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Physics. — “*On the question whether at the absolute zero entropy changes on mixing.*” By Dr. W. H. KEESOM. Supplement N^o. 33 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. The formula for the entropy of the “gramme-molecule” of a mixture of ideal, not reacting gases, for each of which $pV=RT$ is valid, contains the expression

$$-R \sum c_i \ln c_i, \quad . . . , \quad \quad (1)$$

if c_1 represents the number of gramme-molecules of the first component, c_2 that of the second component etc., which are present in the gramme-molecule of the mixture. \sum will indicate in this paper a summation over the different components.

The expression (1) passes unchanged into the formula for the entropy of the mixture, when this is transferred from an ideal gas condition as considered above into other conditions.

According to PLANCK'S version of the NERNST heat theorem the entropy of a one-component substance in a condensed state approaches to a finite value, which is independent of the pressure and of the special state of aggregation, when the absolute temperature approaches to 0. That value may be taken as a suitable zero point for the entropy of that substance in the condensed state.

As it is not immediately evident, how the other terms which occur in the expression for the entropy of a mixture, can on approaching to $T=0$ furnish a compensation of the term written above, it might be imagined, that for a mixture on approaching to $T=0$ the entropy might not become 0, notwithstanding this is the case for the components.

In that case, however, at a temperature which differs little from the absolute zero, any reversible isothermal change of the components, in a condensed state, individually would be connected with a development or absorption of heat, which approaches more rapidly to 0 than the temperature. The reversible mixing of those components, on the other hand, would be accompanied by a heat-effect, which approaches to 0 as rapidly as (eventually more slowly than) the temperature. In other words the mixing heat would be of a different order of magnitude from the heat of each reversible isothermal process performed with the components individually.

It seems to me that it is more natural to assume, that *also for a mixture the entropy at the absolute zero point is equal to 0*, if this is the case for the components by the choice of this point as a zero point for the corresponding entropies.

Probably even the compensation referred to above already takes place in the ideal gas state, at least if the volume of the mixture is not increased at too rapid a rate to ∞ as the temperature decreases to 0.

In accordance with a remark by NERNST¹⁾ we are practically forced to assume that for the molecular translatory motion of a gas on approaching to $T=0$ at last the equipartition laws are no more valid. For the determination of the temperature one can then no more rely upon the gas thermometer. A method for the determination of the temperature, which is then suitable in theory, is this that one derives the temperature from the energy density of the radiation which is in equilibrium with it.

We shall consider the equilibrium between the molecular translatory motion of the gas and the radiation subsequently at two temperatures T and $T + dT$. The most obvious assumption is that to an increase of the energy density of the gas an increase of the energy density of the radiation corresponds which is in a finite ratio to the first, in other words that

$$dU = \gamma T^3 dT, \quad \dots \dots \dots (2)$$

where γ has a finite, and at sufficiently low temperature a constant value. In this equation U may represent the energy of the gram-molecule of the gas. The molecular volume is supposed not to become ∞ on approaching to $T=0$.

From (2) follows that²⁾

$$\text{for } T=0 : \left(\frac{\partial U}{\partial T} \right)_V = 0. \quad \dots \dots \dots (3)$$

The equation (2) has the same form as the corresponding relation for a solid. Indeed it could hardly be assumed that the equilibrium between the molecular motion of the gas molecules in colliding against a solid and the radiation would be governed by quite a different law from the equilibrium between the molecular motion in a solid and the radiation.

From (2) and

$$p = \frac{2U}{3V}, \quad \dots \dots \dots (4)$$

¹⁾ W. NERNST, *Physik. Z.S.* 13 (1912), p. 1066. Cf. also H. KAMERLINGH ONNES and W. H. KEESOM, *Math. Enz.* V 10, Leiden Comm. Suppl. N^o. 23, note 517.

²⁾ It will be noticed that for the validity of (3) a decrease of $\left(\frac{\partial U}{\partial T} \right)_V$ proportionally to T^3 , as is indicated by (2), is not required, but that a decrease proportionally to T would be sufficient.

which relation remains valid, follows for $T = 0$

$$\left(\frac{\partial p}{\partial T}\right)_V = 0, \text{ hence } \left(\frac{\partial S}{\partial V}\right)_T = 0, \dots \dots (5)$$

if S represents the entropy.

If we now calculate the change of entropy which occurs on mixing two ideal gases (i.e. gases, in whose equation of state no members occur which depend on the volume and the mutual attraction of the molecules) by supposing this mixing to take place in a reversible way at constant temperature, it follows from the last mentioned relation that at the absolute zero the entropy change on mixing is equal to 0.

§ 2. The theorem indicated in the former § may be further elucidated by means of relations for the equation of state of an ideal gas which I deduced in Suppl. N^o. 30x (May '13). It seemed, however, desirable to me as the foundations of the considerations of § 1 not to make more assumptions than are strictly necessary. For against several of the special assumptions of Suppl. N^o. 30a, particularly against the use of DEBLIE's method in the way as is done there for an ideal gas, more or less serious objections can be made. All the same the deviations from the equipartition laws, which will become apparent in the equation of state of an ideal monatomic gas, are presumably given rightly in a qualitative sense by those relations. Further it seems to me that one may expect with some confidence that the order of magnitude of those deviations will agree with that of the deviations given by the relations mentioned. For this reason it seems to me to be not quite superfluous to indicate here what may be derived for the entropy of an ideal mixture from those relations.

a. From equation (1) of Suppl. N^o. 30a with (2), (3), and (5) of that paper follows for a *one-component gas*, if molecular rotations and intramolecular motions are left out of account¹⁾,

$$S = \frac{9N}{v^3_{\max}} \int_0^{v_{\max}} \left\{ \frac{1}{T} \frac{h\nu}{e^{h\nu/kT} - 1} - \ln \left(1 - e^{-\frac{h\nu}{kT}} \right) \right\} v^2 dv. \dots (6)$$

With

$$\xi = \frac{h\nu}{kT}, \quad x = \frac{h\nu_{\max}}{kT}, \dots \dots (7)$$

¹⁾ This expression was already given by H. TERRODE, Physik. Z.S. 14 (1913), p. 212.

and integrating partially as regards the second term under the integral sign, (6) changes into

$$S = 3Nk \left\{ \frac{4}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \ln(1 - e^{-x}) \right\} \dots \dots \dots (8)$$

For large values of x this gives:

$$S = 3Nk \left\{ \frac{4\pi^4}{15} \frac{1}{x^3} - 3x \sum_{n=1}^{\infty} e^{-nx} \left(\frac{1}{nx} + \frac{4}{n^2 x^2} + \frac{8}{n^3 x^3} + \frac{8}{n^4 x^4} \right) \right\}, \quad (9)$$

for small values of x :

$$S = -3Nk \left[\ln(1 - e^{-x}) - \frac{4}{3} \left\{ 1 - \frac{3}{8}x + \frac{3}{5} \frac{B_1}{2!} x^2 - \frac{3}{7} \frac{B_2}{4!} x^4 + \dots \right\} \right], \quad (10)$$

if B_1, B_2, \dots denote the Bernoullian coefficients.

a. Low temperatures. If of the development (9) we write down the first term only, we may put $x = \frac{\theta_0}{T}$ with θ_0 according to Suppl. No. 30a equation (18a) or (18b). This gives

$$S = \alpha M^3 V^2 T^3, \dots \dots \dots (11)$$

if M denotes the molecular weight, and α a constant which depends on PLANCK's constants h and k and on the AVOGADRO number.

According to (11), the volume being kept constant, the entropy approaches to 0 for $T = 0$. It does so proportionally to T^3 , which is in agreement with (2). The latter would not have been the case if (see Suppl. No. 30a § 4c) the zero-point energy had not been introduced in the theory, cf. H. TETRODE, Physik. ZS. 14 (1913), p. 214.

β. High temperatures. Retaining in the development for high temperatures only the first term which gives a deviation from the equipartition laws, we obtain:

$$S = -\frac{3Nk}{2} \ln \frac{8}{3} \frac{\theta_0}{T} + 4Nk + \frac{16Nk}{1575} \frac{\theta_0^2}{T^2} \dots \dots \dots (13)$$

or

$$S = Nk \left\{ \frac{3}{2} \ln \beta M T V^{2/3} + 4 + \frac{1}{700} (\beta M T V^{2/3})^{-2} \right\} \dots \dots (14)$$

where β is a constant depending on $h, k,$ and N .

The additive constant $Nk \left(4 + \frac{3}{2} \ln \beta M \right)$, with which the "chemical constant" is connected, agrees with the expression obtained for it by TETRODE l.c. without the assumption of a zero-point energy.

b. From (11) and (14) the entropy of the molecular quantity of

an *ideal mixture*, again leaving molecular rotations and intramolecular motions out of account, may be easily derived if GIBBS' theorem, according to which the entropy of such a mixture is obtained by calculating the entropy for each component as if it were present by itself in the volume occupied by the mixture and adding the values so obtained, is supposed to remain valid when the equipartition laws no longer hold. We then obtain:

α. for *low temperatures*

$$S = aT^3 V^2 \sum \frac{M_1^3}{c_1}, \dots \dots \dots (16)$$

β. for *high temperatures*, retaining the first term which gives a deviation from the equipartition laws:

$$S = Nk \left\{ \frac{3}{2} \ln \beta T V^{3/2} + \frac{3}{2} \sum c_1 \ln M_1 - \sum c_1 \ln c_1 + 4 + \frac{1}{700} (\beta T V^{3/2})^{-2} \cdot \sum c_1^{7/2} M_1^{-2} \right\} \dots \dots \dots (17)$$

If at constant volume the temperature continually decreases, at sufficiently low temperatures (for densities of the order of magnitude of the normal density at extremely low temperatures, cf. Suppl. N^o. 30a § 5b) a positive deviation from the equipartition value begins to develop itself. This deviation finally causes the entropy for a mixture also to approach to 0 proportionally to T^3 as shown by (16) instead of becoming $-\infty$.

Physics. — “*Further experiments with liquid helium. H. On the electrical resistance etc. (continued). VIII. The sudden disappearance of the ordinary resistance of tin, and the super-conductive state of lead.*” By Prof. H. KAMERLINGH ONNES.

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§ 13¹⁾. *First observation of the phenomena. α.* Passing from the investigation of the super-conductive state of mercury to that of the change in the resistance of various other metals when they are cooled to helium temperatures, although I hoped to find more super-conductors, I did not think it likely, judging from our experiences

¹⁾ The §§, tables and figures are numbered successively to those of Comm. VII of this series. (These Proceedings May and June 1913).