On the Specific Heat of Gases

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The classical theory of the specific heat of gases, which right at the beginning obtained such a brilliant confirmation through Kundt and Warburg's determination of the specific heat of mercury vapour, has for a long time produced no new results. It has, in particular, proved impossible to explain the variation of the specific heat with the temperature. It has now, however, become possible to give this theory the extension which has for so long been looked forward to, and which enables the theory to explain the variability of the specific heat.

A few years ago Einstein succeeded in enunciating a formula for the specific heat of *solids* on the basis of the quantum theory. And this formula has, after having been modified by Nernst and Lindemann, proved to apply over a very wide temperature range. It therefore seems probable that also for *gases* the correct formula for the specific heat can be obtained by combining the quantum theory with the kinetic theory. A short time ago Nernst has also given an outline of a formulation of this idea.

The derivation is briefly as follows:

A gas molecule possesses three kinds of energy, the amount of which varies with the temperature: the *energy of translation*, due to its translatory movements, the *energy of rotation*, due to the rotatory movement of the molecule, and the *energy of oscillation*, from the oscillations of the atoms in the molecule.

According to the classical kinetic theory of gases the energy of translation is always equal to $^3/_2$ RT per mole, whether the molecule is mono-, di-, tri-, or tetra-atomic. As to the energy of rotation conditions are different. The magnitude of the energy of rotation may be obtained in the following way: According to the laws of classical statistical mechanics the following rule will apply to the kinetic energy of a molecule: the content of energy of a molecule is the same for each degree of freedom, and as the energy of translation possesses three degrees of freedom and is equal to $^3/_2 RT$, the energy of the molecule must be $^1/_2 RT$ per degree of freedom. In order to obtain the energy of rotation we therefore only have to multiply the number of degrees of freedom of the energy of rotation

by $^1/_2$ RT. The latter number of degrees of freedom is for a monatomic gas 0, for a diatomic gas 2 and for tri- and polyatomic gases 3, because a monatomic molecule may be considered a point-mass, a diatomic molecule can possess energy of rotation about two axes and a tri- or polyatomic gas may possess energy of rotation about all three axes (if it does not happen to be of linear structure).

As regards the energy of oscillation, a monatomic gas molecule cannot possess energy of oscillation. In a diatomic molecule the two atoms may oscillate in relation to each other. There is thus one degree of freedom which, according to the classical theory, corresponds to a kinetic energy of $^1/_2$ RT per mole, and, as an equally large amount of potential energy should be added, a total energy of RT. Here the new theories interfere. According to the quantum hypothesis only a fraction φ of the classical oscillation energy is present, i.e. in this case $RT\varphi$. φ is a function only of the temperature and the frequency of the oscillation in question. According to Einstein we have

$$\varphi = \frac{\dfrac{\beta\,\nu}{T}}{e^{\frac{\beta\nu}{T}} - 1}$$

where $\beta = 4.86 \cdot 10^{-11}$ and ν is the frequency (the number of oscillations per second). Nernst and Lindemann have found that Einstein's function does not apply to solids at low temperatures while the formula

$$\varphi = \tfrac{1}{2}\,\frac{\dfrac{\beta\,\nu}{T}}{e^{\frac{\beta\nu}{T}} - 1} + \tfrac{1}{2}\,\frac{\dfrac{\beta\,\nu}{2T}}{e^{\frac{\beta\nu}{2T}} - 1}$$

agrees closely with the observations.

In the following I shall employ both these functions to find out whether the new one is also to be preferred in case of gases.

Both functions of φ are at the absolute zero equal to nil, and they approach 1 at higher temperatures. At higher temperatures the energy content thus approaches that which is required by the classical theory.

In a triatomic gas molecule the three atoms, which may be denoted A, B, and C, can oscillate in pairs, i.e. A and B in relation to each other and likewise B and C as well as C and A. We must thus consider three different oscillations, and the total energy of oscillation will be: $RT\,(\varphi_1 + \varphi_2 + \varphi_3)$.

Just as a triangle is determined by three elements, the energy of oscillation of a triangular molecule has three degrees of freedom. In analogy with this a tetra-atomic molecule must possess six oscillations, an n-atomic $3n - 6$ oscillations.

Summary

Number of atoms in the molecule	Energy of translation	Energy of rotation	Energy of oscillation
1	$^3/_2 RT$	0	0
2	$^3/_2 RT$	RT	$RT\varphi$
3	$^3/_2 RT$	$^3/_2 RT$	$RT(\varphi_1 + \varphi_2 + \varphi_3)$
4	$^3/_2 RT$	$^3/_2 RT$	$RT\Sigma_6\varphi$

By adding up energy of translation, energy of rotation and energy of oscillation the total energy is obtained. When the total energy is divided by the temperature we obtain the *mean specific heat* reckoned from the absolute zero, and by differentiating with respect to T, we obtain the true specific heat, in all cases at constant volume. Hereby, we have formulated an expression for the specific heat of gases.

In connection with the above derivation the following should be observed: As shown by Nernst, it also applies to the energy of rotation that at low temperatures only a fraction of the amount calculated according to the classical theory, will be present. However, already at temperatures far below 0° C this amount has practically been reached. For the purpose of the present investigation we need not take this into consideration. Another point neglected is the following: Besides the *kinetic energy of rotation E_K*, the molecule must possess *potential energy of rotation E_P*, as the atoms are more or less removed from each other due to the centrifugal force. This contribution of potential energy of rotation will be the smaller the more rigidly the atoms are linked. For a diatomic gas molecule, the internal frequency of which is ν, it can be calculated that

$$\frac{E_P}{E_K} = \frac{RT}{4\,\pi^2\,\nu^2\,Mr^2}$$

Here M is the molecular weight and r the radius of the molecule. According to this expression the potential energy of rotation may usually be taken to equal nil. We have, e.g. for oxygen at ordinary temperature, when we substitute $\nu = 10^{14}$, $M = 32$, and $r = 10^{-8}$,

$$\frac{E_P}{E_K} = 0.00002$$

For the purpose of testing the new expressions for the specific heat of gases, monatomic gases cannot be used as Boltzmann's theory remain applicable to these gases. We can therefore at once proceed to the polyatomic gases. In the case of diatomic gases the specific heat has previously been considered to vary linearly with the temperature. However, the values observed are in very good

agreement with those calculated from the new exponential formulae, as will be seen from tables 1 and 2.

We have for *hydrogen* and *nitrogen* correlated the observed values of the specific heat with the values (E) calculated from Einstein's φ-function and with the

Table 1. Specific heat of hydrogen

t	Observed value	Calculated E $\lambda = 3.0\mu$	Calculated N and L $\lambda = 2.0\mu$
18° C	c 4.9–5.2 from c_p/c_v	c 4.96	c 4.96
	$c_m(0°, t°)$	$c_m(0°, t°)$	$c_m(0°, t°)$
1413	5.34 ⎫	5.37	5.37
1592	5.42 ⎪	5.45	5.44
1835	5.52 ⎬ Pier	5.54	5.52
2017	5.61 ⎪	5.61	5.59
2250	5.72 ⎭	5.69	5.67

Table 2. Specific heat of nitrogen

t	Observed value	Calculated E $\lambda = 3.6\mu$	Calculated N and L $\lambda = 2.59\mu$
18° C	c 4.84 from c_p/c_v	c 4.96	c 4.96
	$c_m(0°, t°)$	$c_m(0°, t°)$	$c_m(0°, t°)$
200	4.73 ⎫	4.97	5.00
630	4.91 ⎪ Holborn	5.10	5.19
1000	5.25 ⎬ Hennig	5.31	5.38
1347	5.31 ⎭	5.50	5.53
2000	5.78 ⎫ Pier	5.78	5.78
2500	5.93 ⎭	5.93	5.93

values (N and L) calculated from Nernst and Lindemann's φ-function. c denotes the true specific heat at constant volume and $c_m(0°, t°)$ the mean specific heat at constant volume between 0° C and $t°$ C.

When the atoms are electrically charged, we must, according to Einstein, expect to find bands in their absorption and emission spectra at wave-lengths corresponding to the frequencies of the atomic oscillations. In the tables, I have therefore given the wave-lengths λ corresponding to the frequencies used for the calculation.

Hydrogen and nitrogen have no infrared bands and the λ-values which have

been calculated according to thermal methods cannot therefore be checked by optical methods. *Carbon monoxide* and *oxygen* seem, however, according to explosion experiments, to have nearly the same specific heat as nitrogen. Their atoms must therefore — as those of nitrogen — oscillate with a frequency corresponding to $\lambda =$ about 3μ. These substances do actually show absorption within this range, namely carbon monoxide at $2.4\ \mu$ and $4.6\ \mu$, and oxygen at $3.2\ \mu$ and $4.7\ \mu$. The oxygen bands are rather weak. The greater the polarity of the molecules the more intense the infrared bands seem to be.

Important material for testing the theory is presented by the triatomic gases, carbon dioxide and water vapour. In the first place the two like atoms can in both gases oscillate in relation to each other. As the forces between these atoms are probably weak, the oscillations will most likely be slow. Secondly, the two oxygen atoms in carbon dioxide can oscillate in relation to the carbon atom and the two hydrogen atoms in water vapour can oscillate in relation to the oxygen atom. We must therefore in these cases expect one slow and two more rapid oscillations, and, considering the uniformity of the valences, the two rapid oscillations are probably identical.

Table 3. Specific heat of carbon dioxide

t	Observed value	Calculated E $\lambda_1 = 14.7\mu$ $\lambda_2 = \lambda_3$ $= 6.2\mu$	Calculated N and L $\lambda_1 = 8.1\mu$ $\lambda_2 = \lambda_3$ $= 5.0\mu$	Calculated N and L $\lambda_1 = 14.7\mu$ $\lambda_2 = 4.3\mu$ $\lambda_3 = 2.7\mu$
18° C	c 7.09 from c_p/c_v	c 6.87	c 6.85	c 7.24
	$c_m(0°, t°)$	$c_m(0°, t°)$	$c_m(0°, t°)$	$c_m(0°, t°)$
200	7.48 ⎫	7.44	7.44	7.67
630	8.60 ⎪ Holborn	8.66	8.67	8.47
1000	9.33 ⎰ Hennig	9.34	9.35	9.00
1364	9.84 ⎭	9.87	9.80	9.40
1611	9.98 ⎫	10.07	10.03	9.62
1839	10.28 ⎬ Pier	10.23	10.21	9.81
2210	10.47 ⎭	10.45	10.43	10.04

From table 3, columns 3 and 4 we may see the good agreement obtained in the case of *carbon dioxide* under these conditions, both according to Einstein's φ-function and according to Nernst and Lindemann's more recent φ-function. As the absorption spectrum of carbon dioxide consists of three bands at 14.7μ, 4.3μ, and 2.7μ, while the thermally calculated values are $14.7\ \mu$ and 6.2μ, respectively 8.1μ and 5.0μ, it may be seen that the orders of magnitude of the optically and thermally determined frequencies agree. The last column in table 3,

which gives the specific heats calculated according to Nernst and Lindemann's
φ-function from the three optical oscillations, shows that the deviations in the
λ-values are insignificant to the calculations of the specific heats. *As will be seen,
we can calculate the specific heat of carbon dioxide from optical measurements with
an accuracy of a few per cent.* When calculating on the basis of the original Einstein
φ-function, the deviation is considerably greater.

The applicability of the new theories to *water vapour* will appear from table 4.
In this case a comparison between optically and thermally determined values of

Table 4. Specific heat of water vapour

t	Observed value		Calculated E $\lambda_1 = 5.5\mu$ $\lambda_2 = \lambda_3 = 2.6\mu$	Calculated N and L $\lambda_1 = \lambda_2 = \lambda_3 = 2.4\mu$
	c		c	c
50° C	5.96		6.04	5.98
270	6.40	Nernst-Levy	6.35	6.32
450	6.80		6.78	6.80
	$c_m(110°, t)$		$c_m(110°, t)$	$c_m(110°, t)$
620	6.51	Holborn	6.59	6.60
1000	6.94	Hennig	7.13	7.17
1327	7.40		7.53	7.58
	$c_m(0°, t)$		$c_m(0°, t)$	$c_m(0°, t)$
1727	7.96		7.89	7.94
2027	8.72	Pier	8.21	8.27
2327	9.68		8.49	8.53

λ cannot, however, be performed, because water vapour has a complicated infra-
red spectrum with bands throughout the range from 1μ to 20μ. It is my opinion
that this unexpectedly complicated spectrum is caused by the presence of double-
molecules of water. At any rate water vapour has bands within the ranges where
they should be expected. A thorough investigation of the spectrum of water
vapour at different temperatures and pressures would be of great interest, as the
bands originating from the simple H_2O-molecule must become more and more
distinctive with decreasing pressure and increasing temperature.

Measurements have also been performed for a tetra-atomic gas — namely
ammonia. Among the six oscillations which its molecule, according to theory,
must possess I have assumed the five rapid ones to have the same frequency.
This assumption is sufficient to obtain agreement with the observations, as shown
in table 5.

Table 5. Specific heat of ammonia

t	Observed value		Calculated E $\lambda_1 = 13.0\mu$ $\lambda_2 = \lambda_3 = \lambda_4 = \lambda_5$ $= \lambda_6 = 3.32\mu$	Calculated N and L $\lambda_1 = 8.9\mu$ $\lambda_2 = \lambda_3 = \lambda_4 = \lambda_5$ $= \lambda_6 = 2.1\mu$
18° C	6.61		6.61	6.62
112	7.09	Nernst	6.98	6.91
466	8.4		8.5	8.6
580	9.2		9.2	9.2

The λ-values found by the thermal methods are 13μ and 3.3μ, respectively 8.9μ and 2.1μ. The infrared spectrum of ammonia extends from 14μ to 3μ and comprises about 20 lines and bands. They are likewise within the range in which they should be according to the thermal measurements.

I have now mentioned all the gases for which detailed investigations are available. For other gases only incomplete thermal and optical measurements are available. We are especially short of absorption measurements in the outermost infrared spectrum. There do not seem, however, to be any cases in which the available measurements contradict the theory.

We may establish as a result of the investigation that the available observations confirm the interdependence between specific heat and spectrum which the quantum theory requires. In most cases the observations are equally well reproduced by means of Einstein's and Nernst-Lindemann's φ-function. But just in the case where the data are best, i.e. in the case of carbon dioxide, the new formula by Nernst and Lindemann proves its superiority.