

surrounding them, and that similar experiments, more recently made by M. REGNAULT, should have led only to the same negative conclusion.

If, on the other hand, the air were neither allowed to take in heat from nor to part with heat to the surrounding matter in any part of the apparatus, it would experience a resultant cooling effect (after arriving at a state of uniformity of temperature as well as pressure) to be calculated by dividing the preceding expression for the quantity of heat which would be required to compensate it, by  $\cdot 17$ , the specific heat of air under constant pressure. The cooling effect on the air itself therefore amounts to

$$0^{\circ}\cdot 27 \times \frac{P-P'}{\Pi}, *$$

which is equal to  $2^{\circ}\cdot 8$ , for air expanding, as in Mr. JOULE's experiment, from 21 atmospheres to half that pressure, and is 900 times as great as the thermometric effect when spread over the water and copper of the apparatus. Hence our present system, in which the thermometric effect on the air itself is directly observed, affords a test hundreds of times more sensitive than the method first adopted by Mr. JOULE, and no doubt also than that recently practised by M. REGNAULT, in which the dimensions of the various parts of the apparatus (although not yet published) must have been on a corresponding scale, or in somewhat similar proportions, to those used formerly by Mr. JOULE.

## SECTION II. *On the Density of Saturated Steam.*

The relation between the heat evolved and the work spent, approximately established by the air-experiments communicated to the Royal Society in 1844, was subjected to an independent indirect test by an application of CARNOT's theory, with values of "CARNOT's function" which had been calculated from REGNAULT's data as to the pressure and latent heat of steam, and the assumption (in want of experimental data), that the density varies according to the gaseous laws. The verification thus obtained was very striking, showing an exact agreement with the relation of equivalence at a temperature a little above that of observation, and an agreement with the actual experimental results quite within the limits of the errors of observation; but a very wide discrepancy from equivalence for other temperatures. The following Table is extracted from the Appendix to the "Account of CARNOT's Theory" in which the theoretical comparison was first made, to facilitate a comparison with what we now know to be the true circumstances of the case.

\* It is worthy of remark that this, the expression for the cooling effect experienced by a mass of atmospheric air expanding from a bulk in which its pressure is  $P$  to a bulk in which, at the same (or very nearly the same) temperature its pressure is  $P'$ , and spending all its work of expansion in friction among its own particles, agrees very closely with the expression,  $\cdot 26 \times \frac{P-P'}{\Pi}$ , for the cooling effect in the somewhat different circumstances of our experiments.

“Table of the Values of  $\frac{\mu(1 + Et)}{E} = [W]$ .”

“Work requisite to produce a unit of heat by the compression of a gas $\frac{[\mu](1 + Et)}{E} = [W]$ .”	“Temperature of the gas <i>t</i> .”	“Work requisite to produce a unit of heat by the compression of a gas $\frac{[\mu](1 + Et)}{E} = [W]$ .”	“Temperature of the gas <i>t</i> .”
ft. lbs. 1357·1	0°	ft. lbs. 1446·4	120°
1368·7	10	1455·8	130
1379·0	20	1465·3	140
1388·0	30	1475·8	150
1395·7	40	1489·2	160
1401·8	50	1499·0	170
1406·7	60	1511·3	180
1412·0	70	1523·5	190
1417·6	80	1536·5	200
1424·0	90	1550·2	210
1430·6	100	1564·0	220
1438·2	110	1577·8	230”

We now know, from the experiments described above in the present paper, that the numbers in the first column, and we may conclude with almost equal certainty, that the numbers in the third also, ought to be each very nearly the mechanical equivalent of the thermal unit. This having been ascertained to be 1390 (for the thermal unit Centigrade) by the experiments on the friction of fluids and solids, communicated to the Royal Society in 1849, and the work having been found above to fall short of the equivalent of heat produced, by about  $\frac{1}{417}$ , at the temperature of the air-experiments at present communicated, and by somewhat less at such a higher temperature as 30°, we may infer that the agreement of the tabulated theoretical result with the fact is perfect at about 30° Cent. Or, neglecting the small discrepancy by which the work truly required falls short of the equivalent of heat produced, we may conclude that the true value of  $\frac{\mu(1 + Et)}{E}$  for all temperatures is about 1390; and hence that if [W] denote the numbers shown for it in the preceding table,  $\mu$  the true value of CARNOT’S function, and  $[\mu]$  the value tabulated for any temperature in the “Account of CARNOT’S Theory,” we must have, to a very close degree of approximation,

$$\mu = [\mu] \times \frac{1390}{[W]}.$$

But if  $[\sigma]$  denote the formerly assumed specific gravity of saturated steam,  $p$  its pressure, and  $\lambda$  its latent heat per pound of matter, and if  $\rho$  be the mass (in pounds) of water in a cubic foot, the expression from which the tabulated values of  $[\mu]$  were calculated is

$$[\mu] = \frac{1 - [\sigma]}{\rho[\sigma]} \frac{1}{\lambda} \frac{dp}{dt};$$

while the true expression for CARNOT’S function in terms of properties of steam is

$$\mu = \frac{1 - \sigma}{\rho\sigma} \frac{1}{\lambda} \frac{dp}{dt}.$$

Hence 
$$\frac{\mu}{[\mu]} = \frac{[\sigma]}{\sigma} \cdot \frac{1-\sigma}{1-[\sigma]}$$

or, approximately, since  $\sigma$  and  $[\sigma]$  are small fractions,

$$\frac{\mu}{[\mu]} = \frac{[\sigma]}{\sigma}$$

We have, therefore, 
$$\frac{\sigma}{[\sigma]} = \frac{[W]}{1390}$$

and we infer that the densities of saturated steam in reality bear the same proportions to the densities assumed, according to the gaseous laws, as the numbers shown for different temperatures in the preceding Table bear to 1390. Thus we see that the assumed density must have been very nearly correct, about 30° Cent., but that the true density increases much more at the high temperatures and pressures than according to the gaseous laws, and consequently that steam appears to deviate from BOYLE'S law in the same direction as carbonic acid, but to a much greater amount, which in fact it must do unless its coefficient of expansion is very much less, instead of being, as it probably is, somewhat greater than for air. Also, we infer that the specific gravity of steam at 100° Cent., instead of being only  $\frac{1}{1693.5}$ , as was assumed, or about  $\frac{1}{1700}$ , as it is generally supposed to be, must be as great as  $\frac{1}{1645}$ . Without using the preceding Table, we may determine the absolute density of saturated steam by means of a formula obtained as follows. Since we have seen the true value of  $W$  is nearly 1390, we must have, very approximately,

$$\mu = \frac{1390E}{1 + Et}$$

and hence, according to the preceding expression for  $\mu$  in terms of the properties of steam,

$$g\sigma = \frac{1-\sigma}{1390E}(1 + Et) \frac{1}{\lambda} \frac{dp}{dt},$$

or, within the degree of approximation to which we are going (omitting as we do fractions such as  $\frac{1}{400}$  of the quantity evaluated),

$$g\sigma = \frac{(1 + Et)}{1390E \cdot \lambda} \frac{dp}{dt}$$

an equation by which  $g\sigma$ , the mass of a cubic foot of steam in fraction of a pound, or  $\tau$ , its specific gravity (the value of  $g$  being 63.887), may be calculated from observations such as those of REGNAULT on steam. Thus, using Mr. RANKINE'S empirical formula for the pressure which represents M. REGNAULT'S observations correctly at all temperatures, and M. REGNAULT'S own formula for the latent heat; and taking  $E = \frac{1}{273}$ ,

we have 
$$g\sigma = \frac{273 + t}{1390} \frac{p \left( \frac{\beta}{(274.6 + t)^2} + \frac{2\gamma}{(274.6 + t)^3} \right) \times .4342945}{(606.5 + 0.305t) - (t + .00002t^2 + .0000003t^3)}$$

with the following equations for calculating  $p$  and the terms involving  $\beta$  and  $\gamma$ ;

$$\log_{10} p = \alpha - \frac{\beta}{t + 274.6} - \frac{\gamma}{(274.6 + t)^2},$$

$$\alpha = 4.950433 + \log_{10} 2114 = 8.275538$$

$$\log_{10} \beta = 3.1851091,$$

$$\log_{10} \gamma = 5.0827176.$$

The densities of saturated steam calculated for any temperatures, either by means of this formula, or by the expression given above, with the assistance of the Table of values of  $[W]$ , are the same as those which, in corresponding on the subject in 1848, we found would be required to reconcile REGNAULT'S actual observations on steam with the results of air-experiments which we then contemplated undertaking, should they turn out, as we now find they do, to confirm the relation which the air-experiments of 1844 had approximately established. They should agree with results which CLAUSIUS\* gave as a consequence of his extension of CARNOT'S principle to the dynamical theory of heat, and his assumption of MAYER'S hypothesis.

SECTION III. *Evaluation of CARNOT'S Function.*

The importance of this object, not only for calculating the efficiency of steam-engines and air-engines, but for advancing the theory of heat and thermo-electricity, was a principal reason inducing us to undertake the present investigation. Our preliminary experiments, demonstrating that the cooling effect which we discovered in all of them was very slight for a considerable variety of temperatures (from about  $0^\circ$  to  $77^\circ$  Cent.), were sufficient to show, as we have seen in §§ I. and II., that  $\frac{\mu(1 + Et)}{E}$  must be very nearly equal to the mechanical equivalent of the thermal unit; and therefore we have

$$\mu = \frac{J}{\frac{1}{E} + t} \text{ approximately,}$$

or, taking for  $E$  the standard coefficient of expansion of atmospheric air, .003665,

$$\mu = \frac{J}{272.85 + t}.$$

At the commencement of our first communication to the Royal Society on the subject, we proposed to deduce more precise values for this function by means of the equation

$$\frac{J}{\mu} = \frac{JK\delta - (P'V' - PV) + w}{\frac{dw}{dt}};$$

where

$$w = \int_v^{v'} p dv;$$

\* POGGENDORFF'S Annalen, April and May 1850.

$v$ ,  $V$ ,  $V'$  denote, with reference to air at the temperature of the bath, respectively, the volumes occupied by a pound under any pressure  $p$ , under a pressure,  $P$ , equal to that with which the air enters the plug, and under a pressure,  $P'$ , with which the air escapes from the plug; and  $JK\delta$  is the mechanical equivalent of the amount of heat per pound of air passing that would be required to compensate the observed cooling effect  $\delta$ . The direct use of this equation for determining  $\frac{J}{\mu}$  requires, besides our own results, information as to compressibility and expansion which is as yet but very insufficiently afforded by direct experiments, and is consequently very unsatisfactory, so much so that we shall only give an outline, without details, of two plans we have followed, and mention the results. First, it may be remarked that, approximately,

$$w = (1 + Et)H \log \frac{P}{P'}, \text{ and } \frac{dw}{dt} = EH \log \frac{P}{P'},$$

$H$  being the "height of the homogeneous atmosphere," or the product of the pressure into the volume of a pound of air, at  $0^\circ$  Cent.; of which the value is 26224 feet. Hence, if  $\mathbf{E}$  denote a certain mean coefficient of expansion suitable to the circumstances of each individual experiment, it is easily seen that  $\frac{w}{\frac{dw}{dt}}$  may be put under the form  $\frac{1}{\mathbf{E}} + t$ , and thus we have

$$\frac{J}{\mu} = \frac{1}{\mathbf{E}} + t + \frac{JK\delta - (P'V' - PV)}{EH \log \frac{P}{P'}},$$

since the numerator of the fraction constituting the last term is so small, that the approximate value may be used for the denominator. The first term of the second member may easily be determined analytically in general terms; but as it has reference to the rate of expansion at the particular temperature of the experiment, and not to the mean expansion from  $0^\circ$  to  $100^\circ$ , which alone has been investigated by REGNAULT and others who have made sufficiently accurate experiments, we have not data for determining its values for the particular cases of the experiments. We may, however, failing more precise data, consider the expansion of air as uniform from  $0^\circ$  to  $100^\circ$ , for any pressure within the limits of the experiments (four or five atmospheres); because it is so for air at the atmospheric density by the hypothesis of the air-thermometer, and REGNAULT's comparisons of air-thermometers in different conditions show for all, whether on the constant-volume or constant-pressure principle, with density or pressure from one-half to double the standard density or pressure, a very close agreement with the standard air-thermometer. On this assumption then, when we take into account REGNAULT's observations regarding the effect of variations of density on the coefficient of increase of pressure, we find that a suitable mean coefficient  $\mathbf{E}$  for the circumstances of the preceding formula for  $\frac{J}{\mu}$  is expressed,

to a sufficient degree of approximation, by the equation

$$E = .0036534 + \frac{.0000441}{3.81} \frac{P - P'}{\Pi \log \frac{P}{P'}}$$

Also, by using REGNAULT'S experimental results on compressibility of air as if they had been made, not at 4°·75, but at 16° Cent., we have estimated P'V' - PV for the numerator of the last term of the preceding expression. We have thus obtained estimates for the value of  $\frac{J}{\mu}$ , from eight of our experiments (not corresponding exactly to the arrangement in seven series given above), which, with the various items of the correction in the case of each experiment, are shown in the following Table.

No. of experiment.	Pressure of air forced into the plug.	Barometric pressure.	Excess.	Cooling effect.	Correction by cooling effect.	Correction by reciprocal coefficient of expansion.	Correction by compressibility (subtracted).	Value of J divided by CARNOT'S function for 16° Cent.
	P.	P'.	P - P'.	δ.	$\frac{JK\delta}{EH \log \frac{P}{P'}}$	$\frac{1}{E} - \frac{1}{E'}$	$\frac{P'V' - PV}{EH \log \frac{P}{P'}}$	$\frac{J}{\mu_{16}}$
I.	20·943	14·777	6·166	0·105	1·031	0·174	0·290	289·4
II.	21·282	14·326	6·956	0·109	0·942	0·168	0·291	289·3
III.	35·822	14·504	21·318	0·375	1·421	0·519	0·412	289·97
IV.	33·310	14·692	18·618	0·364	1·523	0·470	0·372	290·065
V.	55·441	14·610	40·831	0·740	1·892	0·923	0·480	289·705
VI.	53·471	14·571	38·900	0·676	1·814	0·883	0·475	289·59
VII.	79·464	14·955	64·509	1·116	2·272	1·379	0·592	289·69
VIII.	79·967	14·785	65·182	1·142	2·300	1·376	0·586	289·73
							Mean ...	289·68

In consequence of the approximate equality of  $\frac{J}{\mu}$  to  $\frac{1}{E} + t$ , its value must be, within a very minute fraction, less by 16 at 0° than at 16°; and, from the mean result of the preceding Table, we therefore deduce 273·68 as the value of  $\frac{J}{\mu}$  at the freezing-point.

The correction thus obtained on the approximate estimate  $\frac{1}{E} + t = 272·85 + t$ , for  $\frac{J}{\mu}$ , at temperatures not much above the freezing-point, is an augmentation of ·83.

For calculating the unknown terms in the expression for  $\frac{J}{\mu}$ , we have also used Mr. RANKINE'S formula for the pressure of air, which is as follows:—

$$pv = H \frac{C+t}{C} \left\{ 1 - \frac{aC}{(C+t)^2} \left( \frac{1}{\rho v} \right)^{\frac{2}{3}} + \frac{hC}{C+t} \left( \frac{1}{\rho v} \right)^{\frac{1}{3}} \right\},$$

where  $C = 274·6$ ,  $\log_{10} a = .3176168$ ,  $\log_{10} h = \bar{3}·8181546$ ,

$$H = \frac{26224}{1 - a + h};$$

and,  $v$  being the volume of a pound of air when at the temperature  $t$  and under the pressure  $p$ ,  $\rho$  denotes the mass in pounds of a cubic foot at the standard atmospheric pressure of 29·9218 inches of mercury. The value of  $p$  according to this equation,

when substituted in the general expression for  $\frac{J}{\mu}$ , gives

$$\frac{J}{\mu} = C + t + \frac{JKC}{H} \delta + 3h \frac{C^{\frac{3}{2}}}{(C+t)^{\frac{3}{2}}} \left\{ \left( \frac{P}{\Pi} \right)^{\frac{1}{2}} - \left( \frac{P'}{\Pi} \right)^{\frac{1}{2}} \right\} - \frac{13}{3} a \left( \frac{C}{C+t} \right)^{\frac{8}{3}} \left\{ \left( \frac{P}{\Pi} \right)^{\frac{2}{3}} - \left( \frac{P'}{\Pi} \right)^{\frac{2}{3}} \right\} \\ \log \frac{P}{P'}$$

From this we find, with the data of the eight experiments just quoted, the following values for  $\frac{J}{\mu}$  at the temperature 16° Cent.,

289·044, 289·008, 288·849, 289·112, 288·787, 288·722, 288·505, 288·559, the mean of which is 288·82, giving a correction of only ·03 to be subtracted from the previous approximate estimate  $\frac{1}{E} + t$ .

It should be observed that CARNOT'S function varies only with the temperature; and therefore if such an expression as the preceding, derived from Mr. RANKINE'S formula, be correct, the cooling effect,  $\delta$ , must vary with the pressure and temperature in such a way as to reduce the complex fraction, constituting the second term, to either a constant or a function of  $t$ . Now at the temperature of our experiments,  $\delta$  is very approximately proportional simply to  $P - P'$ , and therefore all the terms involving the pressure in the numerator ought to be either linear or logarithmic; and the linear terms should balance one another so as to leave only terms which, when divided by  $\log \frac{P}{P'}$ , become independent of the pressures. This condition is not fulfilled by the actual expression, but the calculated results agree with one another as closely as could be expected from a formula obtained with such insufficient experimental data as Mr. RANKINE had for investigating the empirical forms which his theory left undetermined. We shall see in Section V. below, that simpler forms represent REGNAULT'S data within their limits of error of observation, and at the same time may be reduced to consistency in the present application.

As yet we have no data regarding the cooling effect, of sufficient accuracy for attempting an independent evaluation of CARNOT'S function for other temperatures. In the following section, however, we propose a new system of thermometry, the adoption of which will quite alter the form in which such a problem as that of evaluating CARNOT'S function for any temperature presents itself.

#### SECTION IV. *On an absolute Thermometric Scale founded on the Mechanical Action of Heat.*

In a communication to the Cambridge Philosophical Society\* six years ago, it

\* "On an Absolute Thermometric Scale founded on CARNOT'S Theory of the Motive Power of Heat, and calculated from REGNAULT'S observations on Steam," by Prof. W. THOMSON, Proceedings Camb. Phil. Soc. June 5, 1848, or Philosophical Magazine, Oct. 1848.

was pointed out that any system of thermometry, founded either on equal additions of heat, or equal expansions, or equal augmentations of pressure, must depend on the particular thermometric substance chosen, since the specific heats, the expansions, and the elasticities of substances vary, and, so far as we know, not proportionally with absolute rigour for any two substances. Even the air-thermometer does not afford a *perfect standard*, unless the precise constitution and physical state of the gas used (the density, for a pressure-thermometer, or the pressure, for an expansion-thermometer) be prescribed; but the very close agreement which REGNAULT found between different air- and gas-thermometers removes, for all practical purposes, the inconvenient narrowness of the restriction to atmospheric air kept permanently at its standard density, imposed on the thermometric substance in laying down a rigorous definition of temperature. It appears then that the standard of practical thermometry consists essentially in the reference to a certain numerically expressible quality of a particular substance. In the communication alluded to, the question, "Is there any principle on which an absolute thermometric scale can be founded?" was answered by showing that CARNOT'S function (derivable from the properties of any substance whatever, but the same for all bodies at the same temperature), or any arbitrary function of CARNOT'S function, may be defined as temperature, and is therefore the foundation of an absolute system of thermometry. We may now adopt this suggestion with great advantage, since we have found that CARNOT'S function varies very nearly in the inverse ratio of what has been called "temperature from the zero of the air-thermometer," that is, Centigrade temperature by the air-thermometer increased by the reciprocal of the coefficient of expansion; and we may define temperature simply as the reciprocal of CARNOT'S function. When we take into account what has been proved regarding the mechanical action of heat\*, and consider what is meant by CARNOT'S function, we see that the following explicit definition may be substituted:—

*If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperatures of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of the operations.*

To fix on a unit or degree for the numerical measurement of temperature, we may either call some definite temperature, such as that of melting ice, unity, or any number we please; or we may choose two definite temperatures, such as that of melting ice and that of saturated vapour of water under the pressure 29.9218 inches of mercury in the latitude 45°, and call the difference of these temperatures any number we please, 100 for instance. The latter assumption is the only one that can be made conveniently in the present state of science, on account of the necessity of retaining a connexion with practical thermometry as hitherto practised; but the former is far

\* Dynamical Theory of Heat, §§ 42, 43.



preferable in the abstract, and must be adopted ultimately. In the mean time it becomes a question, what is the temperature of melting ice, if the difference between it and the standard boiling-point be called  $100^\circ$ ? When this question is answered within a tenth of a degree or so, it may be convenient to alter the foundation on which the degree is defined, by assuming the temperature of melting ice to agree with that which has been found in terms of the old degree; and then to make it an object of further experimental research, to determine by what minute fraction the range from freezing to the present standard boiling-point exceeds or falls short of 100. The experimental data at present available do not enable us to assign the temperature of melting ice, according to the new scale, to perfect certainty within less than two- or three-tenths of a degree; but we shall see that its value is probably about  $273\cdot7$ , agreeing with the value of  $\frac{J}{\mu}$  at  $0^\circ$  found by the first method in Section III. From the very close approximation to equality between  $\frac{J}{\mu}$  and  $\frac{1}{E}+t$ , which our experiments have established, we may be sure that temperature from the freezing-point by the new system must agree to a very minute fraction of a degree with Centigrade temperature between the two prescribed points of agreement,  $0^\circ$  and  $100^\circ$ , and we may consider it as highly probable that there will also be a very close agreement through a wide range on each side of these limits. It becomes of course an object of the greatest importance, when the new system is adopted, to compare it with the old standard; and this is in fact what is substituted for the problem, the evaluation of CARNOT'S function, now that it is proposed to call the reciprocal of CARNOT'S function, temperature. In the next Section we shall see by what kind of examination of the physical properties of air this is to be done, and investigate an empirical formula expressing them consistently with all the experimental data as yet to be had, so far as we know. The following Table, showing the indications of the constant-volume and constant-pressure air-thermometer in comparison for every twenty degrees of the new scale, from the freezing-point to  $300^\circ$  above it, has been calculated from the formulæ (9), (10), and (39) of Section V. below.

Comparison of Air-thermometer with Absolute Scale.

Temperature by absolute scale in Cent. degrees from the freezing-point. $t - 273.7.$	Temperature Centigrade by constant-volume thermometer with air of specific gravity $\frac{\Phi}{v}$ . $\theta = 100 \frac{p_t - p_{273.7}}{p_{373.7} - p_{273.7}}$	Temperature Centigrade by constant-pressure air-thermometer $S = 100 \frac{v_t - v_{273.7}}{v_{373.7} - v_{273.7}}$
0	0	0
20	$20 + 0.0298 \times \frac{\Phi}{v}$	$20 + 0.0404 \times \frac{p}{\Pi}$
40	$40 + 0.0403$ "	$40 + 0.0477$ "
60	$60 + 0.0366$ "	$60 + 0.0467$ "
80	$80 + 0.0223$ "	$80 + 0.0277$ "
100	$100 + 0.0000$ "	$100 + 0.0000$ "
120	$120 - 0.0284$ "	$120 - 0.0339$ "
140	$140 - 0.0615$ "	$140 - 0.0721$ "
160	$160 - 0.0983$ "	$160 - 0.1134$ "
180	$180 - 0.1382$ "	$180 - 0.1571$ "
200	$200 - 0.1796$ "	$200 - 0.2018$ "
220	$220 - 0.2232$ "	$220 - 0.2478$ "
240	$240 - 0.2663$ "	$240 - 0.2932$ "
260	$260 - 0.3141$ "	$260 - 0.3420$ "
280	$280 - 0.3610$ "	$280 - 0.3897$ "
300	$300 - 0.4085$ "	$300 - 0.4377$ "

The standard defined by REGNAULT is that of the constant-volume air-thermometer, with air at the density which it has when at the freezing-point under the pressure of 760 mm. or 22.9218 inches of mercury, and its indications are shown in comparison with the absolute scale by taking  $\frac{\Phi}{v} = 1$  in the second column of the preceding Table.

The greatest discrepancy between 0° and 100° Cent. amounts to less than  $\frac{1}{20}$ th of a degree, and the discrepancy at 300° Cent. is only four-tenths. The discrepancies of the constant-pressure air-thermometer, when the pressure is equal to the standard atmospheric pressure, or  $\frac{p}{\Pi} = 1$ , are somewhat greater, but still very small.

SECTION V. *Physical Properties of Air expressed according to the absolute Thermodynamic scale of Temperature.*

All the physical properties of a fluid of given constitution are completely fixed when its density and temperature are specified; and as it is these qualities which we can most conveniently regard as being immediately adjustable in any arbitrary manner, we shall generally consider them as the independent variables in formulæ expressing the pressure, the specific heats, and other properties of the particular fluid in any physical condition.

Let  $v$  be the volume (in cubic feet) of a unit mass (one pound) of the fluid, and  $t$  its absolute temperature; and let  $p$  be its pressure in the condition defined by these elements.

Let also  $e$  be the “mechanical energy\*” of the fluid, reckoned from some assumed standard or zero state, that is, the sum of the mechanical value of the heat communicated to it, and of the work spent on it, to raise it from that zero state to the condition defined by  $(v, t)$ ; and let  $N$  and  $K$  be its specific heats with constant volume, and with constant pressure, respectively. Then denoting, as before, the mechanical equivalent of the thermal unit by  $J$ , and the value of CARNOT’S function for the temperature  $t$  by  $\mu$ , we have†

$$\frac{de}{dv} = \frac{J}{\mu} \frac{dp}{dt} - p \dots \dots \dots (1)$$

$$N = \frac{1}{J} \frac{de}{dt} \dots \dots \dots (2)$$

$$K = \frac{1}{J} \frac{de}{dt} + \frac{1}{J} \left( \frac{de}{dv} + p \right) \frac{\frac{dp}{dt}}{-\frac{dp}{dv}} \dots \dots \dots (3)$$

From these we deduce, by eliminating  $e$ ,

$$K - N = \frac{1}{\mu} \frac{\left( \frac{dp}{dt} \right)^2}{-\frac{dp}{dv}} \dots \dots \dots (4)$$

and

$$\frac{dN}{dv} = \frac{d \left( \frac{1}{\mu} \frac{dp}{dt} \right)}{dt} - \frac{1}{J} \frac{dp}{dt} \dots \dots \dots (5)$$

equations which express two general theorems regarding the specific heats of any fluid whatever, first published‡ in the Transactions of the Royal Society of Edinburgh, March 1851. The former (4) is the extension of a theorem on the specific heats of gases originally given by CARNOT§, while the latter (5) is inconsistent with one of his fundamental assumptions, and expresses in fact the opposed axiom of the Dynamical Theory. The use of the absolute thermo-dynamic system of thermometry proposed in Section IV., according to which the definition of temperature is

$$t = \frac{J}{\mu} \dots \dots \dots (6)$$

simplifies these equations, and they become

$$JK - JN = t \frac{\left( \frac{dp}{dt} \right)^2}{-\frac{dp}{dv}} \dots \dots \dots (7)$$

$$\frac{d(JN)}{dv} = t \frac{d^2 p}{dt^2} \dots \dots \dots (8)$$

\* Dynamical Theory of Heat, Part V.—On the Quantities of Mechanical Energy contained in a Fluid in different States as to Temperature and Density, § 82. Trans. Roy. Soc. Edin., Dec. 15, 1851.

† Ibid. §§ 89, 91.

‡ Ibid. §§ 47, 48.

§ See “Account of CARNOT’S Theory,” Appendix III. Trans. Roy. Soc. Edin., April 30, 1849, p. 565.

To compare with the absolute scale the indications of a thermometer in which the particular fluid (which may be any gas, or even liquid) referred to in the notation  $p, v, t$ , is used as the thermometric substance, let  $p_0$  and  $p_{100}$  denote the pressures which it has when at the freezing and boiling points respectively, and kept in constant volume,  $v$ ; and let  $v_0$  and  $v_{100}$  denote the volumes which it occupies under the same pressure,  $p$ , at those temperatures. Then if  $\theta$  and  $\mathfrak{S}$  denote its thermometric indications when used as a constant-volume and as a constant-pressure thermometer respectively, we have

$$\theta = 100 \frac{p - p_0}{p_{100} - p_0} \dots \dots \dots (9)$$

$$\mathfrak{S} = 100 \frac{v - v_0}{v_{100} - v_0} \dots \dots \dots (10)$$

Let also  $\epsilon$  denote the "coefficient of increase of elasticity with temperature\*," and  $\epsilon$  the coefficient of expansion at constant pressure, when the gas is in the state defined by  $(v, t)$ ; and let  $E$  and  $E$  denote the mean values of the same coefficients between  $0^\circ$  and  $100^\circ$  Cent. Then we have

$$\epsilon = \frac{dp}{p_0 dt} \dots \dots \dots (11)$$

$$\epsilon = \frac{\frac{dp}{dt}}{v_0 \times -\frac{dp}{dv}} \dots \dots \dots (12)$$

$$E = \frac{p_{100} - p_0}{100 p_0} \dots \dots \dots (13)$$

$$E = \frac{v_{100} - v_0}{100 v_0} \dots \dots \dots (14)$$

Lastly, the general expression for  $\frac{J}{\mu}$  quoted in Section II. from our paper of last year, leads to the following expression for the cooling effect on the fluid when forced through a porous plug as in our air experiments :—

$$\delta = \frac{1}{JK} \left\{ \int_v^{v'} \left( t \frac{dp}{dt} - p \right) dv + (P'V' - PV) \right\} \dots \dots \dots (15)$$

$(p, v)$   $(P', V')$   $(P, V)$ , as explained above, having reference to the fluid in different states of density, but always at the same temperature,  $t$ , as that with which it enters the plug.

From these equations, it appears that if  $p$  be fully given in terms of  $v$  and absolute values of  $t$  for any fluid, the various properties denoted by

$$JK - JN, \quad \frac{d(JN)}{dv}, \quad \theta, \quad \mathfrak{S}, \quad \epsilon, \quad \epsilon, \quad E, \quad E, \quad \text{and} \quad \delta,$$

may all be determined for it in every condition. Conversely, experimental investiga-

\* So called by Mr. RANKINE. The same element is called by M. REGNAULT the coefficient of dilatation of a gas at constant volume.

tions of these properties may be made to contribute, along with direct measurements of the pressure for various particular conditions of the pressure, towards completing the determination of the function which expresses this element in terms of  $v$  and  $t$ . But it must be remarked, that even complete observations determining the pressure for every given state of the fluid, could give no information as to the values of  $t$  on the absolute scale, although they might afford data enough for fully expressing  $p$  in terms of the volume and the temperature with reference to some particular substance used thermometrically. On the other hand, observations on the specific heats of the fluid, or on the thermal effects it experiences in escaping through narrow passages, may lead to a knowledge of the absolute temperature,  $t$ , of the fluid when in some known condition, or to the expression of  $p$  in terms of  $v$ , and absolute values of  $t$ ; and accordingly the formulæ (7), (8), and (15) contain  $t$  explicitly, each of them in fact essentially involving CARNOT'S function. As for actual observations on the specific heats of air, none which have yet been published appear to do more than illustrate the theory, by confirming (as MR. JOULE'S, and the more precise results more recently published by M. REGNAULT, do), within the limits of their accuracy, the value for the specific heat of air under constant pressure which we calculated\* from the *ratio of the specific heats*, determined according to LAPLACE'S theory by observations on the velocity of sound, and the *difference of the specific heats* determined by CARNOT'S theorem with the value of CARNOT'S function estimated from MR. JOULE'S original experiments on the changes of temperature produced by the rarefaction and condensation of air†, and established to a closer degree of accuracy by our preliminary experiments on expansion through a resisting solid‡. It ought also to be remarked, that the specific heats of air can only be applied to the evaluation of absolute temperature with a knowledge of the mechanical equivalent of the thermal unit; and therefore it is probable that, even when sufficiently accurate direct determinations of the specific heats are obtained, they may be useful rather for a correction or verification of the mechanical equivalent, than for the thermometric object. On the other hand, a comparatively very rough approximation to JK, the mechanical value of the specific heat of a pound of the fluid, will be quite sufficient to render our experiments on the cooling effects available for expressing with much accuracy, by means of the formula (15), a thermo-dynamic relation between absolute temperature and the mechanical properties of the fluid at two different temperatures.

Let us now assume

$$p = \frac{1}{v} \left\{ At + \phi_0(v) + \frac{\phi_1(v)}{t} + \frac{\phi_2(v)}{t^2} + \&c. \right\} \dots \dots \dots (16)$$

as an empirical formula, where  $A$  is a constant and  $\phi_0(v)$ ,  $\phi_1(v)$ , &c. are functions of the volume to be determined by comparisons with experimental results. In doing so

\* Philosophical Transactions, March 1852, p. 82.

† Royal Society Proceedings, June 20, 1844; or Phil. Mag., May 1845.

‡ Ibid. Dec. 1850.

we adopt the form to which Mr. RANKINE was led by his theory of molecular vortices, and which he has used with so much success for the expression of the pressure of saturated steam and the mechanical properties of gases; with this difference, that the series we assume proceeds in descending powers of the absolute thermo-dynamic temperature, while Mr. RANKINE'S involves similarly the temperature according to what he calls "the scale of the perfect gas-thermometer."

Now any variable part of  $\phi_0(v)$ , and the whole series of terms following it, must correspond to deviations from the gaseous laws, since the general expression of these laws would be simply  $pv=At+B$ , if A and B be constant. Hence for atmospheric air any variable part that  $\phi_0(v)$  can have, and all the terms following it in the series, must be very small fractions of  $pv$ . We shall see immediately that the various deviations from the gaseous laws which have been established by experiment, as well as the cooling effects which we have observed, are all such as to be represented by expressions derived from the preceding formula, if the variable part of  $\phi_0(v)$ , and the whole functions  $\phi_1(v)$ ,  $\phi_2(v)$ , &c. be taken each of them simply proportional to the density directly, or to the volume ( $v$ ) of a pound inversely. We may then, to avoid unnecessary complications, at once assume

$$pv=At+B+\left(C+\frac{D}{t}+\frac{G}{t^2}\right)\frac{\Phi}{v} \dots \dots \dots (17)$$

where A, B, C, D and G are all constants to be determined by the comparison with experimental results, and  $\Phi$  denotes a particular volume corresponding to a standard state of density, which it will be convenient to take as 12.387 cubic feet, the volume of a pound when under the atmospheric pressure  $\Pi$  (=2117 lbs. per square foot) of 29.9218 inches of mercury in latitude 45°. The series is stopped at the fifth term, because we have not at present experimental data for determining the coefficients for more. The experimental data which we have, and find available, are (1) the results of REGNAULT'S observations on the coefficients of expansion at different constant densities, (2) the results of his observations on the compressibility, at a temperature of 4°.75 Cent., and (3) our own experimental results now communicated to the Royal Society. These are expressed within their limits of accuracy (at least for pressures of from one to five or six atmospheres, such as our experiments have as yet been confined to), by the following equations:—

$$E=.003665+\frac{.0000441}{3.81}\left(\frac{\Phi}{v}-1\right),$$

or 
$$E=.00365343+.000011575\frac{\Phi}{v} \dots \dots \dots (18)$$

$$PV-P'V'=.008163\frac{P-P'}{\Pi}PV, \text{ at temperature } 4^\circ.75 \text{ Cent.}, \dots \dots (19)$$

and 
$$\delta=.26\frac{P-P'}{\Pi}, \text{ at temperature } 17^\circ \text{ Cent.} \dots \dots \dots (20)$$

Now, by the empirical formula (17), with equations (13) and (15), neglecting squares and products of the small quantities C, D, G, we find

$$E = \frac{100A - \left\{ D \left( \frac{1}{t_0} - \frac{1}{t_0 + 100} \right) + G \left[ \frac{1}{t_0^2} - \frac{1}{(t_0 + 100)^2} \right] \right\} \frac{\Phi}{v}}{100 \left\{ At_0 + B + \left( C + \frac{D}{t_0} + \frac{G}{t_0^2} \right) \frac{\Phi}{v} \right\}} \quad (21)$$

$$= \frac{A}{At_0 + B} - \frac{1}{100(At_0 + B)} \left\{ \frac{100A}{At_0 + B} \left( C + \frac{D}{t_0} + \frac{G}{t_0^2} \right) + D \left( \frac{1}{t_0} - \frac{1}{t_0 + 100} \right) + G \left( \frac{1}{t_0^2} - \frac{1}{(t_0 + 100)^2} \right) \right\} \frac{\Phi}{v}$$

$$\left( \frac{P'V' - PV}{PV} \right)^{4.75} = \frac{- \left( C + \frac{D}{t_{4.75}} + \frac{G}{t_{4.75}^2} \right) \left( \frac{\Phi}{V} - \frac{\Phi}{V'} \right)}{At_{4.75} + B + \left( C + \frac{D}{t_{4.75}} + \frac{G}{t_{4.75}^2} \right) \frac{\Phi}{V}} = \frac{- \left( C + \frac{D}{t_{4.75}} + \frac{G}{t_{4.75}^2} \right) \left( \frac{\Phi}{V} - \frac{\Phi}{V'} \right)}{At_{4.75} + B} \quad (22)$$

$$= - \frac{At_0 + B}{(At_{4.75} + B)^2} \left( C + \frac{D}{t_{4.75}} + \frac{G}{t_{4.75}^2} \right) \left( \frac{P}{\Pi} - \frac{P'}{\Pi} \right) \quad (23)$$

and 
$$\delta = \frac{1}{JK} \left\{ -B \log \frac{V'}{V} - \left( 2C + \frac{3D}{t} + \frac{4G}{t^2} \right) \left( \frac{\Phi}{V} - \frac{\Phi}{V'} \right) \right\} \quad (24)$$

$$= \frac{1}{JK} \left\{ -B \log \frac{P}{P'} - \frac{At_0 + B}{At + B} \left( 2C + \frac{3D}{t} + \frac{4G}{t^2} \right) \left( \frac{P}{\Pi} - \frac{P'}{\Pi} \right) \right\} \quad (25)$$

From the last, and the equation of condition (20), we find

$$B = 0 \quad (26)$$

and 
$$- \frac{1}{JK} \frac{t_0}{t_0 + 17} \left( 2C + \frac{3D}{t_0 + 17} + \frac{4G}{t_0 + 17} \right) = .26 \quad (27)$$

Again, by equations (21) and (18) similarly used, we have

$$\frac{A}{At_0 + B} = .00365343 \quad (28)$$

and 
$$\frac{-1}{100(At_0 + B)} \left\{ \frac{100A}{At_0 + B} \left( C + \frac{D}{t_0} + \frac{G}{t_0^2} \right) + D \left( \frac{1}{t_0} - \frac{1}{t_0 + 100} \right) + G \left( \frac{1}{t_0^2} - \frac{1}{(t_0 + 100)^2} \right) \right\} = .000011575 \quad (29)$$

From (26) and (28), we have

$$\left. \begin{aligned} \frac{1}{t_0} &= .00365343 \\ t_0 &= 273^{\circ}.72 \end{aligned} \right\} \quad (30)$$

That is, from the thermo-dynamic experimental result (20), and the experimental result (18) characteristic of the difference of temperature which we choose to call 100 from the freezing-point upwards, showing the effect on the pressure of air, we have determined the absolute thermo-dynamic temperature of the freezing-point. The result agrees within one-twentieth of a degree with that which we obtained in Section II. by the first plan, in which the same data as regards the increase of pressure of air from  $t_0$  to  $t_0 + 100^\circ$  were used, but taken into account on different and apparently less satisfac-

tory principles. From (22) and its equation of condition (19) we derive only a single equation among the constants, which is as follows:—

$$-\frac{At_0+B}{(At_{4.75}+B)^2} \left( C + \frac{D}{t_{4.75}} + \frac{G}{t_{4.75}^2} \right) = .008163. \quad (31)$$

Another equation besides the three, (27), (29), and (31), is required to determine the four remaining unknown constants, A, C, D, G; and is afforded by a determination of the density of air, which has been most accurately given by REGNAULT, who finds that the weight of 26224 cubic feet of air at constant temperature 0° Cent. and constant atmospheric pressure, in lat. 45°, amounts to the same as the pressure per square foot, a result which is expressed by the equation

$$\Pi\Phi = 26224.$$

Here  $\Pi$  denotes the value of  $p$  in the empirical formula (17), which corresponds to  $t=t_0$ , (the absolute temperature of the freezing-point,) and  $v=\Phi$ . Hence we have the equation

$$At_0+B+C+\frac{D}{t_0}+\frac{G}{t_0^2}=26224. \quad (32)$$

Calling 26224, H, (the “height of the homogeneous atmosphere”) for brevity, and denoting the true value of  $At_0$  by  $\mathfrak{H}$ , which must be very nearly equal to H, we may simplify the treatment of the four equations by taking the approximate value H for  $At_0$ , in three of them, (27), (29), (31), without losing accuracy, and we may afterwards use (32) to determine the exact value of  $\mathfrak{H}$ . Accordingly (and to avoid subsequent confusion of algebraic signs in the numerical results) it is convenient to assume

$$C = -\mathfrak{H}\alpha, \quad D = \mathfrak{H}\beta, \quad G = -\mathfrak{H}\gamma. \quad (33)$$

Then, taking everywhere  $B=0$  as we have found it, we have, instead of (32), (27), (29), (31) respectively,

$$\mathfrak{H} \left( 1 - \alpha + \frac{\beta}{t_0} - \frac{\gamma}{t_0^2} \right) = H \quad (34)$$

$$2\alpha - \frac{3\beta}{t_0+17} + \frac{4\gamma}{(t_0+17)^2} = \frac{JK}{H} \cdot \frac{t_0+17}{t_0} \times .26 \quad (35)$$

$$100\alpha - \left( \frac{100}{t_0} + 1 - \frac{t_0}{t_0+100} \right) \beta + \left( \frac{100}{t_0^2} + \frac{1}{t_0} - \frac{t_0}{(t_0+100)^2} \right) \gamma = 100t_0 \times .000011575 \quad (36)$$

and

$$\alpha - \frac{\beta}{t_0+4.75} + \frac{\gamma}{(t_0+4.75)^2} = \left( \frac{t_0+4.75}{t_0} \right)^2 \times .008163. \quad (37)$$

Reducing to numbers the coefficients of  $\alpha, \beta, \gamma$ , and the other terms, by using the value 273.72 found above (30) for  $t_0$ ; 1390 for J; and .238 for K according to the observations and theoretical conclusion regarding the absolute value of the specific heat of air under constant pressure, published in Notes to Mr. JOULE’s paper on the



Air-Engine, since confirmed by REGNAULT'S observations ; we have three simple equations for determining the three unknown quantities,  $\alpha$ ,  $\beta$ ,  $\gamma$ ; and then a single simple equation (34) for determining  $H$ . By solving these, we find

$$\left. \begin{aligned} \alpha &= .0012811 \\ \beta &= 1.3918 \\ \gamma &= 353.20 \\ H &= 26247.9 \end{aligned} \right\} \dots \dots \dots (38)$$

Using these and (33) in (17), we have

$$pv = H \left\{ t - \left( .0012811 - \frac{1.3918}{t} + \frac{353.2}{t^2} \right) \frac{\Phi}{v} \right\}, \dots \dots \dots (39)$$

an empirical formula which represents the pressure of air, in terms of its temperature on the absolute thermo-dynamic scale and its density, consistently with REGNAULT'S observations on the increase of pressure from 0° to 100° Cent. and on the compressibility at 4°·75 Cent., and consistently with our own on the thermal effects of air at the temperature 17° Cent., forced with various pressures through a porous body.

It also agrees perfectly with REGNAULT'S observations on the expansion of air under constant pressure.

The only other observations on the variations of pressure and density available for testing the formula, are REGNAULT'S comparisons of different air-thermometers. The Table at the end of Section IV., which has been calculated from our empirical formula (39), shows, in its second and third columns, the indications to be expected of constant-volume and of constant-pressure air-thermometers in terms of temperature on the absolute thermo-dynamic scale; and the differences between the numbers show the discrepancies to be expected between different air-thermometers themselves. These discrepancies, although considerably greater than have been observed by REGNAULT on thermometers with air at different densities or pressures of from half to double those of the standard, appear to be within, or scarcely to exceed, the limits of errors of observation. If further examination of this subject proves that there is in reality a closer agreement between air-thermometers than shown in the Table, it will be necessary to introduce another equation of condition to reconcile them, and to determine another constant in the general empirical formula for  $p$ . At present however we do not think it necessary to take up this question, as we hope soon to have much more extensive experimental data on the cooling effects, with more varied pressures and at different temperatures ; which should both show whether any other functions of the density than that of simple proportionality will be required, and enable us to determine other terms of the series in descending powers of  $t$ , and will so give us probably a much more exact empirical formula for air than all the data at present available enable us to obtain.

We have also calculated formulæ for the specific heats of air under constant pressure and constant volume, by which the variations of these elements with the tempe-

rature and density are determined. Should they turn out to be inconsistent with facts, other equations of condition will have to be introduced and other constants of the empirical formula determined, to do away with the discrepancies; but probably no experiments have yet been made of sufficient accuracy to test them.

The following expressions are derived from the general equations (7) and (8) for the mechanical values of the specific heats of a fluid, by substituting for  $p$  the particular expressions for the case of air afforded by the empirical formula (39), and integrating the second of the two results with reference to  $v$ :—

$$J(K-N) = \frac{H}{t_0} + \frac{2H}{t} \left( \alpha - \frac{2\beta}{t} + \frac{3\gamma}{t^2} \right) \frac{\Phi}{v} \dots \dots \dots (40)$$

$$JN = J\mathcal{N} + \frac{2H}{t} \left( \frac{-\beta}{t} + \frac{3\gamma}{t^2} \right) \frac{\Phi}{v}, \dots \dots \dots (41)$$

in the second of which,  $J\mathcal{N}$  denotes the value of  $JN$  when  $v = \infty$ . Using a similar notation  $J\mathcal{K}$  with reference to the specific heat of air at constant pressure, we have from these two equations,

$$J\mathcal{K} = J\mathcal{N} + \frac{H}{t_0} \dots \dots \dots (42)$$

$$JK = J\mathcal{K} + \frac{2H}{t} \left( \alpha - \frac{3\beta}{t} + \frac{6\gamma}{t^2} \right) \frac{\Phi}{v}; \dots \dots \dots (43)$$

or with  $\frac{p}{\Pi} \frac{t_0}{t}$  instead of  $\frac{\Phi}{v}$ ,

$$JK = J\mathcal{K} + \frac{2Ht_0}{t^2} \left( \alpha - \frac{3\beta}{t} + \frac{6\gamma}{t^2} \right) \frac{p}{\Pi} \dots \dots \dots (44)$$

Lastly, denoting the ratio of the specific heats,  $\frac{K}{N}$ , by  $k$ , and the particular value,  $\frac{\mathcal{K}}{\mathcal{N}}$ , corresponding to the case of extreme dilatation, by  $\mathcal{k}$ , we have, to the same degree of approximation as the other expressions,

$$k = \mathcal{k} + \frac{2H}{JNt} \left\{ \alpha - \frac{(3-k)\beta}{t} + \frac{(6-3k)\gamma}{t^2} \right\} \frac{\Phi}{v} \dots \dots \dots (45)$$

In the Notes to Mr. JOULE's paper on the Air-Engine\*, it was shown that if MAYER's hypothesis be true we must have approximately,

$$K = \cdot 2374 \text{ and } N = \cdot 1684,$$

because observations on the velocity of sound, with LAPLACE's theory, demonstrate that

$$k = 1\cdot 410$$

within  $\frac{1}{700}$  of its own value. Now the experiments at present communicated to the Royal Society prove a very remarkable approximation to the truth in that hypothesis (see above, Section I.), and we may therefore use these values as very close approximations to the specific heats of air. The experiments on the friction of fluids and solids

\* Philosophical Transactions, March 1852, p. 82.

made for the purpose of determining the mechanical value of heat\*, give for  $J$  the value 1390; and we therefore have  $JN=234.1$  with sufficient accuracy for use in calculating small terms. Calculating accordingly, with this for  $JN$ , and with the value 1.41 for  $k$ , the coefficient of  $\frac{\Phi}{v}$  in (45), we find,

$$\left. \begin{aligned} \text{for } t=273.7 \text{ (temperature } 0^\circ \text{ Cent.)}, \quad k &= \mathbf{k} + .00126 \times \frac{\Phi}{v} \\ \text{and for } t=293.7 \text{ (temperature } 20^\circ \text{ Cent.)}, \quad k &= \mathbf{k} + .00076 \times \frac{\Phi}{v} \end{aligned} \right\} \dots \dots \dots (46)$$

Now according to REGNAULT we have, for dry air at the freezing-point, in the latitude of Paris,

$$H=26215;$$

and since the force of gravity at Paris, with reference to a foot as the unit of space and a second as the unit of time, is 32.1813, it follows that the velocity of sound in dry air at 0° Cent. would be, according to NEWTON'S unmodified theory,

$$\sqrt{26215 \times 32.1813} = 918.49,$$

or in reality, according to LAPLACE'S theory,

$$\sqrt{k} \cdot \sqrt{26215 \times 32.1813}.$$

But according to BRAVAIS and MARTINS it is in reality

$$1090.5, \text{ which requires that } k=1.4096,$$

or according to MOLL and VAN BECK

$$1090.1, \text{ which requires that } k=1.4086.$$

The mean of these values of  $k$  is 1.4091. If this be the true value of  $k$  for 0° Cent. and the standard density ( $\frac{\Phi}{v}=1$ ), the correction shown in (46) above would give

$$\mathbf{k}=1.40784;$$

or if it be the true value of  $k$  for air of the standard density, and the temperature 20° Cent., the correction will give

$$\mathbf{k}=1.40834.$$

Which of these hypotheses is most near the truth, might possibly be ascertained by reference to the original observations on the velocity of sound from which the preceding results reduced to the temperature 0° were obtained, but as the actual temperatures of the air must in all probability have been between 0° and 20° Cent., without going into the details of the calculations by which the reductions to 0° have been made, we may feel confident that  $\mathbf{k}$  cannot differ much from either of the two preceding estimates, and we may take their mean,

$$\mathbf{k}=1.4081, \dots \dots \dots (47)$$

as probably a very close approximation to the truth. Now we have seen above that

\* Philosophical Transactions, 1849.

$H=26247.9$ , and since  $t_0=273.7$ , we have, by (42),

$$JK - JN = 95.9003. \dots \dots \dots (48)$$

From this, and the preceding value of  $k$  (or  $\frac{K}{D}$ ), we have

$$\left. \begin{aligned} JN &= 134.9921 \\ JK &= 330.8924 \end{aligned} \right\} \dots \dots \dots (49)$$

Using these, and the values of  $\alpha$ ,  $\beta$ , and  $\gamma$  obtained above, in the preceding expressions (40), (41), (45) and (44), and calculating for every 20° of temperature from 0° Cent. to 300°, we obtain the results shown in the following Table; the assumptions

$$\left. \begin{aligned} f &= \frac{2H}{t} \left( \alpha - \frac{2\beta}{t} + \frac{3\gamma}{t^2} \right) \\ g &= \frac{2H}{t} \left( \frac{-\beta}{t} + \frac{3\gamma}{t^2} \right) \end{aligned} \right\} \dots \dots \dots (50)$$

being made merely for convenience in exhibiting the formulæ and mode of calculation along with the results.

Table of the Specific Heats of Air.

Temperature from freezing-point, $t-t_0$ .	I.	II.	III.	IV.
	Difference of mechanical values of specific heats, $JK - JN = \frac{H}{t_0} + f \frac{\Phi}{v}$ .	Mechanical value of specific heat at constant volume, $JN = JN + g \frac{\Phi}{v}$ .	Ratio of specific heats, $k = k + \frac{1}{JN} (f + g - kg) \frac{\Phi}{v}$ .	Mechanical value of specific heat at constant pressure, $JK = JK + \frac{t_0}{t} (f + g) \frac{p}{\Pi}$ .
0	95.9003 + 1.0080 $\times \frac{\Phi}{v}$	234.9921 + 1.7376 $\times \frac{\Phi}{v}$	1.4081 + .001262 $\times \frac{\Phi}{v}$	330.8924 + 2.7457 $\times \frac{p}{\Pi}$
20	95.9003 + .7306 "	234.9921 + 1.3486 "	1.4081 + .000759 "	330.8924 + 1.9376 "
40	95.9003 + .5314 "	234.9921 + 1.0594 "	1.4081 + .000404 "	330.8924 + 1.3880 "
60	95.9003 + .3862 "	234.9921 + .8408 "	1.4081 + .000177 "	330.8924 + 1.0064 "
80	95.9003 + .2792 "	234.9921 + .6731 "	1.4081 + .000014 "	330.8924 + .7369 "
100	95.9003 + .1994 "	234.9921 + .5426 "	1.4081 - .000098 "	330.8924 + .5435 "
120	95.9003 + .1396 "	234.9921 + .4401 "	1.4081 - .000175 "	330.8924 + .4030 "
140	95.9003 + .0944 "	234.9921 + .3587 "	1.4081 - .000225 "	330.8924 + .2997 "
160	95.9003 + .0601 "	234.9921 + .2934 "	1.4081 - .000256 "	330.8924 + .2331 "
180	95.9003 + .0345 "	234.9921 + .2412 "	1.4081 - .000275 "	330.8924 + .1663 "
200	95.9003 + .0141 "	234.9921 + .1977 "	1.4081 - .000285 "	330.8924 + .1223 "
220	95.9003 - .0010 "	234.9921 + .1625 "	1.4081 - .000288 "	330.8924 + .0895 "
240	95.9003 - .0125 "	234.9921 + .1334 "	1.4081 - .000286 "	330.8924 + .0644 "
260	95.9003 - .0211 "	234.9921 + .1094 "	1.4081 - .000282 "	330.8924 + .0453 "
280	95.9003 - .0275 "	234.9921 + .0893 "	1.4081 - .000274 "	330.8924 + .0306 "
300	95.9003 - .0322 "	234.9921 + .0726 "	1.4081 - .000263 "	330.8924 + .0193 "

The mean value of JK for air at constant pressure  $p$ , and for the range of temperature from  $t'$  to  $t$  obtained by integrating equation (44) with reference to  $t$  between those limits, and dividing by  $t-t'$ , is

$$JK + \frac{HC}{t-t'} \left\{ 2\alpha \left( \frac{1}{t'} - \frac{1}{t} \right) - 3\beta \left( \frac{1}{t'^2} - \frac{1}{t^2} \right) + 2\gamma \left( \frac{1}{t'^3} - \frac{1}{t^3} \right) \right\} \frac{p}{\Pi};$$

and this divided by J expresses the element actually observed in experiments such as

have hitherto been made on the specific heat of air at constant pressure. The theoretical results, according to this expression and to the determination 1390 for  $J$ , are as follow for several particular cases:—

Range of temperature.	Mean specific heat of air at atmospheric pressure.	Mean specific heat of air at five times the atmospheric pressure.
Cent. degrees.		
0 to 100	·2390	·2428
0 to 300	·2384	·2396

The comparison of these results with sufficiently accurate direct experiments on the specific heat of air at the atmospheric pressure, might lead to a correction on the value 1390 found for  $J$  by direct experiments on the generation of heat by friction; but it must depend on the evidence afforded by accounts of the experimental details, whether the value of the mechanical equivalent of the thermal unit is to be corrected from them, or whether we may assume the preceding results as nearer the truth than the results which they indicate. No such evidence, nor any demonstrating whether or not the influence of change of pressure is such as shown in the preceding Tables, has as yet been published.

CHART N° I.

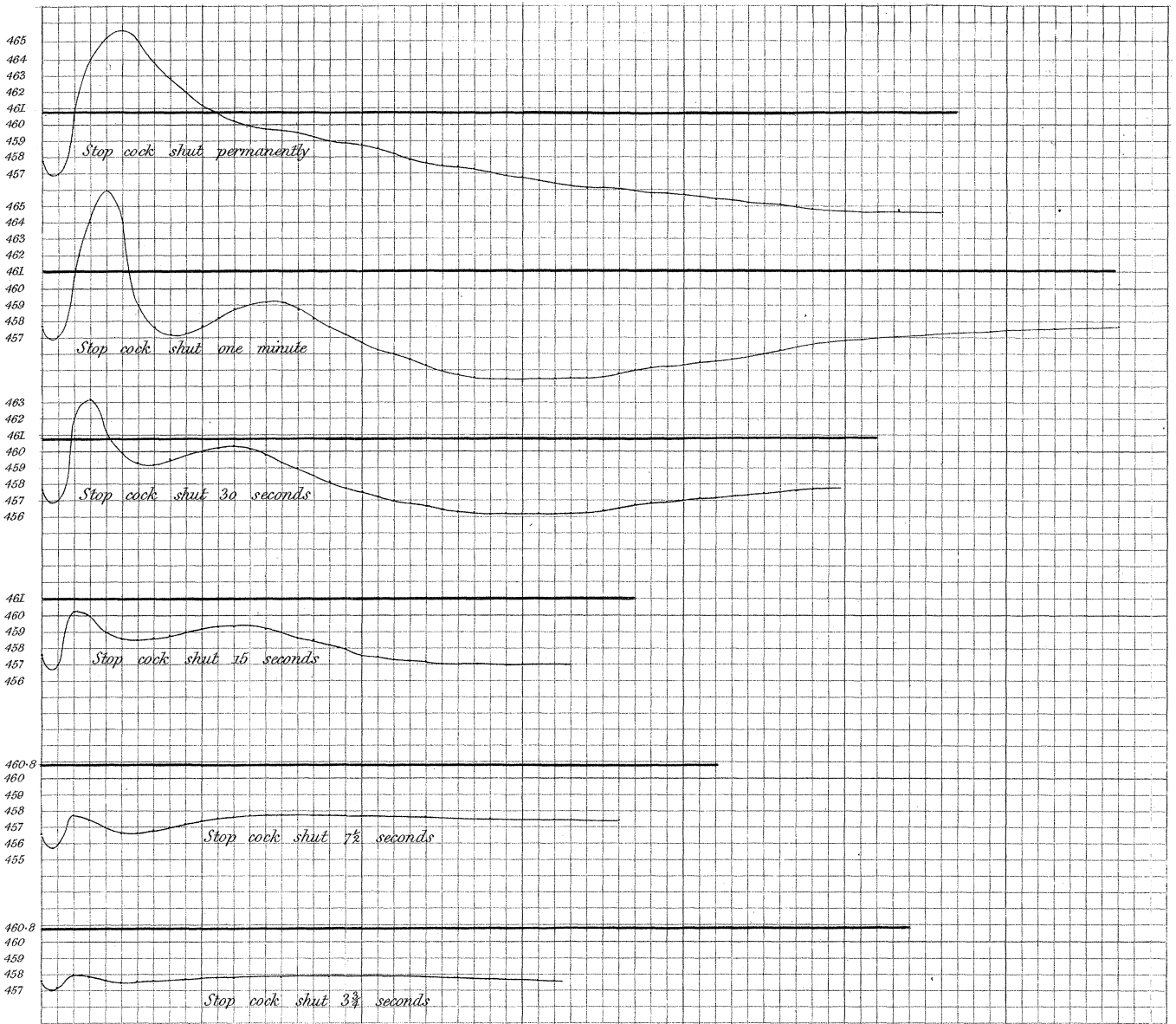


CHART N° 3.

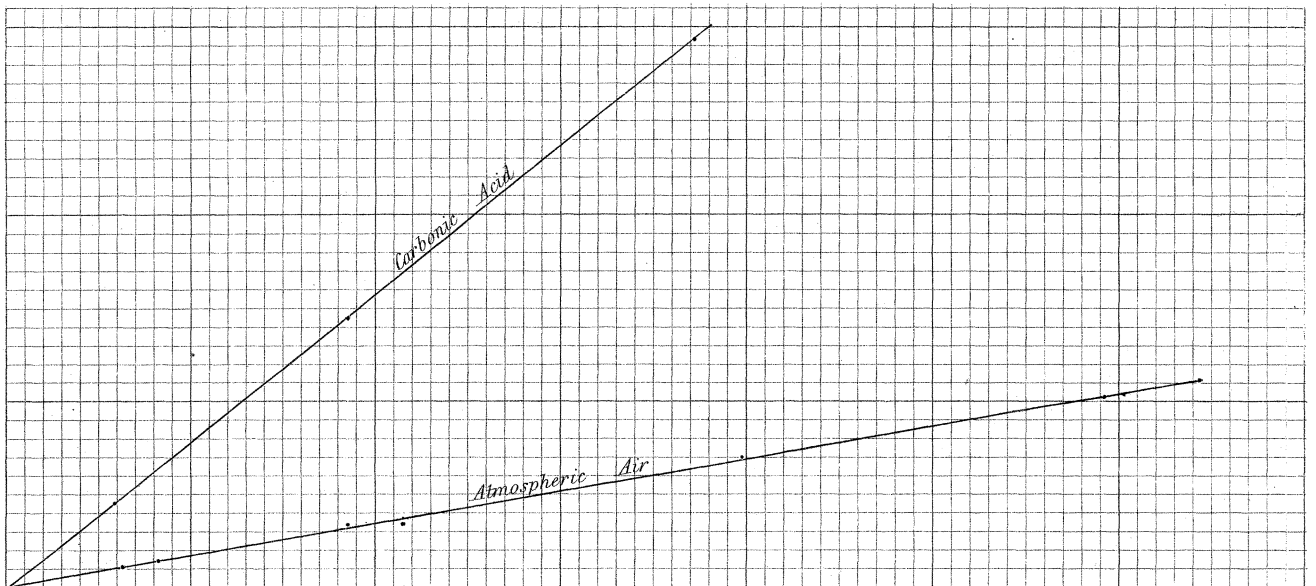


CHART N<sup>o</sup> 2.

