

ON A HEURISTIC VIEWPOINT OF THE CREATION AND MODIFICATION OF LIGHT

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**Über einen der Erzeugung und Verwandlung des Lichtes
betreffenden heuristischen Gesichtspunkt**

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INTRODUCTION

Between the conceptions that physicists have of gases and other ponderable matter *vis-à-vis* MAXWELL's theory of electromagnetic processes transpiring in so-called 'empty space,' there exists a deep formal distinction. While for the state of a material body the specification of the position and velocity of a very large but still finite number of atoms and electrons suffices, for the specification of the state of an electromagnetic field in a given space, continuous functions are used, so that a finite number of quantities is seen as insufficient for the complete description of its state. According to MAXWELL theory, for all purely electromagnetic phenomena, in particular for light, energy is expressed as a continuous function in space, whereas for particles nowadays physicists consider that energy is a sum over atoms and electrons. The energy of ponderable matter cannot be divided into arbitrarily small portions, but the energy of a ray from a point light source, according to MAXWELL theory or wave theory generally, is propagated over a continuously expanding volume.

The wave theory of light employing continuous functions has been verified through its description of purely optical effects so excellently, that it will never be replaced by some other theory. Nevertheless, it is to be kept in mind, that optical observations constitute averages, not instantaneous values; and, despite the verification of the theory by its description of the phenomena of deflection, reflection, diffraction, dispersion, etc., it is still conceivably possible, that experiments could uncover conflicts with theory when applied to the generation and modification of light.

It seems to me in fact, that observations on "black body radiation," photo luminescence, the generation of cathode rays by ultraviolet light and other means of light generation or modification appear to be more comprehensible with the assumption that light energy is discontinuously distributed in space. According to the notion proposed here, for propagation of light from a point source, its energy is not continuously dispersed over ever larger volumes in space, rather there should exist a finite number of spatially localized energy quanta, which propagate without dividing and can be generated and absorbed only as a whole.

In the following I shall describe my logic, as well as the effects that led me to this conclusion, in the hope, that this view point will be useful for researchers.

1. ON A DIFFICULTY IN THE THEORY OF “BLACK BODY” RADIATION

Let us consider the following case first from a viewpoint based on MAXWELL’s theory and the existence of electrons. Suppose that a number of gas molecules and electrons are enclosed within a fully reflecting cavity. Let the particles move freely while exercising conservative forces on one another when they closely approach each other, that is, they scatter off one another like molecules according to kinetic gas theory.¹ A number of additional electrons are envisioned to be farther away and bound to distant fixed points in the volume by forces proportional to their separation from these same points. These additional electrons also interact with the free electrons and molecules via conservative forces when approached. Let us call these bound electrons “resonators;” they are taken to emit and absorb electromagnetic waves of a particular frequency.

In accord with current views on the generation of light, which were founded on consideration of dynamical equilibrium in MAXWELL theory, radiation in the above mentioned cavity must be identical with “black body” radiation — at least in the presence of resonators for all relevant frequencies.

To begin, let us ignore the radiation emitted and absorbed by the resonators and investigate the interaction (the scatterings) between the molecules and electrons under the conditions of dynamical equilibrium. The kinetic theory of gases for the latter conditions requires that the average live force of resonant electrons equals the average kinetic energy of a mobile gas molecules. If we resolve the motion of the electrons into three orthogonal oscillations, we find the average, \bar{E} , of the energy of such linear oscillators to be:

$$\bar{E} = \frac{R}{N}T,$$

where R is the absolute gas constant, N the number of “actual molecules” in a gram equivalent and T the absolute temperature. The energy, \bar{E} equals, because of the equality of the time average of kinetic and potential energy, $2/3$ of the live force of a free, single atom molecule. Were it now via some cause — in the case considered here: radiation — that a resonator had time average energy either larger or smaller than \bar{E} , then the scatterings with free electrons and molecules would not lead to a net null energy exchange with the gas. In other words, for the situation considered here, dynamical equilibrium is possible only if each resonator has an average energy of \bar{E} .

We now make the same argument for the interaction between resonators and radiation in the cavity. PLANCK has derived the conditions for dynamical equilibrium for radiation,²

¹This assumption is equivalent to the supposition, that the average kinetic energy of the gas molecules and electrons is equal at thermal equilibrium, an assumption with which DRUDE has derived theoretically the thermal and electrical conductivity of metals.

²M. PLANCK, *Ann. d. Phys.* **1** (1900), p. 99.

under the conditions, that the radiation can be considered a random process.³ He found

$$\bar{E}_\nu = \frac{L^3}{8\pi\nu^2} \rho_\nu,$$

where \bar{E}_ν is the average energy of a resonator with frequency ν (per degree of freedom), L the speed of light and $\rho_\nu d\nu$ the average energy per unit volume of that part of the radiation for which the frequency is between ν and $\nu + d\nu$.

Should the radiation energy at frequency ν on the whole not be either increased or diminished, the following must then obtain:

$$\begin{aligned} \frac{R}{N} T = \bar{E} = \bar{E}_\nu &= \frac{L^3}{8\pi\nu^2} \rho_\nu, \\ \rho_\nu &= \frac{R}{N} \frac{8\pi\nu^2}{L^3} T. \end{aligned}$$

These equations, as the determining conditions for dynamical equilibrium, not only have no empirical verification, they indicate, in accord with our understanding, that there cannot exist a specific energy distribution between radiation (aether) and matter. The broader the spectral band considered, the larger the total energy must be, and in the limit we get

$$\int_0^\infty \rho_\nu d\nu = \frac{R}{N} \frac{8\pi}{L^3} \int_0^\infty \nu^2 d\nu = \infty.$$

2. ON PLANCK'S DETERMINATION OF THE BASIC QUANTUM.

In the following I wish to show that PLANCK's determination of the basic quanta is to a degree independent of his theory of "black body" radiation.

All experiments have verified PLANCK's formula⁴ for ρ_ν , which is

$$\rho_\nu = \frac{\alpha \nu^3}{e^{\frac{\alpha \nu}{T}} - 1},$$

where

$$\alpha = 6.10 \times 10^{-55}.$$

For large values of T/ν , that is for long wave lengths and large radiation densities, this formula becomes

$$\rho_\nu = \frac{\alpha}{\beta} \nu^2 T.$$

³This condition can be formulated as follows: We expand the Z -component of the electric force (Z) at an arbitrary point in the cavity between the times $t = 0$ and $t = T$ (where T is taken as very large in comparison to all cycle times) in a FOURIER series

$$F = \sum_{\nu=1}^{\infty} A_\nu \sin\left(2\pi\nu \frac{t}{T} + \alpha_\nu\right),$$

where $A_\nu \geq 0$ and $0 \leq \alpha_\nu \leq 2\pi$. If one now considers an ensemble of such expansions at this point at various initial times, then the quantities A_ν and α_ν will have various values. There will be then a (static) probability of occurrence for the various combinations of values for the quantities A_ν and α_ν of the form

$$dW = f(A_1, A_2, \dots, \alpha_1, \alpha_2, \dots).$$

The radiation will be then the most random if

$$f(A_1, A_2, \dots, \alpha_1, \alpha_2, \dots) = F_1(A_1) F_2(A_2) \dots f(\alpha_1) f(\alpha_2) \dots,$$

that is, if the probability of a particular value of one of the quantities A or α has, is independent of the values of all other quantities A and α . The better the condition that individual pairs of the quantities A_ν and α_ν depend on emission and absorption from *particular* resonator groups is satisfied, the greater is the validity of the assumption that the radiation is "random."

⁴M. PLANCK, *Ann. d. Phys.* **4**, 561 (1901).

One sees that this latter version coincides with that from MAXWELL theory as presented in §1. By setting the coefficients in both formulas equal, one gets

$$\frac{R}{N} \frac{8\pi}{L^3} = \frac{\alpha}{\beta},$$

or

$$N = \frac{\beta}{\alpha} \frac{8\pi R}{L^3} = 6.17 \times 10^{23},$$

that is, one atom of hydrogen weights $1/N$ gram = 1.62×10^{-24} g. This is precisely the value found by PLANCK, which also coincides with the value found using other methods.

Thus, we are led to the conclusion: the larger the energy density and wavelength, the more accurate our current theories; but, for lower densities and shorter wavelengths, they fail completely.

In what follows we consider "black body" radiation in view of experiments without regard to its generation and propagation.

3. ON THE ENTROPY OF RADIATION

The following consideration is to be found in a famous article from WIEN and will be repeated here for the sake of continuity of presentation.

Consider an emission which fills the volume v . We shall assume that the perceptible characteristics of this emission are completely known if the radiation density $\rho(v)$ for all frequencies is given.⁵ In that radiation in various frequencies can be seen as independent with respect to doing work or delivering heat, the entropy of the emission can be written in the form

$$S = v \int_0^\infty \varphi(\rho, v) dv,$$

where φ is a function of the variables ρ and v . φ can be reduced to a function of only one variable by means of the assumption, that through adiabatic compression of radiation contained between reflecting walls, its entropy is not altered. However, we do not want to take this option, rather we wish to investigate how the function φ can be extracted from the black body law.

For "black body" radiation ρ is function of v , for which the entropy of the given energy is maximum, that is:

$$\delta \int_0^\infty \varphi(\rho, v) dv = 0,$$

if

$$\delta \int_0^\infty \rho dv = 0.$$

From this, it follows that for each choice of $\delta\rho$ as a function of v , we may write

$$\int_0^\infty \left(\frac{\partial \varphi}{\partial \rho} - \lambda \right) \delta\rho dv = 0,$$

where λ is independent of v . For black body radiation $\partial\varphi/\partial\rho$ is also independent of v .

For a temperature increase of black radiation in a volume $v = 1$ about dT , the following equation holds:

$$dS = \int_{v=0}^\infty \frac{\partial \varphi}{\partial \rho} d\rho dv,$$

⁵This assumption is arbitrary. One is naturally inclined to stick to this assumption, however, so long as experiments allow.

or, in that $\partial\varphi/\partial\rho$ is independent of ν

$$dS = \frac{\partial\varphi}{\partial\rho} dE.$$

In that dE equals the invested heat and the process is irreversible, it is also true that

$$dS = \frac{1}{T} dE.$$

By comparison, one then gets

$$\frac{\partial\varphi}{\partial\rho} = \frac{1}{T}.$$

This is the black body law. In summary, one can get the black body law from the function φ , or, in reverse, by integrating the black body law get the function φ by taking into account that for $\rho = 0$, φ vanishes.

4. THE FUNDAMENTAL LAW OF ENTROPY FOR A MONOCHROMATIC RAY OF LOW DENSITY.

From the preceding observations on "black body" radiation it is evident, that WEIN's law for black body radiation, namely

$$\rho = \alpha\nu^3 e^{-\beta\frac{\nu}{T}},$$

is not exactly correct, even though for large values of ν/T it has been empirically verified. We shall take this law as the foundation for our calculations, while keeping in mind, that our result will be valid only within certain limits.

From this formula one immediately gets:

$$\frac{1}{T} = -\frac{1}{\beta\nu} \lg \frac{\rho}{\alpha\nu^3}$$

and by then by using the relation found in the preceding paragraph:

$$\varphi(\rho, \nu) = -\frac{\rho}{\beta\nu} \left\{ \lg \frac{\rho}{\alpha\nu^3} - 1 \right\}.$$

Let there be a ray with energy E , for which the frequency is between ν and $\nu + d\nu$. Suppose this radiation fills volume ν . The entropy then of this radiation is

$$S = \nu\varphi(\rho, \nu)d\nu = -\frac{E}{\beta\nu} \left\{ \lg \frac{E}{\nu\alpha\nu^3 d\nu} - 1 \right\}.$$

We now focus on investigating the dependence of the entropy from the volume occupied, and denote the entropy with the letter S ; for which, if the radiation occupies volume ν , we get

$$S - S_0 = \frac{E}{\beta\nu} \lg \left(\frac{\nu}{\nu_0} \right).$$

This equation shows that the entropy of monochromatic radiation of sufficiently low density varies according to the same law as the entropy of an ideal gas or a sparse solution. This equation will be interpreted in terms of BOLTZMANN's principle, according to which the entropy of a system is a function of the probability of its state.

5. A INVESTIGATION OF THE DEPENDENCY OF THE ENTROPY OF GASES AND SPARSE SOLUTIONS ON THE VOLUME ON THE BASIS OF MOLECULAR THEORY

In connection with calculations of the entropy on the basis of molecular theory, the term "probability" is used in a sense that does not conform with its use in probability theory. In particular "states of equal probability" are frequently considered for situations where the hypothetical circumstances are actually specified well enough to justify deterministic deductions. I will show in another article, that for analysis of thermal processes, the so-called "statistical probability" is fully adequate, and I hope therefore, to have removed a logical objection impeding application of BOLTZMANN's principle. In this work, however, only its general formulation and a very particular application will be discussed.

If it makes sense to talk about the probability of the state of a system, and if, further, entropy increases with transformation to more probable states, then the entropy S_1 of a system is a function of the probability W_1 of the momentary state. If there are two non interacting systems S_1 and S_2 , one can write

$$\begin{aligned} S_1 &= \varphi_1(W_1), \\ S_2 &= \varphi_2(W_1). \end{aligned}$$

If one considers these systems as a single system with entropy S and probability W , then

$$S = S_1 + S_2 = \varphi(W),$$

and

$$W = W_1 \times W_2.$$

The latter relations states, that the states of the two systems are independent of each other. From this equation it follows

$$\varphi(W_1 \times W_2) = \varphi_1(W_1) + \varphi_2(W_2),$$

and therefore finally:

$$\begin{aligned} \varphi_1 &= C \lg(W_1) + \text{const.} \\ \varphi_2 &= C \lg(W_2) + \text{const.} \\ \varphi &= C \lg(W) + \text{const.} \end{aligned}$$

The quantity C is a universal constant; it has, as follows from the kinetic theory of gases, the value R/N , where the constants R and N have the same meaning as above. If S_0 denotes the entropy for a given starting state of the considered system and W is the relative probability of a state with entropy S , then in general we get:

$$S - S_0 = \frac{R}{N} \lg W.$$

Let us consider first the following special case. In a volume v_0 let there be a number (n) of mobile points (e.g., molecules), for which our considerations are to pertain. In addition, in this space there may be still other mobile points of an arbitrary nature. We make no assumption regarding the law regulating the motion of these points, except to the extent that there shall be no privileged position or direction. The number of points of the first type is to be so low that their influence on one another may be neglected.

For this system, which could be, for example, an ideal gas or a sparse solution, there is a certain entropy S_0 . Now let us consider that all n points are so displaced that they become confined to a sub volume v of v_0 , without, however, any other changes being introduced. For this state, obviously, there is a distinct of entropy (S), and we seek to determine the difference in entropy with the help of BOLTZMANN's principle.

We ask: how large is the probability of the latter state in comparison to the former one? Or: how large is the probability, that at an arbitrarily selected moment all n particles accidentally are located in the sub volume v ?

For the probability, which is a “statistical probability,” one gets the value

$$W = \left(\frac{v}{v_0} \right)^n,$$

from with the BOLTZMANN principle one gets

$$S - S_0 = R \left(\frac{n}{N} \right) \lg \left(\frac{v}{v_0} \right).$$

It is noteworthy, that the derivation of this equation, from which the BOYLE-GAY-LUSSAC law and the identically named law of osmotic pressures also can be easily derived thermodynamically,⁶ requires no assumption to the effect that the molecules need be in motion.

6. AN INTERPRETATION OF THE EXPRESSION FOR THE DEPENDENCE OF THE ENTROPY OF MONOCHROMATIC RADIATION ON THE VOLUME ACCORDING TO BOLTZMANN'S PRINCIPLE

In §4 we found for the dependence of the entropy of monochromatic radiation, the expression:

$$S - S_0 = \frac{E}{\beta v} \lg \left(\frac{v}{v_0} \right).$$

If one writes this equation in the form

$$S - S_0 = \frac{R}{N} \lg \left[\left(\frac{v}{v_0} \right)^{\frac{N}{R} \frac{E}{\beta v}} \right],$$

and then compares it with the general expression for the BOLTZMANN principle,

$$S - S_0 = \frac{R}{N} \lg W,$$

one comes to the conclusion:

If monochromatic radiation of frequency ν and energy E is enclosed in a volume v_0 (with reflecting walls), then the probability, that at an arbitrarily chosen moment the total radiation energy in a sub volume v of the total volume v_0 equals

$$W = \left(\frac{v}{v_0} \right)^{\frac{N}{R} \frac{E}{\beta v}}.$$

Further, we conclude:

⁶If E is the energy of the system, then one gets

$$-d(E - TS) = pdv = TdS = R \frac{n}{N} \frac{dv}{v},$$

that is

$$pv = R \frac{n}{N} T.$$

Monochromatic radiation of low density (within the zone of validity of WIEN'S Law) conforms to the theory of thermal transformations as if it consisted of mutually independent quanta of energy of the magnitude $R\beta v/N$.

We wish to compare the average magnitude of the energy quanta of "black body radiation" with the average live force of the center of mass motion of a molecule at a particular temperature. The latter quantity is $\frac{3}{2}(R/N)T$, while one has for the average magnitude of energy quantum from WIEN'S formula

$$\frac{\int_0^\infty \alpha v^3 e^{-\frac{\beta v}{T}} dv}{\int_0^\infty \frac{N}{R\beta v} \alpha v^3 e^{-\frac{\beta v}{T}} dv} = 3 \frac{R}{N} T.$$

If monochromatic radiation of sufficiently low density behaves as if the entropy depended on the volume as if it were a discontinuous medium, and for which energy quanta have the magnitude $R\beta v/N$, then it is natural to investigate whether the laws of generation and modification of light are so constructed, as if light itself consisted of such energy quanta. This shall be the focus of considerations it what follows.

7. ON STOKES' LAW

Let us consider monochromatic light shifted by the photo luminescence effect to another frequency, where, in accord with the above, it is taken that both before and after the frequency change, light consists of light energy quanta of the magnitude $(R/N)\beta v$, where v is the relevant frequency. The change can then be understood as follows. Each input energy quantum of frequency v_1 is absorbed and then gives — at least for sufficiently low intensity of input radiation — an energy quantum of frequency v_2 ; possibly also quanta of other frequencies v_3, v_4 , etc. as well as other types of energy, e.g., heat, may be generated. Other possible intermediary stages are immaterial. If the photo luminescence media is not to serve as an energy source, conservation of energy implies that the energy of the generated quantum cannot be larger than that of the input; i.e., the following must hold

$$\frac{R}{N} \beta v_2 \leq \frac{R}{N} \beta v_1$$

or

$$v_2 \leq v_1.$$

This is the well known STOKES' Law.

It is to be emphasized, that for low intensity, the quantity of generated light must be proportional, under similar circumstances, to the input, as each input energy quantum is an elementary process of the type described above, independent of the effect of all other input quanta. In particular, there is no lower boundary for the intensity of the input light below which it would be unable to generate an output.

Deviations from STOKES' Law are imaginable under the following circumstances:

1. if the number of simultaneous input quanta per unit volume is so large, that a generated quantum may equal several input quanta;
2. if the input (or generated) light is not in the portion of the energy spectrum subject to WIEN'S Law for "black body radiation," for example if the temperature of source for the input quanta is so high that WIEN'S Law is not valid.

The latter possibility is particularly interesting. According to the above development, it is not excluded, that a "non WEIN-type emission," even at low intensity, behaves in

energy relationships differently from “black body radiation” within the range of validity of WIEN’S Law.

8. ON THE GENERATION OF CATHODE RAYS BY ILLUMINATING A SOLID BODY

The usual formulation, i.e., the one in which light energy is considered continuously distributed throughout space, encounters serious difficulties in explaining light::charged-particle phenomena, especially those described in a pioneering work by LENARD.⁷

Following the conception that stimulating light is comprised of energy quanta $(R/N)\beta v$, fosters an understanding of the generation of cathode rays of the following sort. Light energy quanta are taken to penetrate the superficial layer of a solid body and at least a part of their energy is transformed to electron kinetic energy. The simplest conception is, that an individual quantum delivers all its energy to a single electron; and, we shall make the assumption, that indeed this case does arise. But, it is not excluded that electrons adsorb only a portion of the quantum’s energy. A portion of an interior electron’s energy will be absorbed within the solid by the time it reaches the superficial layer. Moreover, it will be assumed, that each electron, in order to escape the body, must expend a specified amount of work P (characteristic of the solid). Electrons initially directly on the solid’s surface and ejected perpendicular to it will exhibit the largest velocity. The kinetic energy of these electrons is given by

$$\frac{R}{N}\beta v - P$$

If the body is at potential Π and surrounded by conductors at null potential and if Π is sufficient to prevent a loss of charge from the body, then it must be

$$\Pi \epsilon = \frac{R}{N}\beta v - P,$$

where ϵ is the charge of the electron, or

$$\Pi E = R\beta v - P'$$

where E is the total charge of a gram equivalent of a single charged ion, and P is the potential of this quantity of negative charge in relation to the solid body.⁸

If one sets $E = 9.6 \times 10^3$, then $\Pi \times 10^{-8}$ is the potential in volts which evokes radiation from the body.

To check if this result conforms with measurements, let us set $P' = 0$ and $v = 1.03 \times 10^{15}$ (corresponding to the limit of sun shine toward the ultraviolet) and $\beta = 4.866 \times 10^{-11}$. We get $\Pi \times 10^7 = 4.3$ volts, which does in fact correspond well with results obtained by LENARD.⁹

If the derived formula is correct, then Π must be, as a function of the frequency of the stimulus light given in Cartesian coordinates, linear with slope characteristic of the solid.

The notions introduced here, as far as I can see, are not in conflict with observations made by LENARD on the characteristics of the light::charge interaction. If each energy quantum of the generated light independent of all others gives its energy to an electron, then the velocity distribution of electrons, that is, the quality of the generated cathode rays is independent of the intensity of the stimulus; otherwise the number of ejected electrons

⁷P. LENARD, *Ann. d. Phys.* **8**, 169, 170 (1902).

⁸If one assumes, that the single electron from a neutral molecule is ejected by light via an expenditure of a particular quantity of work, then one need not modify the derived expression except that P' is to be then a sum of two terms.

⁹P. LENARD, *Ann. d. Phys.* **8**, 165 & 184 Tab. I, Fig. 2 (1902).

is proportional to the intensity of the stimulus light.¹⁰ On the presumed validity limits regarding these considerations, the same sort of comments can be made as those concerning presumed deviations from STOKES' Law.

In the above it was assumed, that the energy, or at least a portion of the energy, would be completely transferred to a single electron. If one does not make this simplifying assumption, then one gets, in place of the above equation, the following one:

$$\Pi E + P' \leq R\beta v.$$

For cathode luminescence, which is the inverse to that considered, one gets by analogous reasoning the following equation:

$$\Pi E + P' \geq R\beta v.$$

For the substances investigated by LENARD, PE is always significantly larger than $R\beta v$, in that the potential which the cathode rays have traversed in order to generate visible light, requires several hundred, in some cases even thousands of volts.¹¹ Thus, it seems reasonable, that the kinetic energy of an electron converts to several light quanta.

9. ON THE IONIZATION OF GASES BY ULTRAVIOLET LIGHT

We shall have to assume, that for ionization of a gas by ultraviolet light each absorbed quantum leads to one ionized gas molecule. This leads directly to the conclusion, that the work of ionization (e.g., the theoretically required work) of a molecule cannot be larger than the energy of the absorbed quantum. If one denotes by J the (theoretical) ionization work per gram equivalent, then it must be so that

$$R\beta v \geq J.$$

According to LENARD's results the largest effective wave length for air is about 1.9×10^{12} cm. that is,

$$R\beta v = 6.4 \times 10^{12} \text{ erg} \geq J.$$

An upper limit for the ionization work can be obtained from the ionization potential in sparse gases. According to J. STARK,¹² the smallest measured ionization potential (on platinum anodes) for air is ca. 10 volts¹³ Thus, the upper limit for J is 9.6×10^{12} , which is nearly identical to what was found above. There is one other consequence, for which verification by experiment seems to me to be of great importance. If each absorbed light quantum ionizes one molecule, then between the absorbed light quantity L and the number j of gram molecules, the equation

$$j = \frac{L}{R\beta v}$$

holds. This relationship must, if our notions correspond to reality, hold for every gas, which (for the considered frequency) shows no noticeable absorption other than for ionization.

Bern, 18 March 1905

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¹⁰P. LENARD, *l.c.* p. 150 and 166-168.

¹¹P. LENARD, *Ann. d. Phys.* **12**, 469 (1903).

¹²J. STARK, *Electricity in gases* (Leipzig, 1902) p. 57.

¹³Within the gas, however, the ionization potential for negative ions is five time larger.