a test-animal — likewise sensitized with extract from a cowbloodspot — but which previously has not been tried with another serum.

Then I have also anaphylactised guineapigs with the extract from spots of human blood. Now as for trying these animals in the subcutaneous or intraperitoneal way rather a great deal of human serum would be necessary, I have examined them upon hypersensibility in the intracerebral way or by preference by intravenous injection. Thus they can very well stand  $\frac{1}{5}$  cM.<sup>3</sup> of serum from horse, cattle or rabbit, but the same quantity of human serum, injected into the carotis, kills these animals certainly within a few minutes.

I am busy continuing this investigation, in the hope of rendering the method simpler and more practicable. Meanwhile I have already now intended to point out the principle of this method, because I think it may perhaps find a place by the side of the well-known methods of judicially medicinal investigation of blood.

**Physics.** — “*Researches on the JOULE-KELVIN-effect, especially at low temperatures. 1. Calculations for hydrogen.*” By J. P. DALTON, M.A., B.Sc., Carnegie Research Fellow. Communication N<sup>o</sup>. 109<sup>a</sup> from the Physical Laboratory, Leiden.

(Communicated in the meeting of March 27, 1909).

§ 1. The present calculations form part of a research which was undertaken <sup>1)</sup> with a view to devising an apparatus for determining the JOULE-KELVIN-effect obtained in expanding helium at the temperature of liquid hydrogen, and thus to lead to some decision regarding the

<sup>1)</sup> The beginning of the research was already referred to in Comm. N<sup>o</sup>. 108 (Proc. Aug. 1908).

possibility of liquefying helium — an open question at that time. To test the apparatus, expansion experiments were first to be made with air at ordinary temperature, and with hydrogen at the temperature of liquid oxygen; but in the construction of the apparatus it had always to be kept in view that it was eventually to be used in liquid hydrogen. Preliminary experiments showed that the apparatus in its original form did not give a true JOULE-KELVIN-effect, and thus led to a special investigation of the thermodynamics of expansion through a valve and how a valve apparatus has to be arranged so that the enthalpy <sup>1)</sup> before and after expansion remains the same. The results of this investigation will be published in this and following communications, for they lose none of their interest by the circumstance that the original object of the research has been disposed of by the liquefaction of helium. <sup>2)</sup>

§ 2. Since the experiments of JOULE and KELVIN <sup>3)</sup> of 50 years ago very little experimental work upon similar expansions of gases has been published. This lack of confirmation is rather surprising when we consider the importance of the JOULE-KELVIN experiments in gas-thermometry and the frequency with which their results are employed in various theoretical thermodynamical investigations. With the exception of some rough experiments by REGNAULT <sup>4)</sup> upon various gases, and the work of E. NATANSON <sup>5)</sup> and KESTER <sup>6)</sup> upon CO<sub>2</sub>, no further measurements of the JOULE-KELVIN effect seem to have been made. REGNAULT did not obtain results sufficiently definite to lead to any theoretical conclusions, and the results obtained by the other experimenters are not in agreement.

§ 3. Although JOULE and KELVIN began their experiments by allowing the expansion to take place through a small aperture, they soon abandoned that form of apparatus, and used instead a porous plug so as to ensure, by friction in the plug, the immediate conver-

<sup>1)</sup> This name has been suggested by KAMERLINGH ONNES to indicate the function  $(\epsilon + pv)$  — the "Heat function" of GIBBS. H. L. CALLENDAR (Phil. Mag. [6]. 5. p. 48. (1903)) calls this expansion "Adiabathermal".

<sup>2)</sup> H. KAMERLINGH ONNES: Comm. Phys. Lab. Leiden. N<sup>o</sup>. 108. (Proc. June 1908).

<sup>3)</sup> JOULE and KELVIN: Phil. Mag. [4]. 4. p. 481. (1852); Phil. Trans 143. p. 357. (1853); 144. p. 321. (1854); 152. p. 579. (1862).

<sup>4)</sup> V. REGNAULT: C. R. 69. p. 780 (1869).

<sup>5)</sup> E. NATANSON: Wied. Ann. 31 p. 502 (1887).

<sup>6)</sup> F. E. KESTER: Physik. Zeits. 6 p. 44 (1905).  
Phys. Rev. 21 p. 260 (1905).

sion into heat of the energy generated, and also to ensure that the expanded gas should issue in a "quiet tranquil stream without jets or rapids". (See § 6, note 1). NATANSON and KESTER also used a porous plug.

More recently OLSZEWSKI has determined "inversion-points" for various gases, and has returned to the original reduction-valve form of apparatus; but while JOULE and KELVIN's highest initial pressure was not greater than 6 atmospheres, OLSZEWSKI expanded from considerably higher pressures. Since the apparatus to be used in my research resembled that used by OLSZEWSKI, a careful examination of his experimental results and of the criticisms concerning them which have been published was necessary.

§ 4. OLSZEWSKI's first determination <sup>1)</sup> was of an "inversion-point" for hydrogen. This result was subsequently used by PORTER <sup>2)</sup> as a means of discriminating between the validity of certain equations of state. Later OLSZEWSKI investigated <sup>3)</sup> the dependence of inversion temperature upon initial pressure in the case of air and nitrogen, and found that the inversion temperature decreased with falling initial pressure. The results of this research have been criticised in a theoretical investigation recently published by HAMILTON DICKSON. <sup>4)</sup> DICKSON reached the conclusion that OLSZEWSKI's experiment differs fundamentally from that of JOULE and KELVIN. This difference he attributed to the different kinetic energies possessed by the gas in the OLSZEWSKI experiment before and after expansion. It will be shown in a subsequent paper that conduction of heat and loss of pressure in OLSZEWSKI's experiments are probably much more important factors in the result than the change of kinetic energy.

§ 5. DICKSON's criticism was based upon calculations made from VAN DER WAALS's equation of state, but, as this equation is not quantitatively correct, the results obtained are of doubtful value. But if we calculate from the real isothermals of the experimental gas, we ought to obtain close correspondence between the calculated and experimental values of the JOULE-KELVIN effect, in so far as no uncertainty is introduced by errors in the experimental

<sup>1)</sup> K. OLSZEWSKI: Phil. Mag. [6]. 3. p. 535. (1902).

" Ann. Phys. 7. p. 818. (1902).

<sup>2)</sup> A. W. PORTER: Phil. Mag. [6]. 11. p. 554 (1906).

<sup>3)</sup> K. OLSZEWSKI: Phil. Mag. [6]. 13. p. 723 (1907).

<sup>4)</sup> I. D. HAMILTON DICKSON: Phil. Mag. [6]. 15. p. 126. (1908).

data. To effect such calculations KAMERLINGH ONNES<sup>1)</sup> has given empirical equations of state, which, if specialised for the experimental gas, and, if necessary, between definite limits of temperature and pressure, represent the actual isotherms of the gas to the limits of accuracy of the observations, and in a form easy to manipulate. In this equation the product  $pv$  is expressed as a series of five powers of the density; thus

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} \dots \quad (1),$$

where  $p$  is expressed in atmospheres,  $v$  in terms of the theoretical normal volume as unit, and the "virial-coefficients"  $A, B, C$ , etc., are calculated as functions of the temperature from the experimental isotherms of the gas in question, in conjunction with the isotherms of other substances which are brought into relation with the one investigated by means of the law of corresponding states. On this account the equation is usually given in the so-called reduced form:

$$\lambda pv = \mathfrak{A} + \frac{\mathfrak{B}}{\lambda v} + \frac{\mathfrak{C}}{\lambda^2 v^2} + \frac{\mathfrak{D}}{\lambda^3 v^3} + \frac{\mathfrak{E}}{\lambda^4 v^4} + \frac{\mathfrak{F}}{\lambda^5 v^5} \dots \quad (2)$$

where  $\lambda$  is equal to  $\frac{T_k}{p_k v_k}$ ,  $p$  and  $v$  the reduced pressures and volumes respectively, and

$$\mathfrak{A} = \frac{A}{T_k}; \mathfrak{B} = \frac{B}{T_k^2} p_k; \mathfrak{C} = \frac{C}{T_k^3} p_k^2; \text{ etc.}$$

§ 6. If the two following experimental conditions are fulfilled, viz.:

1. that the difference between the kinetic energies of the gas before and after expansion is negligible; and
2. that the conduction of heat from the apparatus to the expanding gas is also negligible;

then the expansion process will be represented by the equation

$$\varepsilon_1 + p_1 v_1 = \varepsilon_2 + p_2 v_2 \dots \quad (3)$$

(where  $\varepsilon$  = internal energy of the gas, and the subscripts 1 and 2 refer to the initial and final states respectively) quite independently of whether the expansion has taken place through a valve or a plug<sup>2)</sup>, or from a high or low initial pressure. Equation (3) repre-

<sup>1)</sup> H. KAMERLINGH ONNES: These Proc. June 1901, and Arch. Néerl. S. II, T. VI, 1901. Comm. Phys. Lab. Leiden. No. 71 and 74.

<sup>2)</sup> In expansion through a valve, since in parts of the jet the kinetic energy temporarily reaches values which are not negligible, intermediate stages of the process are not characterised by equal values of the enthalpy; in expansion through a plug the process, if it agrees with the theoretical suppositions, becomes *isenthalpic*.

senting an expansion which is characterised by equal values of enthalpy in the initial and final states may by the usual methods<sup>1)</sup> be transformed into

$$\bar{C}_v (T_1 - T_2) = \int_{v_1}^{v_2} \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dv + p_2 v_2 - p_1 v_1 \dots \dots (4)$$

or

$$\bar{C}_p (T_1 - T_2) = - \int_{p_1}^{p_2} \left[ T \left( \frac{\partial v}{\partial T} \right)_p - v \right] dp \dots \dots \dots (5)$$

where

$$\bar{C} (T_1 - T_2) = \int_{T_2}^{T_1} C dT.$$

Since  $T_1$  and  $T_2$  never differ much in value, and since, in any case,  $C$  varies very slowly with temperature, the difference between  $\bar{C}$  and  $C$  must be extremely small.

For the present calculation equation (4) seems at first sight more directly applicable than (5), but the evaluation of  $v_2$  would necessitate the use of successive approximations; it is, therefore, better to use equation (5). For this purpose, the following transformation, valid as long as excessive densities are not reached, may be applied to equation (2); this equation may be written in terms of reduced pressure as

$$\lambda pv = \mathfrak{A}(\nu) + \mathfrak{B}(\nu)p + \mathfrak{C}(\nu)p^2 + \mathfrak{D}(\nu)p^3 + \mathfrak{E}(\nu)p^4 + \text{etc.} \dots (6)$$

if

$$\mathfrak{A}(\nu) = \mathfrak{A} \dots \dots \dots (7)$$

$$\mathfrak{B}(\nu) = \frac{\mathfrak{B}}{\mathfrak{A}} \dots \dots \dots (8)$$

$$\mathfrak{C}(\nu) = \frac{\mathfrak{C}\mathfrak{A} - \mathfrak{B}^2}{\mathfrak{A}^3} \dots \dots \dots (9)$$

$$\mathfrak{D}(\nu) = \frac{2\mathfrak{B}^3 - 3\mathfrak{A}\mathfrak{B}\mathfrak{C}}{\mathfrak{A}^5} \dots \dots \dots (10)$$

$$\mathfrak{E}(\nu) = \frac{\mathfrak{D}\mathfrak{A}^4 - 5\mathfrak{B}^4 - 2\mathfrak{A}^2\mathfrak{C}^2 + 10\mathfrak{A}\mathfrak{B}^2\mathfrak{C}}{\mathfrak{A}^7} \dots \dots (11)$$

etc.

Equation (5) in reduced magnitudes becomes

$$\bar{C}_p (T_1 - T_2) = - T_k \lambda \int_{p_1}^{p_2} \left[ t \left( \frac{\partial v}{\partial t} \right)_p - v \right] dp \dots \dots (12)$$

<sup>1)</sup> See: J. P. KUENEN Die Zustandsgleichung, pp. 106—9 Vieweg 1907.

Since

$$t \frac{d\mathfrak{A}}{dt} - \mathfrak{A} = 0 \dots \dots \dots (13)$$

equations (12) and (6) give the relation

$$\begin{aligned} \bar{C}_p (T_1 - T_2) = & \frac{T_k}{p_k} \left( t \frac{d\mathfrak{B}^{(\rho)}}{dt} - \mathfrak{B}^{(\rho)} \right) (p_1 - p_2) + \frac{T_k}{2p_k^2} \left( t \frac{d\mathfrak{C}^{(\rho)}}{dt} - \mathfrak{C}^{(\rho)} \right) (p_1^2 - p_2^2) \\ & + \frac{T_k}{3p_k^3} \left( t \frac{d\mathfrak{D}^{(\rho)}}{dt} - \mathfrak{D}^{(\rho)} \right) (p_1^3 - p_2^3) + \text{etc.} \dots \dots (14) \end{aligned}$$

Hence, if we return to the original coefficients by means of (8), (9), (10), (11) and (13), we obtain an expression for the heat-effect in terms of the virial-coefficients, and the initial and final pressures; and if the expansion takes place against atmospheric pressure, this relation becomes

$$\begin{aligned} (T_1 - T_2) = & \frac{t \frac{d\mathfrak{B}}{dt} - 2\mathfrak{B}}{\mathfrak{A}} \cdot \frac{T_k}{\bar{C}_p p_k} (p_1 - 1) + \\ & + \frac{\mathfrak{A} \left( t \frac{d\mathfrak{C}}{dt} - 3\mathfrak{C} \right) - 2\mathfrak{B} \left( t \frac{d\mathfrak{B}}{dt} - 2\mathfrak{B} \right)}{2\mathfrak{A}^3 p_k} \cdot \frac{T_k}{\bar{C}_p p_k} (p_1^2 - 1) + \\ & + \frac{3 \left( t \frac{d\mathfrak{B}}{dt} - 2\mathfrak{B} \right) (2\mathfrak{B}^2 - \mathfrak{A}\mathfrak{C}) - 3\mathfrak{A}\mathfrak{B} \left( t \frac{d\mathfrak{C}}{dt} - 3\mathfrak{C} \right)}{3\mathfrak{A}^5 p_k^2} \cdot \frac{T_k}{\bar{C}_p p_k} (p_1^3 - 1) + \\ & + \frac{20 \left( t \frac{d\mathfrak{B}}{dt} - 2\mathfrak{B} \right) (\mathfrak{A}\mathfrak{B}\mathfrak{C} - \mathfrak{B}^3) + \left( t \frac{d\mathfrak{C}}{dt} - 3\mathfrak{C} \right) (10\mathfrak{A}\mathfrak{B}^2 - 4\mathfrak{A}^2\mathfrak{C}) + \mathfrak{A}^3 \left( t \frac{d\mathfrak{D}}{dt} - 5\mathfrak{D} \right)}{4\mathfrak{A}^7 p_k^3} \\ & \cdot \frac{T_k}{\bar{C}_p p_k} (p_1^4 - 1) \dots \dots \dots (15) \end{aligned}$$

which is the equation to be used in calculating the heat-effects.

§ 7. As a first example I have taken hydrogen, and from equation (15) have calculated the heat effects produced when hydrogen is expanded against atmospheric pressure under various conditions of initial temperature and pressure. The values of the virial-coefficients, specialised to fit the isotherms of KAMERLINGH ONNES and BRAAK <sup>1)</sup> down to  $-217^\circ \text{C.}$  and not yet published, were kindly placed at my disposal by Professor ONNES. These coefficients are

<sup>1)</sup> H. KAMERLINGH ONNES and C. BRAAK: Comm. Phys. Lab. Leiden. No's 95—101.

$$\begin{aligned}
\mathfrak{A} &= 0.0036618 t \\
10^8 \mathfrak{B} &= 168.982 t - 435.381 - 722.848 \frac{1}{t} + \\
&\quad + 420.696 \frac{1}{t^3} - 118.456 \frac{1}{t^5} \\
10^{11} \mathfrak{C} &= 50.3923 t + 131.386 + 131.2531 \frac{1}{t} + \\
&\quad + 199.2748 \frac{1}{t^3} - 50.6347 \frac{1}{t^5} \\
10^{14} \mathfrak{D} &= 434.680 t - 131.462 - 903.004 \frac{1}{t} + \\
&\quad + 367.7055 \frac{1}{t^3} - 178.5625 \frac{1}{t^5}
\end{aligned} \tag{16}$$

The values of the critical constants used in the reduction were  $p_k = 15$  atm. and  $T_k = 29^\circ$  abs.; but as the reduction is ultimately reversed the accuracy or otherwise of these constants is immaterial. The WIEDEMANN value of  $\bar{C}_p = 3.41$  cal. has been used. An estimate of the change of  $\bar{C}_p$  with temperature was obtained by combining equation (2) with the well-known thermodynamical relation

$$C_p - C_v = T \frac{\partial p}{\partial T_v} \frac{\partial v}{\partial T_p} \dots \dots \dots (17)$$

and regarding  $C_v$  as independent of the temperature.<sup>1)</sup> This showed that down to  $-190^\circ$  C. the variation in  $C_p$  at 1 atm. was less than 1%; hence it appeared that a sufficiently high degree of accuracy was reached by retaining the constant value 3.41 throughout these calculations.

For the calculations four terms of equation (2) were found sufficient, for the greatest influence of the  $\mathfrak{D}$ -term on the values shown in Table I of  $T_1 - T_2$  at 100 atm. pressure was not greater than  $0^\circ.15$ . Table I<sup>2)</sup> contains the results of the calculations; from it has been constructed the series of  $(T_1 - T_2, p_1 - 1)_{T = \text{const}}$  curves shown in fig. 1 and also the series of  $(T_1 - T_2, T_1)_{p_1 = \text{const}}$  curves of fig. 2.

<sup>1)</sup> Cf. A. W. WITKOWSKI: Bull. de l'Acad. d. Sciences de Crac. Oct.-Nov. 1895.

The comparatively great change of  $C_v$  and  $C_p$  with temperature deduced by H. LE CHATELIER and E. MALLARD. (Séanc. Soc. de Phys. p. 308. (1888)) from experiments at high temperatures cannot be applied to low temperatures without further investigation.

<sup>2)</sup> The calculation is not extended beyond the limits of density at each temperature at which powers higher than those occurring in (15) must be taken into account.



T A B L E I.

$t$	10	9	8	7	6.5	6	5	4	3	2
$T_{abs}$	290	261	232	203	188.5	174	145	116	87	58
$t^{\circ} C$	+ 17	- 12	- 41	- 70	- 84.5	- 99	-128	-157	-186	-215
$(p_1 - 1)$ atm.	$T_1 - T_2$									
1	- 0.026	- 0.019	- 0.011	- 0.001	+ 0.006	+ 0.015	+ 0.037	+ 0.073	+ 0.141	+ 0.291
5	- 0.128	- 0.098	- 0.059	- 0.006	+ 0.028	+ 0.071	+ 0.189	+ 0.361	+ 0.698	+ 1.466
10	- 0.259	- 0.198	- 0.121	- 0.016	+ 0.051	+ 0.135	+ 0.351	+ 0.711	+ 1.382	+ 2.951
20	- 0.526	- 0.407	- 0.254	- 0.049	+ 0.081	+ 0.247	+ 0.668	+ 1.371	+ 2.694	+ 5.957
30	- 0.799	- 0.625	- 0.400	- 0.100	+ 0.092	+ 0.335	+ 0.951	+ 1.991	+ 3.931	.
40	- 1.080	- 0.852	- 0.558	- 0.166	+ 0.083	+ 0.400	+ 1.200	+ 2.538	+ 5.073	
50	- 1.367	- 1.088	- 0.729	- 0.249	+ 0.056	+ 0.444	+ 1.418	+ 3.044	+ 6.108	
60	- 1.662	- 1.333	- 0.909	- 0.347	+ 0.011	+ 0.467	+ 1.603	+ 3.497	+ 7.023	
70	- 1.963	- 1.587	- 1.102	- 0.460	- 0.052	+ 0.468	+ 1.757	+ 3.897		
80	- 2.270	- 1.849	- 1.306	- 0.587	- 0.132	+ 0.450	+ 1.881	+ 4.246		
90	- 2.584	- 2.119	- 1.520	- 0.729	- 0.229	+ 0.413	+ 1.976	+ 4.544		
100	- 2.904	- 2.398	- 1.744	- 0.885	- 0.343	+ 0.356	+ 2.043	+ 4.793		

( 870 )

§ 8. Considering the  $\alpha$  of his equation as a function of the temperature, VAN DER WAALS<sup>1)</sup> deduced the following expression for the JOULE-KELVIN effect :

$$T_1 - T_2 = \frac{2}{mC_p} \times 273 \left[ \frac{a}{v_1} \{2f(T_1) - T_1 f'(T_1)\} - \frac{RT_1 b}{v_1 - b} \right]. \quad (18)$$

and drew attention to the fact that "at a given value of  $T_1$  we may give  $p_1$  such a value that the cooling has a maximum value". The foregoing calculations, the results of which are embodied in Table I, lead to the same conclusion, and show that as the initial pressure increases, the cooling effect (if any) increases, reaches a maximum, diminishes, and finally at high pressures (as long as  $t_2 > 1$ ) changes into a heating effect. They show moreover that except in the neighbourhood of temperatures determined by the relation

$$t \frac{d\mathfrak{B}}{dt} - 2\mathfrak{B} = 0 \quad (19)$$

or at very high pressures, the subsequent terms of the right-hand member of equation (15) are very small compared with the first, and it is therefore only under these circumstances that the progressive change from cooling to heating could be experimentally realised; but if the critical pressure of the gas is low, as in the case of hydrogen, high reduced pressures are easily attainable, and these changes become of importance. In fact, this warming effect obtained in expansions from high pressures explains the fact that TRAVERS<sup>2)</sup> found hydrogen "a perfect gas down to very low temperatures"; for, in his experiments expansions were made from the comparatively high initial pressure of 200 atm. And in this connection it is also worth remarking that in the liquefaction of helium KAMERLINGH ONNES<sup>3)</sup> found that if the expansion pressure exceeded a certain value, the expanding gas no longer showed a cooling effect. The curves (fig. 1 and 2) further show that at lower pressures and at temperatures not in the neighbourhood of those defined by equation (19), the cooling effect remains practically proportional to the pressure-difference, and decreases in magnitude as the temperature of the compressed gas is increased. It was under conditions such as these that the JOULE-KELVIN experiments were carried out, and their results embodied in their well-known empirical equation

<sup>1)</sup> J. D. VAN DER WAALS. Proc. Kon. Akad. van Wetens. Amsterdam II. p. 379. (1900).

<sup>2)</sup> MORRIS W. TRAVERS : Experimental Study of Gases ; p. 197 (1901).

<sup>3)</sup> loc. cit.

$$T_1 - T_2 = \frac{A}{T^2} (p_1 - p_2) \dots \dots \dots , \quad (20)$$

are in agreement with the foregoing conclusions. The value of  $A$  for hydrogen at  $+5^\circ$  C. was given by JOULE and KELVIN as  $-0.03$  which is somewhat greater than the above calculated value of  $-0.023$ ; but numerical non-correspondence is in this case of no great importance seeing that JOULE and KELVIN's results for hydrogen were very irregular, and the authors declared them to be less trustworthy than those obtained with other gases.

§ 9. With regard to "inversion-points", it is at once evident that the inversion temperature is a function of the initial pressure, and that it does not reach the value  $T_{inn} = 7T_k$  (see table I). From the curves of fig. 2 have been read the following inversion temperatures corresponding with various initial pressures.

T A B L E II.

Pressure-difference	Inversion temperature.
1 atm.	$-72^\circ.6$ C.
5 "	$-73.2$ "
10 "	$-74.1$ "
20 "	$-75.8$ "
30 "	$-77.8$ "
40 "	$-79.9$ "
50 "	$-81.9$ "
60 "	$-83.6$ "
70 "	$-85.9$ "
80 "	$-88.3$ "
90 "	$-90.0$ "
100 "	$-91.7$ "

Thus the relation between inversion-temperature and pressure-difference is practically linear (fig. 3), and with increasing initial pressure the inversion temperature falls. If we extrapolate the above table we obtain for a pressure of 115 atm. an inversion temperature of  $-95^\circ$  C., where OLSZEWSKI found  $-80^\circ.5$  C. It is worth noting that NAKAMURA<sup>1)</sup> calculating from REINGANUM's equation of state found

<sup>1)</sup> S. NAKAMURA: refer. Journ. de Physique (4). 2 p. 704. (1903).

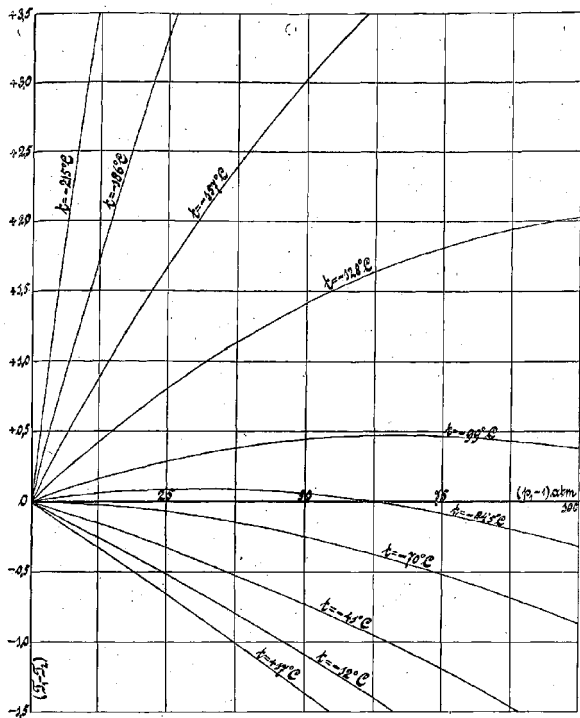


Fig. 1

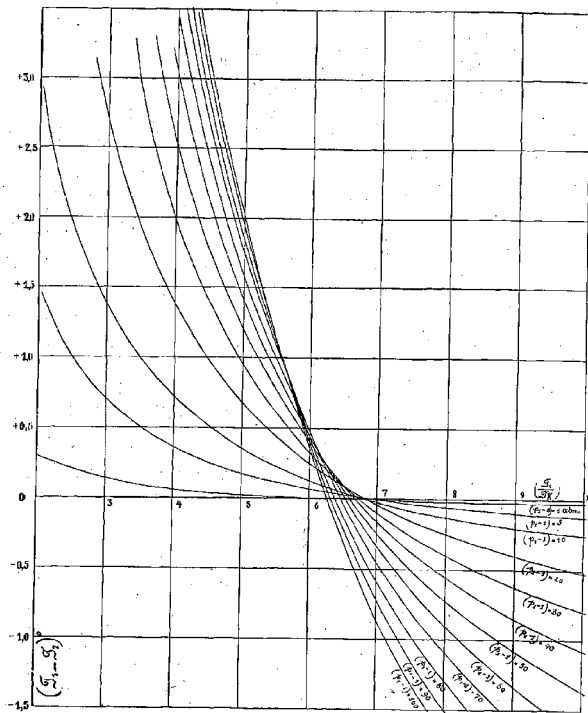


Fig. 2

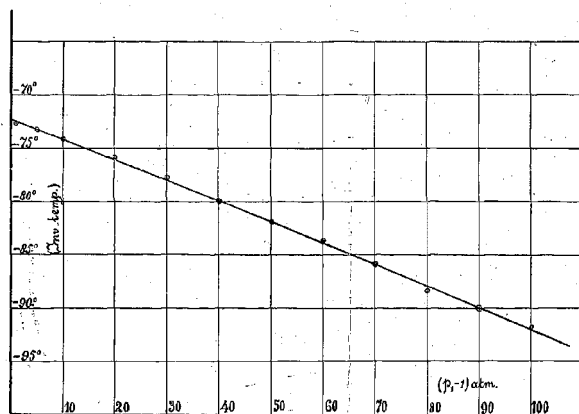


Fig. 3

a value of  $-79^{\circ}$  C. for the inversion point; but in his calculation he seems to have taken no account of the influence of initial pressure and his result is valid only for 1 atmosphere.

The results obtained by OLSZEWSKI for air and nitrogen are in marked contrast to those here obtained for hydrogen. The diagrams by which he shows graphically the relation between inversion-temperature and pressure, are lines that are strongly curved, and they exhibit, moreover, an inversion temperature increasing with increasing initial pressure. The calculations given above throw some doubt upon these results. For JOULE and KELVIN found for air at ordinary temperatures a linear relation between cooling-effect and pressure difference; this, compared with the foregoing result for hydrogen at  $-215^{\circ}$  C. renders it highly probable that air and hydrogen follow the law of corresponding states in the JOULE-KELVIN effect, as was to be expected from the facts that their equation of state follows that law, and that both gases are bi-atomic without any chemical complication in the molecule<sup>1</sup>).

Keeping in view this thermodynamic similarity of hydrogen with air or nitrogen it may be inferred from equations (4) or (5) that the inversion temperature curves for all three gases must have the same general properties, and exhibit a relation between inversion temperature and pressure approximately linear; and it can be seen that the small uncertainty in the changes of specific heat with temperature for the different gases cannot account for OLSZEWSKI's finding an opposite effect of initial pressure.

Thus we must conclude that expansion through a reduction-valve of the same construction as that used by OLSZEWSKI does not satisfy the conditions embodied in equations (3) and (15) governing a process at the beginning and end of which the enthalpy has the same value.

A subsequent paper dealing with the experimental portion of this research will show that the cause of this discrepancy can lie in the conditions under which the expansions in OLSZEWSKI's experiments were carried out.

<sup>1</sup>) Cf. H. KAMERLINGH ONNES: Zitt. Versl. Januari 1896, Comm. Phys. Lab. Leiden. No. 23.

DANIEL BERTHELOT: Journ. de Phys. Mars (1903); and

EDGAR BUCKINGHAM: Bull. Bur. Stand. (3), 2, (1907).