[8] A. Glaser, *Dissertation*, Münich, 1924.

[9] S. J. Barnett, *Physic. Rev.*, **25**, 835, 1925.

[10] This can, for instance, be seen from Darwin's Lagrangian and Hamiltonian functions for atoms in magnetic fields, *Phil. Mag.*, **39**, 537, 1920.

[11] P. Tartakowsky, *Zeits. f. Physik*, **34**, 216, 1925.

[12] P. Debye, *Physic. Rev.*, **25**, 586A, 1925.

[13] A. Pascal, numerous references listed in *Jahr. d. Rad. and Elektr.*, **17**, 184, 1920.

[14] The value $\epsilon = 1.0000693$ for He is that obtained by Herzfeld and Wolf, *Ann. d. Physik*, **76**, 71 and 567, 1925, by extrapolating refractive indices to infinite wave-length, and is probably more accurate than direct determinations. The value $\epsilon = 1.000273$ for H_2 is that obtained directly by Tangl. This value apparently is for 0°C. rather than 20°C., contrary to the statement in the Landolt-Bornstein tables (5th ed., p. 1041) and so is in good agreement with dispersion data.

[15] If the field were strong enough for spacial quantization, the values of Z obtained from diamagnetism with the old quantum theory would be 1.14 and 0.78 instead of 0.93 and 0.64. We suppose the electric but not the magnetic field adequate for spacial quantization in the old theory.

[16] Wills and Hector, *Physic. Rev.*, **23**, 209, 1926; Hector, *Ibid.*, **24**, 418.

[17] Soné, *Phil. Mag.*, **39**, 305, 1920.

[18] E. Lehrer, *Ann. Physik*, **81**, 229, 1926.

[19] C. W. Hammar, *Proc. Nat. Acad. Sci.*, **12**, 594 and 597, 1926.

[20] J. H. Jones, *Proc. Roy. Soc.*, **105A**, 650, 1924.

ON THE EQUILIBRIUM BETWEEN RADIATION AND MATTER

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1. *Introduction.*—The theories of stellar evolution of Eddington, Jeans and Russell apparently necessitate the transformation of matter into radiation in order to account for the great life span of the sun and other stars. Such a process, however, immediately implies the existence of the reverse change of radiation into matter, and thus leads to the possibility of an equilibrium between these two forms of energy under suitable conditions of concentration and temperature.

By applying the laws of thermodynamics to an equilibrium mixture of radiation and matter Stern[1] has attacked this problem in a very stimulating and original manner, and derived an expression for the concentration of perfect gas which would be in equilibrium with radiation at any given temperature. He obtains the surprising result that, even at a temperature of one hundred million degrees, only one electron per cubic centimeter could be present at equilibrium. For a mixture containing equal numbers of electrons and protons, such as would presumably have to form from radiation in order to maintain electrical neutrality, the equilibrium concentrations would be even enormously lower. This result seems somewhat unsatisfactory, since it might seem reasonable to expect that the change of matter into radiation in the interior of a star would take place at a rate high enough to maintain a concentration of matter not greatly in excess of equilibrium. Taking the sun as an example, we then find, however, that its mean density of 1.4 grams per cubic centimeter and internal temperature of the order of forty million degrees are very far from being in agreement with the Stern result.

The purpose of the present note is as follows. To obtain his derivation Stern has had to apply all three laws of thermodynamics, not only the dependable first and second laws of classical thermodynamics, but also the less certainly formulated third law or Nernst heat theorem. It will be shown below, however, that by applying merely the first two laws of thermodynamics it is possible to obtain an equation connecting concentration and temperature of the same form as Stern's, but containing, as might be expected, a constant which cannot be evaluated from the principles of classical thermodynamics. It will then be shown that the introduction of the third law in the form used by Stern leads indeed to his value of this constant. Arguments will be presented, however, which indicate that there might be a more correct manner of introducing the third law which would lead to a very much higher value of this constant.

2. *The Pressure-Temperature Relation for Matter and Radiation.*—Consider a cylinder provided with a sliding piston and with walls which can be kept at a constant temperature and can interchange radiation with the space inside. Let us start with zero volume behind the piston and with the walls at temperature T, and then withdraw the piston until the volume v is included behind it. If the process is carried out reversibly with respect to the emission of radiation and with respect to the equilibrium between radiation and matter, the work done will be

$$W = pv \tag{1}$$

where p is the combined pressure of matter and radiation at temperature T, and the heat absorbed will be

$$Q = E + pv \tag{2}$$

where E is the total energy of the matter and radiation thus produced inside the cylinder. Hence the combined entropy of this matter and radiation will be

$$S = \frac{E + pv}{T}. \tag{3}$$

We have now, however, as the condition of thermodynamic equilibrium that the entropy of our system must be a maximum for any variations at constant energy content and constant volume, and hence, taking T

and v as the independent variables, can write the simultaneous equations

$$\delta S = \left(-\frac{E + pv}{T^2} + \frac{1}{T}\frac{dE}{dT} + \frac{v}{T}\frac{dp}{dT}\right)\delta T = 0$$

$$\delta E = \frac{dE}{dT}\delta T = 0$$

and by combination obtain the result

$$v\frac{dp}{dT} = \frac{E + pv}{T}. \tag{4}$$

This is a general expression for the dependence of pressure on temperature in the case of any equilibrium mixture of matter and radiation. The equation can also be simply and directly derived from the Carnot principle, since a reversible cycle operating between temperatures $T + dT$ and T can be set up in which vdp is the work done and $E + pv$ the heat transferred from the upper to the lower temperature.

3. *The Pressure-Temperature Relation for Matter in Equilibrium with Radiation.*—If now we consider a temperature at which the concentration of matter is low enough so that the energy of the radiation is given by the Stefan-Boltzmann equation

$$E_R = avT^4 \tag{5}$$

and its partial pressure by the equation

$$p_R = {}^1/_3 aT^4 \tag{6}$$

we may evidently write for the radiation alone an equation of exactly the same form as (4), namely

$$v\frac{dp_R}{dT} = \frac{E_R + p_R v}{T}. \tag{7}$$

Hence by subtraction from equation (4) we can then obtain for the *matter alone* an equation of that same form, namely

$$v\frac{dp_M}{dT} = \frac{E_M + p_M v}{T} \tag{8}$$

connecting the partial pressure of this matter with its energy and temperature.

4. *Concentration of a Perfect Gas in Equilibrium with Radiation.*—In case we consider the matter to be present in the form of a perfect gas, we can easily integrate equation (8). We have for the pressure-volume product

$$pv = NkT \tag{9}$$

where N is the number of atoms present. And for the total energy including that necessary to form N atoms of mass m, can write

$$E = \frac{3}{2} NkT + Nmc^2. \tag{10}$$

Substituting in (8) we obtain

$$kT\frac{dN}{dT} + Nk = \frac{3}{2} Nk + \frac{Nmc^2}{T} + Nk \tag{11}$$

and integrating easily find our final expression

$$\frac{N}{v} = bT^{3/2}e^{-\frac{mc^2}{RT}}. \tag{12}$$

where b arises from the constant of integration. This equation for the number of atoms present at equilibrium has the same form as that of Stern, but sets no requirements on the magnitude of the constant b.

5. *Discussion of the Constant b.*—To obtain a value of the constant b, we should have in some way to introduce the third law of thermodynamics, through a consideration of the absolute entropy of the gas. Returning, however, to the process discussed in section 2, it is evident, when we produce a mixture of radiation and matter by drawing out the piston through the volume v at temperature T, that the absolute entropy of the contents produced will be

$$S = \frac{E + pv}{T} \tag{13}$$

and this must be the *absolute entropy* of the radiation and matter formed, in the most precise sense that we can use that term, since at the start of the process the cylinder had no volume nor contents, and the above quantity is certainly the entropy that has flowed from the walls into the volume created behind the piston. Hence with concentrations of gas low enough so that the partial entropy of the radiation itself is given by an equation of the form of (13), we can write as an absolutely certain expression for the absolute entropy of the gas

$$S = \frac{E + pv}{T} = \frac{{}^3/_2NkT + Nmc^2 + NkT}{T}. \tag{14}$$

Hence, if we had some suitable theoretical expression for the absolute entropy of our gas, we should at once be in a position to obtain an absolute value of the equilibrium concentration by equating with (14).

Now Stern's deduction is apparently equivalent to setting the above value for the absolute entropy of our gas equal to the Sackur-Tetrode expression for the entropy of a monatomic gas

$$S = kN \log \left\{ \frac{e^{5/2}v}{h^3 N} (2\pi mkT)^{3/2} \right\}. \tag{15}$$

Equating expressions (14) and (15) we then easily obtain the Stern result

$$\frac{N}{v} = \left(\frac{2\pi mk}{h^2}\right)^{3/2} T^{3/2} e^{-\frac{mc^2}{kT}}. \tag{16}$$

Such a use of the Sackur-Tetrode formula in this connection, however, seems far from justified since the theoretical derivations of this equation are based on considerations which do not contemplate the possibility of changes in the total number of atoms N. Thus if we follow Planck's[2] latest procedure, we may express the absolute entropy of a system by the equation

$$S = k \log P \tag{17}$$

where P is the total number of stationary states of the system whose energy does not exceed the total energy available; and, as he has shown, may then derive the Sackur-Tetrode expression for the entropy of a monatomic gas by considering all stationary states in which the *number of atoms* retains the *constant* value N and the *kinetic energy* does not exceed the value $E - Nmc^2$.

In the case of interest, however, the *number of atoms* could change at will from one to E/mc^2, the *kinetic energy* available for different configurations in the phase space changing at the same time from $E - mc^2$ to zero. Hence, it would seem that an application of the Planck method, correctly made for our purposes, would lead to a value of the absolute entropy much greater than that given by the Sackur-Tetrode formula, and hence to a value of the constant b in equation (12) much larger than that obtained by Stern.

Under the circumstances it may not be unreasonable to try to apply an equation of the form of (12) to the interpretation of astro-physical phenomena, leaving the absolute value of the constant as a problem for later investigation.

[1] Stern, *Zs. Elektrochem.*, **31**, 448 (1925); *Trans. Farad. Soc.*, **21**, 477 (1925–26).

[2] Planck, *Zs. Physik*, **35**, 155 (1925).