The Variation in the Ratio of the Specific Heats of a Gas at the Temperature of Liquid Air.

By C. M. Smith.

Introduction.—The value of the ratio of the specific heat of a gas at constant pressure, to the specific heat at constant volume, $k = \dfrac{C_p}{C_v}$, has occupied the attention of physicists since the time of Newton. It was well understood by him that the values for the velocity of sound in a gas as calculated from his formula $V = \sqrt{\dfrac{elasticity}{density}}$, were not in accord with observed values, and being impressed by this discordance he was moved to make certain violent assumptions concerning the relative magnitudes of the gas molecules and the inter-molecular spaces, together with the relative velocities of sound in each. The true explanation of the discordance was first suggested by LaGrange, who pointed out that the elasticity of a gas might be augmented faster than its density, under compression, although it remained for LaPlace, in 1816, to develop the complete theory, and elucidate the necessity for regarding the adiabatic changes in volume, the modified equation being $V = \sqrt{\dfrac{elasticity}{density}} \times k$, where k is the ratio of the adiabatic and isothermal elasticities, likewise the ratio of the specific heats. Since that time more than a score of investigators have occupied themselves with the determination of the value of k[1], under the various conditions of temperature and pressure, and the importance attached to the determination of k will be apparent from the following considerations.

With a value of k assumed as known, its use in Newton's equation is convenient for studying various physical constants of a gas, and in small quantities of the gas, values of the velocity of sound and specific heats may be determined or compared. Furthermore a knowledge of the

[1] For an exhaustive review of the history of the problem, see Maneuvrier, Jour. de Physique, 4, 1895.

value of k is important because of its entrance into several of the fundamental equations of thermodynamics, and also because it furnishes an excellent criterion for the correctness of the assumptions made in the kinetic gas theory, concerning the distribution of the energy within the molecule. In view of these intimate correlations of the value of k with other fundamental factors it is important to study its variation under different conditions of pressure and temperature for the same gas.

For constant pressure Wüllner[2] found practically a constant value of k between 0° and 100° C., for air. Witkowski[3] has found evidence of a variation in k with both temperature and pressure, from theoretical considerations. Luduc[4] shows that k should decrease with rising temperature and with falling pressure. Stevens[5] finds a value of 1.34 for k at 1000°, and Kalähne[6] shows that k decreases with rising temperature, reaching a value 1.39 for 900°. S. R. Cook,[7] working with liquid air temperatures, finds the value of k for air to be 1.35 (nearly), and Valentiner[8] in an exhaustive study of the dependence of k in nitrogen upon pressure, at liquid air temperatures, finds the value of k to increase, approximately in proportion to the ratio of the pressure to the saturation pressure for the temperature used.

In this connection it was suggested to the writer by Professor Röntgen, that a study of the value of k should be undertaken for constant pressure and liquid air temperature, and under his direction the present work was carried out during the winter and spring semesters of 1901, in the Physical Institute at Munich. Two series of observations were carried through:

I. For constant pressure, the ratio of values of k for the temperatures of melting ice and boiling water was determined, the gas used being air, free from moisture and CO_2. Values under these conditions had been determined by Wüllner (loc. cit.), and were here repeated as a means of checking the method.

II. For constant pressure, the same ratio was determined over a range of temperature from that of the room, about 20° C., to that

[2] Ann. der Physik 4, 1878.
[3] Sci. Abs. 3, 1900, p. 387.
[4] Sci. Abs. 3, 1900, p. 29.
[5] Sci. Abs. 4, 1901. p. 847.
[6] Ann. der Physik 11. 1903, p. 225.
[7] Phys. Rev. 23, 1906, p. 232.
[8] Ann. der Physik 15, 1904.

of liquid air, boiling freely under atmospheric pressure, about —190° C., the gas in this series being pure nitrogen.

Values were calculated for both series using the simple relations given in equation (6), and for series I the results were in close agreement with those of Wüllner. The assumption that Gay Lussac's law holds for nitrogen at low temperatures was however regarded as questionable, and results for series II were not at that time published. Subsequently the density-pressure relation for low temperatures was investigated for nitrogen by Bestelmeyer and Valentiner[9] in the Institute at Munich, and resulted in the establishment of the following empirical relation between pressure volume and temperature:—

$pv = h_1T — (h_2 — h_3T)p$, where T is the absolute temperature, p is the pressure, and v is the specific volume, the constants having values $h_1=0.27774$, $h_2=0.03202$, and $h_3=000253$. This relation introduced into the general equations gives (13). Making use of (13) the data of series II have been recomputed, and the results are given in table IV.

Subsequent to the experimental work of I and II, Valentiner[10] has made use of the same apparatus used by the writer, with certain modifications and improvements, for investigating the dependence of k upon pressure, for nitrogen, at liquid air temperatures.

THEORY.—The method used was that of Kundt's dust figures. Two glass tubes, maintained at different temperatures, had set up in them systems of standing waves by means of the longitudinal vibrations of the same glass rod. The frequency of the waves was the same within both tubes, and from measurements of the wave lengths, as shown by the dust figures, the variations in k could be determined.

The velocity of sound in any homogeneous medium is given by the equation

$$V^2 = — v^2 \frac{\partial p}{\partial v} = 4n^2 l^2. \tag{1}$$

where v is the specific volume, and p is the pressure, the negative sign meaning that a decrease in pressure corresponds to an increase in specific volume. It must be remembered that the standing wave in the tube has a wave length half as great as that for the progressive wave of the same

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[9] Ann. der Physik, 15, p. 61.

[10] Ann. der Physik, 15, p. 74.

frequency, and throughout λ will be used to mean the inter-nodal distance for the systems of standing waves. For a perfect gas the adiabatic equation $(pv^k=constant)$ must be used, whence

$$\frac{\partial p}{\partial v} = -\frac{pk}{v}. \tag{2}$$

Substituting this value in (1)

$$V^2 = \frac{v^2 pk}{v} = kpv = 4n^2\lambda^2. \tag{3}$$

Let equation (3) refer to the tube B. Fig. 1, in series I, which contains air, and is at $0°$ C., and let a similar equation with subscripts apply to the tube A in the steam bath.

$$V^2{}_1 = k_1\, p_1\, v_1 = 4\, n^2{}_1\, \lambda^2{}_1. \tag{4}$$

Dividing (4) by (3) and solving for the ratio $\dfrac{k_1}{k}$.

$$\frac{k_1}{k} = \frac{\lambda^2{}_1\, v}{\lambda^2\, v_1}. \tag{5}$$

From Gay Lussac's law specific volumes are directly proportional to absolute temperatures, whence

$$\frac{k_1}{k} = \frac{\lambda^2{}_1\, T}{\lambda^2\, T_1}. \tag{6}$$

From (6) the results given in table I are calculated.

For series II however, using nitrogen at liquid air temperature, the p–v–T relation to *Bestelmeyer and Valentine was used,*

$$p\ v=0.27774\ T-(0.03202-0.000253\ T)p \tag{7}$$

Substituting in the fundamental equation

$$\left(\frac{\partial p}{\partial v}\right)_Q = k\left(\frac{\partial p}{\partial v}\right)_T \tag{8}$$

the value of $\dfrac{\partial p}{\partial v}$ for constant temperature, as determined by differentiating (7),

$$\left(\frac{\partial p}{\partial v}\right)_Q = \frac{k\,p}{v + (h_2 - h_3\, T)} \tag{9}$$

and substituting this in (1).

$$V^2 = \frac{v^2 \, k \, p}{v + (h_2 - h_3 \, T)} = \frac{k \, p^2 \, v^2}{h_1 \, T} = 4 \, n^2 \, \lambda^2 \tag{10}$$

Writing equation (10) with subscripts referring to the tube B Fig. 1, as used in series II with nitrogen, at a temperature of liquid air,

$$\frac{k_1 \, p^2_1 \, v^2_1}{h_1 \, T_1} = 4 \, n^2_1 \, \lambda^2_1 \tag{11}$$

Dividing (11) by (3),

$$\frac{k_1 \, p^2_1 \, v^2_1}{k \, p \, v} = \frac{4 \, n^2_1 \, \lambda_1 \, h_1 \, T_1}{4 \, n^2 \, \lambda^2} \quad \text{whence} \quad \frac{k_1}{k} = \frac{p \, v \, h_1 \, T_1 \, \lambda^2_1}{p^2_1 \, v^2_1 \, \lambda^2} \tag{12}$$

For normal conditions $pv = 76 \, (1+at)$, whence

$$\frac{k^1}{k} = \frac{\lambda^2_1}{\lambda^2} 76 \, (1 + a \, t) \frac{h_1 \, T_1}{p^2_1 \, v^2_1} \tag{13}$$

The product $p_1^2 v_1^2$, referring as it does to nitrogen at liquid air temperature, must be computed from the empirical equation (7). Equation (13) is used for the calculation of results for series II, given in table IV.

DESCRIPTION OF APPARATUS AND METHOD.—A general view of the apparatus as mounted for use is shown in Fig. 1, the essential features of which are shown in Fig. 2. Two glass tubes, A and B, Fig. 2, about 3.2 cm. in diameter, were bent at right angles, about 30 cm. from the ends, the horizontal portions being about 80 cm. long. These were mounted on a rectangular frame of wood, a a a a. This frame was hung with its plane vertical, and was capable of rotation about a pivot at the point O. The entire structure could be tilted forward slightly about an axis XX'. A glass rod e f g, 100 cm. long, with enlarged ends, was clamped at points $\frac{1}{4}$ and $\frac{3}{4}$ of its length from its ends, the supports for the rod at these points being of rubber, and serving at the same time to close the ends of the tubes. Through these rubber stoppers were passed small delivery tubes, for introducing the gas used. Adjustable pistons were inserted through similar rubber stoppers at c and d. The upper tube was surrounded by a double walled vessel made of tinned copper, and covered with a layer of heavy felt. This vessel had a closely fitting double cover, provided with mica windows through which the thermometers were read. It was also provided with inlet, outlet and drainage tubes, so that steam could be passed in and the temperature of boiling water indefinitely maintained about the enclosed tube A. A long trough was made of such dimensions that it could be raised up about the lower tube B, and when filled with

melting ice the temperature of B could be held at 0° throughout the necessary time interval. For the series II, a trough of special design to contain liquid air was used. This was made of three layers of thin sheet tin, with
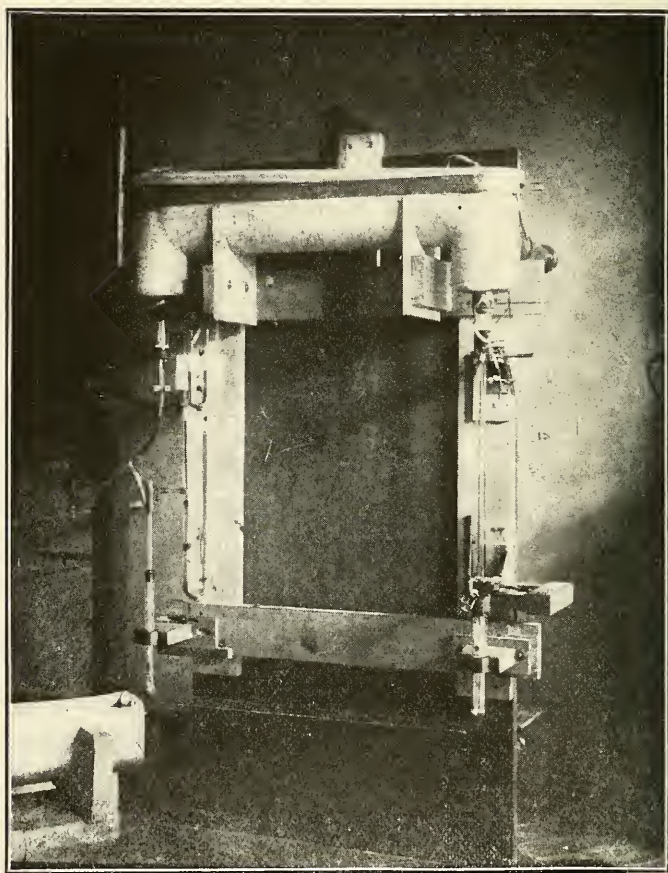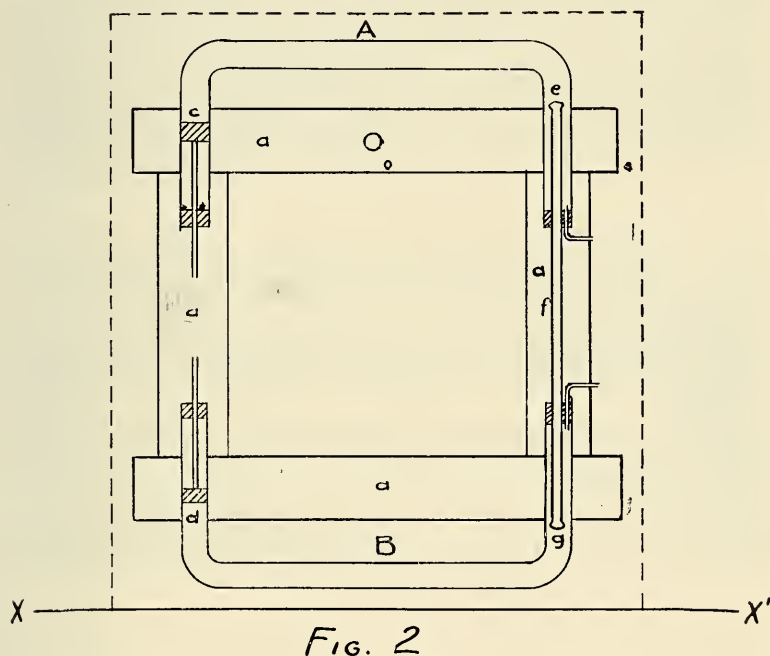

Fig. 1.

a U shaped cross section, nested together with thick layers of felt between. This is shown in the lower part of Fig. 1.

A small quantity of anhydrous quartz powder was placed in the tubes A and B, and uniformly distributed in a thin line along the bottom of the tubes by rocking the frame about O, and gently tapping the tubes with a

pencil. After this linear distribution of the powder the entire structure
was tilted forward slightly about XX', and the line of the powder was made
to seek the lowest part of the tubes by gentle tapping. On tilting the
frame back to its vertical position, the line of powder was raised slightly
along the side of the tubes, and when the glass rod e f g was rubbed at
its middle point with a piece of moistened flannel, its longitudinal vibra-
tion was communicated to the gas in both tubes, setting up systems of

FIG. 2

stationary waves, and causing the powder to fall down at the points of
maximum disturbance as shown in Fig. 3. These festoon like figures were
sharp and uniform, and capable of accurate measurement, the inter-nodal
distances giving the wave lengths of the standing waves within the tubes.
Each of the tubes carried near the ends of the horizontal portions, a pair
of felt covered brass rings. To the under side of these rings could be
quickly attached by means of set screws, the brass meter scale for measur-
ing the figures. A sliding sleeve which could be slipped over the tube was
provided with a vernier reading to one-tenth mm., which played over the

brass scale beneath, and on the sleeve was a fiducial line, in the form of a fine black wire. Three independent settings were made on each nodal point, the mean being taken as the position of the node. Since the figures were formed at temperatures different from those at which they were measured, the corresponding corrections for the expansion and contraction of the glass tubes were applied.
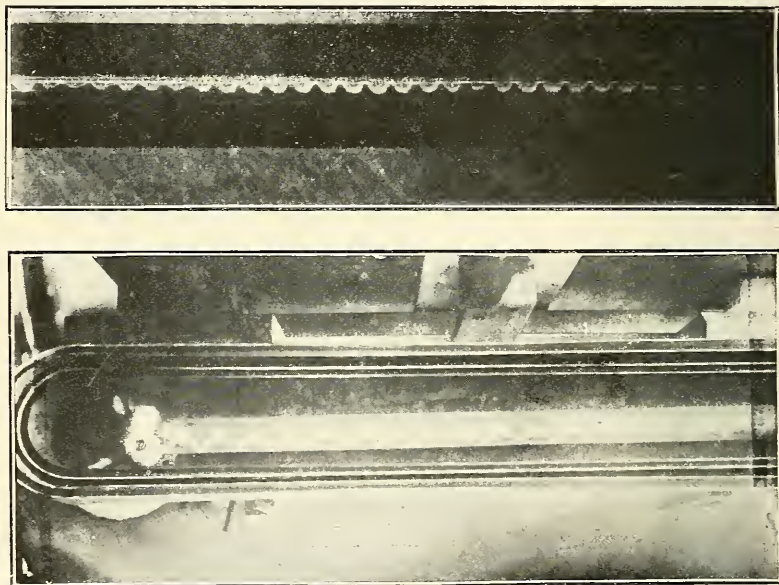
Fig. 3.

From such a series of measured inter-nodal distances the most proba-ble value of the wave length was calculated from the formula,

$$\frac{(n-1)\,(a.-a_1)+(n-3)\,(a_{n-1}-a_2)\;\cdots\cdots\cdots\cdots}{\dfrac{n\,(n^2-1)}{1\,.\,.\,.3}}$$

where n is the number of settings, and $a_1\text{-}a_2\text{-}a_3$ are the respective settings.

The writer is indebted to Mr. P. P. Koch for a complete calibration of the brass scale used, in terms of the standard meter bar belonging to the Institute. Corresponding corrections have been computed and applied to all the measurements of both series.

Procedure, Series I.—For this series of measurements the tube A was kept at steam temperature, while the tube B was packed in melting ice. The tubes were first carefully cleaned, washed with acid and alkali solutions, rinsed and dried, then mounted in place as in Fig. 2. Dry air free from CO_2 was drawn through them for some time, meanwhile gently warming them with bunsen burners. A small amount of the quartz powder, previously heated and cooled in a dessicator, was introduced, and the dry air suction continued for some time. The apparatus was then rocked and tilted as described above in order to effect a proper distribution of the powder, steam was admitted about A and the ice bath placed about B. After a period ranging from one to two hours, with both tubes open to the atmosphere through the drying train, the glass rod was rubbed, the temperatures and atmospheric pressure were observed and the steam and ice baths were withdrawn. After some hours the figures were measured in the manner above described. The thermometers used were frequently compared with standards, and the temperature in the steam jacket was constantly checked from standard barometer readings. One complete set of average wave length measurements is given in table I, and the data for eight such experiments, together with calculated values of $\dfrac{k_0}{k_{100}}$ are given in table II.

Tube A, in Steam.		Tube B, in Melting Ice.	
55.43	λ	63.73	λ
93.50	38.07	96.47	32.74
132.13	38.63	129.23	32.76
170.37	38.24	162.03	32.80
208.80	38.43	194.50	32.47
246.80	38.00	227.60	33.10
285.13	38.33	260.80	33.20
323.47	38.34	293.77	32.97
361.60	38.13	326.03	32.26
399.95	38.35	358.97	32.94
438.17	38.22	391.63	32.66
476.23	38.06	424.93	32.30
514.33	38.10	457.87	32.94
553.10	38.77	490.50	32.63
591.20	38.10	523.10	32.60
		556.00	32.90
		589.17	33.17
Most probable value of		Most probable value of	
$\lambda = 38.262$ mm. $\pm$ 0.01,		$\lambda = 32.838$ mm. $\pm$ 0.01,	
e $=$ 0.225 mm.		e $=$ 0.279.	

Table 1.

From the mean value of λ from table II, it would appear that the value does not vary from unity by more than one-tenth of one per cent. An unfavorable combination of errors could affect the single values by three-tenths of one per cent.

	Tube A, in Steam.			Tube B, in Ice Bath.			
Exp.	λ meas.	λ cor.	T. abs.	λ meas.	λ cor.	T. abs.	$\dfrac{k_0}{k_{100}}$
1	38.287	38.325	370.80	32.862	32.867	272.5	1.000758
2	38.262	38.299	370.76	32.838	32.842		1.000485
3	38.303	38.339	371.12	32.860	32.864		1.000707
4	38.234	38.271	370.49	32.846	32.851		1.001770
5	38.252	38.288	370.67	32.843	32.848		1.001180
6	38.275	38.312	370.87	32.807	32.811		0.998216
7	38.231	38.268	370.84	32.863	32.869		1.003972
8	38.291	38.328	370.91	32.865	32.869		1.001020
						mean 1.001013 $\pm$ 0.000376	

Table 2.

Procedure, Series II. For the second series of measurements the procedure was substantially the same as that for the first. Carefully dried and purified nitrogen was introduced into the tubes. The upper tube surrounded by cotton and enclosed in the double walled jacket, was allowed to assume the temperature of the room, its thermometer being read through the mica windows. The lower tube, 2.2 cm. in diameter, was immersed in the liquid air bath, the top of the tube being 2 or 3 cm. below the surface. Temperatures of the liquid air were read by means of a constantan-iron thermo-junction and a sensitive millivoltmeter, which was provided with a calibration curve from the Reichsanstalt. These temperatures were checked by evaporating samples of the liquid air, mixing with hydrogen and exploding by means of an electric spark in a eudiometer tube. From percentages of oxygen thus found temperatures were interpolated from Baly's curves.[11]

[11] Phil. Mag. 49, June 1899.

Tube A, at Room Temp.		Tube B, in Liquid Air.	
	λ	179.12	λ
44.88	34.30	196.75	17.63
79.38	33.69	215.03	18.28
113.07	34.83	233.33	18.30
147.90	34.55	251.37	18.04
182.45	34.70	270.20	18.83
217.15	34.72	288.27	18.07
251.87	34.35	306.15	17.88
286.22	33.63	324.37	18.22
319.85	34.72	342.60	18.23
354.57	35.03	360.18	17.58
389.60	34.10	378.80	18.62
423.70	33.45	396.72	17.92
457.15	35.02	415.43	18.71
492.17	34.30	433.32	17.89
526.47	34.95	451.18	17.86
561.42		469.55	18.37
		487.75	18.20
		505.75	18.00
		524.03	18.28
		541.97	17.94
		559.82	17.85
		587.15	18.35

Most probable value of
$\lambda = 34.421 \pm 0.016$,
$e = 0.44$.

Most probable value of
$\lambda = 18.152 \pm 0.007$,
$e = 0.32$.

Table 3.

	Tube A, in Liquid Air.					Tube B, in Room Temp.				
Exp.	Vm.	T. abs.	λ meas.	λ cor.		T. abs.	λ meas.	λ cor.	p.	$\dfrac{k_1}{k}$
1	7.21	83.46	18.152	18.133		293.59	34.421	34.433	72.55	1.0477
2	7.23	82.85	18.096	18.076		294.84	34.502	34.514	72.4	1.0498
3	7.285	81.18	17.938	17.917		295.24	34.555	34.572	72.1	1.0553
4	7.225	83.00	18.011	17.994		296.84	34.704	34.706	72.0	1.0336
5	7.200	83.76	18.195	18.176		296,04	34.593	34.606	72.0	1.0464
6	7.200	83.76	18.237	18.118		296.64	34.608	34.623	72.5	1.0523
										mean 1.0475 $\pm$ 0.002

Table 4.

[13—26988]

About five liters of liquid air were required for an experiment. The tube was left in the bath for about one hour before the glass rod was sounded. Corrections were applied for scale errors and for the expansion of the tube prior to measurement. The coefficient of expansion[12] for glass at liquid air temperature was taken as 0.0000073.

One complete set of average wave length measurements for an experiment is given in table III, and the assembled data together with the calculated values of $\dfrac{k_1}{k}$ are given in table IV. The subscripts relate to liquid air temperatures. All temperatures are referred to $-273°.04$ as the absolute zero[13].

Any change in T will alter $\dfrac{k_1}{k}$ inversely in about the same ratio. Temperatures were probably accurate to one-fifth of one per cent. An unfavorable combination of errors might invest $\dfrac{k_1}{k}$ with an error of onehalf of one per cent.

From the results in table IV it would appear that k for liquid air temperature is something more than four per cent greater than for ordinary temperatures, about $22°$ C.

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[12] Phil. Mag. 49, June, 1899.

[13] Ann. der Physik 9, p. 1149.

Purdue University, Dec., 1910.