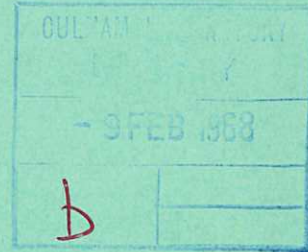
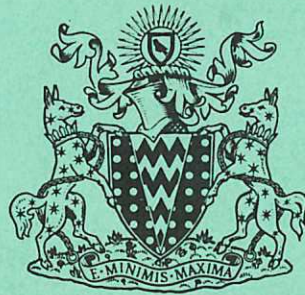


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DEPARTURES FROM LOCAL THERMODYNAMIC EQUILIBRIUM

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1967

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DEPARTURES FROM LOCAL THERMODYNAMIC EQUILIBRIUM

by

R.W.P. McWHIRTER

A B S T R A C T

This paper starts with a definition of local thermodynamic equilibrium and points out the relationship between local and complete thermodynamic equilibrium. It is shown that electron collisions are essential for the establishment of LTE and a relationship is derived for the minimum electron density at which collision processes are just sufficiently frequent to cause the plasma to be in LTE in face of the competing radiative processes. This relationship is derived for an optically thin plasma. The effect of radiation trapping is considered and some figures given by which the effect of this can be taken into account in assessing the validity of LTE in such cases. Account is now taken of the finite time required for the atomic collision processes to establish the plasma in LTE. A numerical example is worked out which shows that these considerations can be very important for plasmas of rapidly varying temperature. Mention is also made of departures from LTE caused by inhomogeneities in the plasma and by the positive ions having a different kinetic temperature from the electrons. Finally, it is remarked that even if the criteria for LTE to be valid are not met then the Saha and Boltzmann equations may still be applied to describe the population densities of the upper levels of individual species of atoms or ions.

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1. INTRODUCTION - DEFINITION OF LOCAL THERMODYNAMIC EQUILIBRIUM

We start by considering the state of a plasma that is contained within a vessel having 100% reflecting walls. Because the walls reflect both the particles and the radiation there is no leakage of energy from the plasma. The problem of calculating how the energy of the plasma is distributed among the various states available to it may be treated by the methods of statistical mechanics. The statistical mechanical calculation of the distribution does not require information about the details of the processes by which energy is transferred from one state to another. All that is required is that the total energy be conserved in each transition process. The calculation says nothing about the rate at which an equilibrium distribution is set up. The assumption is that sufficient time is allowed for the energy states to exchange with each other to establish such an equilibrium distribution. In assessing the distribution account is taken of (a) radiation energy, (b) kinetic energy of the particles, (c) energy of excitation of the atoms and ions, and (d) energy of ionization of the atoms and ions. The methods of statistical mechanics may be used to answer the question, 'what is the energy distribution which when slightly disturbed returns to the original distribution?'. Thus we may derive the following equations which describe the distribution among the energy states:

- (a) The radiation is described by the Planck function as follows:

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\exp(hc/\lambda kT) - 1} \quad \dots (1)$$

where λ is the wavelength of the radiation and T is the temperature of the plasma.

- (b) Particles of the plasma have velocities v described by Maxwell's equation:

$$dn(v) = n 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \exp(-mv^2/2kT) v^2 dv \quad \dots (2)$$

where n is the particle density.

- (c) The distribution of population densities among the excited levels of an atom or ion is described by Boltzmann's equation:

$$\frac{n(p)}{n(q)} = \frac{\omega(p)}{\omega(q)} \exp\left(-\frac{\chi(p,q)}{kT}\right) \quad \dots (3)$$

(p is the upper and q the lower level)

where $n(p)$ and $n(q)$ are the population densities of levels p and q of statistical weights $\omega(p)$ and $\omega(q)$ and having a difference of excitation potential of $\chi(p,q)$.

- (d) The state of ionization of the particles of the plasma is described by Saha's equation which when taken with Boltzmann's equation may be expressed:

$$\frac{n(z+1, g)n_e}{n(z, g)} = \frac{\omega(z+1, g)}{\omega(z, g)} 2 \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \exp\left(-\frac{\chi(z, g)}{kT}\right) \quad \dots (4)$$

where the symbols z and $z+1$ refer to the charge on the ion and $\chi(z,g)$ is the ionization potential of an ion of charge z in its ground level g .

The hypothetical plasma that is described by these equations is said to be in Complete Thermodynamic Equilibrium. In practice it can never be achieved in an absolute sense but nevertheless some of the equations may be used to a limited extent to describe real situations.

It turns out to be easier in real plasmas to contain the particles than the radiation. This is partly because particles have much larger collision cross-sections than radiation and because when the particles are charged they are subject to forces due to magnetic and electric fields. When the particle density is large enough the rate of exchange among the energy states available to the particles can be sufficiently rapid by collisions alone that the leakage of energy by radiation is a small perturbation compared with the total rate of exchange. Under these conditions it is possible to meet the requirements for thermodynamic equilibrium for the energy states available to the particles although not for the radiation, i.e. in each collisional transition process the total energy of the particles taking part is conserved. Thus we may expect plasmas of sufficiently high density to be described to some degree of approximation by the equations (2), (3) and (4) above. Such a system is said to be in Local Thermodynamic Equilibrium (LTE). It is the purpose of this paper to investigate some of the physical conditions that must be met before a system of particles may be adequately described by the equations of LTE. These conditions will be discussed from a theoretical stand-point although it is hoped that some of the conclusions are of practical value.

The restriction is adopted that the plasma should be more than about 1% ionized as this introduces some simplifications in the treatment that follows. Thus the conclusions apply to plasmas at temperatures greater than about 10^4 °K.

2. DEPARTURES DUE TO THE PARTICLE DENSITY BEING TOO LOW

Consider a long-lived plasma whose particles are contained in some way such that the plasma is homogeneous in temperature and density. Thus it may be assigned specific values of these quantities. Because of the elevated temperature it will be composed of electrons, positive ions and possibly atoms. A particle can make a transition to another energy state either by having a collision with one of the neighbouring particles, or by absorbing or emitting radiation. In discussing departures from LTE it is necessary to consider the details of these mechanisms by which transitions occur between energy states. We start with collisions and consider all classes of binary processes (including as a special case three-body recombination).

Elastic collisions are the most important of the mechanisms that give rise to transitions between the kinetic energy states of the particles. Charged particles because of their Coulomb fields have a much greater cross-section for such collisions than neutral atoms. Thus it may be possible to use equation (2) to describe, for example, the electron velocity distribution but it may fail to give an adequate description of the atom velocities. The relaxation time required for Coulomb collisions to cause some significantly large change in a given velocity distribution is a problem discussed by Spitzer⁽¹⁾.

He shows that the relaxation time for collisions between like particles is shorter than for unlike particles because when the masses are equal a larger amount of energy can be transferred in a collision. For about equal kinetic energies of electrons and positive ions, the electrons have a shorter relaxation time by a factor of about 50 as compared with the ions since their velocities are that much greater. Because of their different masses thermalization between electrons and ions is slower by a factor of about 2000 as compared with the relaxation time for the electrons alone. Spitzer quotes simple formulae which may be used to calculate these times. The self-collision time for like particles is given by:

$$t_c = \frac{m^{1/2}(3kT)^{3/2}}{8 \times 0.714 \pi n e^4 Z^4 \ln \Lambda} = \frac{11.4 A^{1/2} T^{3/2}}{n Z^4 \ln \Lambda} \text{ seconds} \quad \dots (5)$$

For unlike particles the time of equipartition of energy is given by:

$$t_{eq} = 5.87 \frac{AA_1}{n_1 Z^2 Z_1^2 \ln \Lambda} \left(\frac{T}{A} + \frac{T_1}{A_1} \right)^{3/2} \text{ seconds} \quad \dots (6)$$

In equations (5) and (6) A is the atomic weight (equal to $1/1823$ for electrons), T is the temperature in $^{\circ}\text{K}$, n is the particle density, Z is the charge of the particles in units of the electronic charge and $\ln \Lambda$ is a quantity tabulated by Spitzer and equal to 10 (to a factor two) for most practical cases. In equation (6) the suffix 1 denotes the field particles.

For the plasma to be described by a unique temperature value it is necessary that the relaxation times given by equations (5) and (6) be short compared with other relevant times. Otherwise it is often useful to adopt the concept of different temperatures for the different groups of particles. Of these the electrons are most important since they in most cases dominate the collision rates that determine the distribution among the energy states described by the Saha and Boltzmann equations (3) and (4). Thus while strictly all the particle velocities should be described by equation (2) with the same value of T it is essential for the electrons to have a Maxwellian distribution before the plasma may be said to be in LTE. An important test therefore for a real plasma to be in LTE is that the self-collision time for the electrons as given by equation (5) is short compared with the time for example for an electron to gain kT_e of energy from an external source.

We consider now those collision processes that lead to redistribution among the internal energy levels of the atoms (and ions). That is collisions which cause the bound electrons to move from one level of excitation to another including ionization and recombination transitions. For basically the same reasons as before, and because in this case too the target particles are electrons (even although they are bound to the atoms), the most efficient impinging particles are also electrons. (A special case where positive ion collisions are important is discussed later).

Consider a species of atom (or ion) with at least one bound electron, present in a plasma having an electron density $n_e \text{ cm}^{-3}$ and an electron temperature $T_e \text{ }^{\circ}\text{K}$. The ions will be subject to electron collisions which will cause transitions of those electrons in level p to some other level q at a rate given by the product of n_e with the relevant excitation coefficient $X(p,q)$. Here $X(p,q)$ is the average product of the

collision cross-section with the electron velocity over the velocity distribution assumed Maxwellian. The problem of calculating excitation cross-sections is one that has occupied atomic physicists for the last three or four decades and even now it is not entirely solved. In the present case we seek a general expression but we do not require very good accuracy. It turns out that there are a number of such expressions that are considered to be accurate to about a factor three and here we choose one due to Seaton⁽²⁾ based on the Bethe approximation. The others lead to similar conclusions as those that will be presented. Seaton's expression gives the following formula for $X(p,q)$:

$$X(p,q) = \langle Q(p,q) \times v_e \rangle_{\text{Maxwell}} = \frac{6.5 \cdot 10^{-4}}{\chi(p,q) \cdot T_e^{1/2}} f(q,p) \exp\left(-\frac{\chi(p,q)}{kT_e}\right) \text{cm}^3 \text{sec}^{-1} \quad \dots (7)$$

In this formula $f(p,q)$ is the absorption oscillator strength, T_e is the electron temperature in $^{\circ}\text{K}$, $\chi(p,q)$ is the excitation potential in electron volts and the other symbols have their usual meaning. Thus the lifetime of an atom in level p against a collisional transition to level q is $1/n_e X(p,q)$. All such collisional transitions are accompanied by their inverse processes which by the principle of detailed balance exactly equals the rate of the forward process when the levels have the populations they would have in thermodynamic equilibrium. Thus the comparison of the lifetime against collisional decay with some other unbalanced decay process gives some indication of whether this process causes departure from LTE.

The most important of these unbalanced processes for laboratory plasma is radiative decay giving rise to spectral lines and in the considerations that follow we shall compare the radiative lifetime with the lifetime against collisional decay. Before doing so however it should be pointed out that there are other mechanisms by which a plasma produces radiation. Apart from interaction with a magnetic field only those in which an electron and a positive ion interact to form a dipole produce significant amounts of radiation. If the electron is free the radiation forms part of the continuum spectrum either as bremsstrahlung or as recombination radiation. If it is bound then line radiation results. The lifetime of an electron to produce continuum radiation may be compared with its self-collision lifetime (equation (5)) and shown to be less restrictive than the corresponding comparison for bound electrons. Radiation may also be re-absorbed by the atoms of the plasma but initially we shall adopt the optically thin approximation and assume that such absorption processes are entirely negligible.

The comparison of the collisional lifetime of an electron in a bound level with its radiative lifetime may now be taken up again. The radiative lifetime is simply the reciprocal of the sum of the Einstein A coefficients which are related to the corresponding f -values by the well known formula. Supposing arbitrarily that for LTE to be adequately satisfied, the collisional lifetime for a transition between a pair of levels p and q should be less than a tenth of the corresponding radiative lifetime we have the following inequality:

$$n_e X(p,q) > 10 A(p,q) \quad \dots (8)$$

Using equation (7) for $X(p,q)$ this may be expressed in terms of a limiting electron density that must be exceeded for LTE to hold, as follows:

$$n_e > 1.6 \cdot 10^{12} T_e^{1/2} \chi(p,q)^3 \text{ cm}^{-3} \quad \dots (9)$$

where T_e is in $^{\circ}\text{K}$ and $\chi(p,q)$ is in eV. In deriving this criterion a very large number of additional processes have been neglected so it is useful to compare the results using this simple formula with the predictions of the more sophisticated calculations in which all the possible collision and radiative transitions have been taken into account. The latter have been done for hydrogen-like ions by Bates, McWhirter et al.⁽³⁾ and the electron densities that they predict for 10% departure of the ground level from its LTE value may be compared with the result of applying the equation (9) to the ground level and the first excited level of a hydrogen-like ion. Very good agreement is found. The agreement is certainly better than was to be expected from the relatively crude way in which the criterion (9) was derived.

The way in which the electron density influences the mechanisms of population of the ground level of a hydrogen-like ion is illustrated in Fig.1 which shows clearly how radiative processes give way completely to collisional transitions as the density is raised above the critical value for LTE.

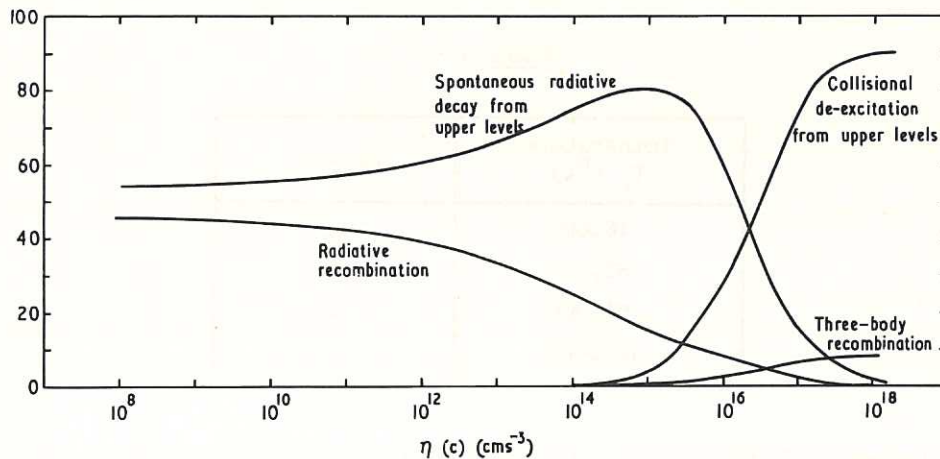


Fig. 1 (CLM-P 150)
The relative magnitudes of the four processes which populate the ground level of hydrogen-like ions at a plasma temperature (T/Z^2) of $32,000^{\circ}\text{K}$. The critical density for LTE is $3.0 \times 10^{17} \text{ cm}^{-3}$ (inequality 9)

Although there are minor differences in the way in which the criteria are expressed both Wilson⁽⁴⁾ and Griem⁽⁵⁾ have used similar arguments to derive LTE criteria. It turns out that their criteria are both less stringent than inequality (9) but in any case agree with it to a factor 2 in density.

The inequality (9) above can be expected to apply with adequate accuracy to non-hydrogen-like atoms and ions. The most critical value of $\chi(p,q)$ to take is that for the largest energy gap in the term scheme of the atom or ion.

The treatment so far has been in the optically thin approximation. That is, we have assumed that there has been no absorption of radiation in the plasma. We presume that the most intense source of local radiation is that due to the plasma itself, and the problem that we now turn to is the re-absorption of plasma radiation and in particular of resonance radiation. This provides an additional mechanism to those considered above for the

population of the upper level of the transition. Ultimately, of course, for plasmas of sufficiently large physical size (probably astronomical size) the emission and absorption of radiation will take over from collision processes as the dominant mechanisms for producing transitions among the bound levels. For even larger physical size the free electrons will interact with the radiation in the same way. The radiation density in the interior of such a plasma will have the spectral shape of a black body, i.e. be described by Planck's equation. Thus the effects of radiation trapping can be to compensate entirely for the effects of too low an electron density in causing departures from LTE. To assess properly the effect of trapping of radiation in the case considered above by Bates, McWhirter et al.⁽³⁾ requires the simultaneous solution of the collision equations with the equations of radiative transfer for each level of the ion or atom. Hearn⁽⁶⁾ has done a numerical solution of this problem for a plane parallel plasma of hydrogen-like ions in the steady-state. In order to define the extent of the trapping Hearn has chosen as a parameter the opacity at the core of the Lyman alpha line. This in turn has allowed the physical dimensions of the plasma to be calculated and hence a self-consistent-set of opacities for the other lines to be used in the calculation. These calculations show that for a hydrogen plasma of three or four centimetres in extent to be adequately described by the LTE equations, the criterion given above for an optically thin plasma may be relaxed by the factors given in Table 1. Thus at an electron temperature of 16,000⁰K an optically

TABLE 1

Temperature T_e (⁰ K)	Factor
16,000	20
32,000	5
64,000	2
> 100,000	1

thick hydrogen plasma of three or four centimetres in size will be in LTE at an electron density one twentieth of that given by inequality (9).

An approximate treatment of the effect of radiation trapping is due to Bates, et al.⁽³⁾. They did not attempt to derive a consistent set of opacities for the lines of a hydrogen plasma but simply adopted the approximation that all the Lyman lines are optically thick and, in their collisional-radiative calculation, put the corresponding radiative transition probabilities equal to zero. The result of this calculation gives steady-state population densities in good agreement with the results of Hearn's⁽⁶⁾ more sophisticated treatment when applied to plasmas of just over one centimetre in extent. This agreement for typical laboratory size plasma must be regarded as fortuitous. It will be seen as particularly fortunate when we come to use the results of Bates et al. to treat the problem of calculating the population distribution for a time-varying plasma which is optically thick.

The extension of these results for optically thick plasmas to non-hydrogen-like ions has not yet been attempted. In the absence of this an estimate of the effect of trapping for such ions is extremely difficult. However, the reduction in the minimum density for

LTE to hold as compared with the optically thin limiting value is unlikely to be as great as in the case of hydrogen.

The results of this section are summarised in Fig.2 where the range of applicability of the LTE model is shown on a plot of electron density against electron temperature. On the same diagram the regimes of operation of some of the well-known plasma producing devices are shown. The extension of the region of LTE due to the trapping of resonance radiation is comparatively small. Thus, for a four centimetre hydrogen plasma at $16,000^{\circ}\text{K}$ the region would extend down to about 10^{16} cm^{-3} electron density. The diagram shows clearly that none of the high temperature plasmas approach the LTE region and that, in particular, laser produced plasmas which have been reported to have densities as high as 10^{20} cm^{-3} are not in LTE.

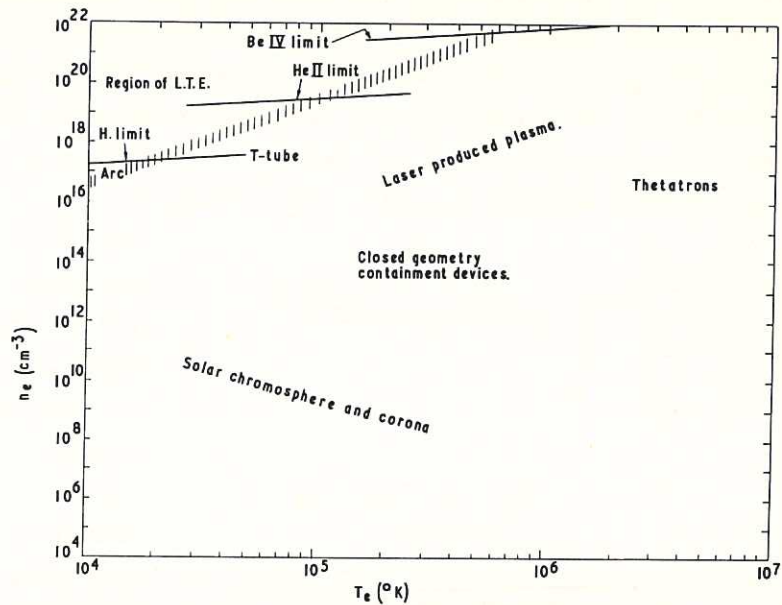


Fig. 2 (CLM-P 150)
 On this temperature/density diagram the limit of the range of applicability of the LTE approximation is shown thus:-----. The limits for particular ions to be in LTE are also shown. For comparison the ranges of operation of various plasma machines are also plotted as is the estimated density and temperature of the sun's atmosphere

It should be noted that the criteria have been derived with the assumption that the plasmas are in a steady-state. All laboratory plasmas of course have a finite lifetime and many of them are extremely short. It will be seen in the next section of this paper that in the cases of transient plasmas there are important additional criteria that must be met before the LTE equations may be applied to them with confidence.

3. DEPARTURES DUE TO THERE BEING INSUFFICIENT TIME FOR THE PLASMA TO ADJUST TO A CHANGE IN CONDITIONS

In our original consideration of a fully contained plasma in complete thermodynamic equilibrium it was remarked that one of the assumptions was that there was sufficient time for the plasma to relax to a steady-state. We turn now to a consideration of the time required by a real plasma to reach such a state. The question that we ask here is, 'what is the relaxation time for the population distribution among the excited levels of the atoms or ions to take up the values appropriate to the new conditions following a sudden change in these conditions?' The rates are determined by the nature of the collisional and radiative processes by which transitions take place between the levels. For levels that can decay radiatively the lifetimes are equal to or are shorter than the radiative lifetimes because besides the possibility of radiative decay these levels may also decay collisionally. The relaxation time constant of the ground level of an atom or ion on the other

hand is determined by the appropriate ionization of recombination coefficient. These time-constants are very much longer than the time-constants for the excited levels and are therefore the time-constants that determine the relaxation time necessary for LTE to be established following a discontinuity in the plasma conditions. The appropriate coefficients for hydrogen and hydrogen-like ions have been calculated by Bates et al. for both the optically thick and optically thin approximations. To illustrate the effect of these relaxation times consider a pure helium plasma initially at a temperature of $128,000^{\circ}\text{K}$ which suddenly drops to $32,000^{\circ}\text{K}$. This situation is illustrated diagrammatically in Fig.3

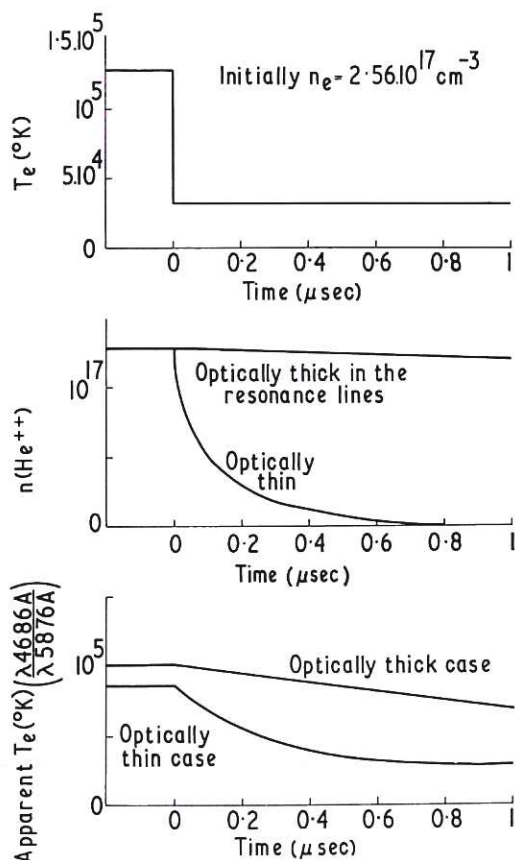


Fig. 3 (CLM-P 150)
 This diagram illustrates the way in which the rates of the atomic processes determine the rates of change of the populations of the ions following an abrupt change in the electron temperature. If the erroneous assumption is made that such a plasma is in LTE and its temperature estimated from the intensity ratio of two spectral lines then the result can differ from the 'true' value by as much as a factor two

intensities are now analysed as if the plasma was in LTE and the resulting apparent electron temperature plotted for comparison with the values initially postulated. The results are shown in Fig.3. The discrepancy between the postulated and the apparent values of the electron temperature in the initial period before it drops to the lower value is due to the fact that the plasma density is too low to sustain LTE. To meet the criterion given above the electron density would have to be about 2 orders of magnitude greater than that taken. The effect of the plasma being optically thick is illustrated by the apparent electron temperature for this case being closer than the optically thin case to the postulated value. However, the effect of the greater opacity in inhibiting recombination is

The values chosen are typical of those in the plasma produced by the magnetically driven shock in a T-tube. However, the example is hypothetical. Since the temperature and densities are specified it is possible to compute the population densities of the excited levels of the helium ions that will be formed. This has been done using the collisional-radiative approximation of Bates et al. and the resulting populations of the ground states shown in the same figure. In the laboratory the relative intensities of the helium II 4686 Å line and the helium I 5876 Å line have been used to determine the electron temperature of plasma such as that produced in a T-tube. In the present example the population densities of the upper levels of these transitions have been calculated as functions of time and up to this point care has been taken to do a proper time-dependent collisional-radiative calculation of the population densities. It has been done in both the optically-thin and optically-thick-in-resonance-lines approximation. The object of the calculation is to illustrate what happens if the erroneous assumption of LTE is made in analysing the spectral intensity ratio. Thus the computed spectral

seen in the longer time required for the plasma to reach its new steady-state population distribution. In fact for the cases chosen the optically-thick time constant is about 100 times longer than the optically thin. This example illustrates clearly the sort of errors that might be expected to arise if the LTE assumption is made in such conditions where it is not justified. While errors of about a factor 2 in the absolute value of the electron temperature can arise, probably more important is the danger of erroneous impressions about the rate of change of the electron temperature of the plasma.

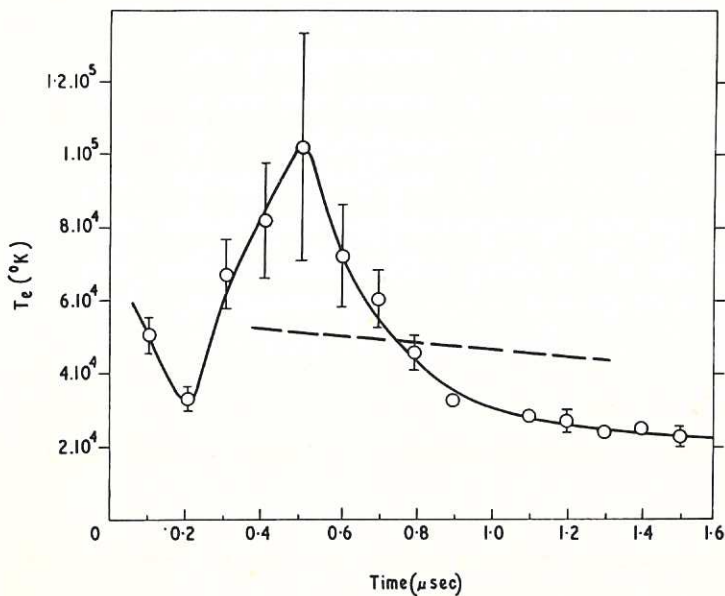


Fig. 4 (CLM-P 150)
The solid curve joining the experimental points is the electron temperature of a T-tube plasma measured by a method that does not depend on the assumption of LTE while the dashed curve illustrates the values obtained if LTE is erroneously assumed. After Eckerlie and McWhirter⁽⁷⁾

An example of the sort of error that can arise in a practical case when the LTE assumption is made in circumstances where it is not justified is shown in Fig.4 (Eckerlie and McWhirter⁽⁷⁾) in which the measured electron temperature is plotted as a function of time. The curve joining the experimental points shows how the temperature, determined from the intensity of the continuum without assuming LTE, varies during the period when the shock is passing the point of observation. The dotted curve shows the electron temperature variation as determined from the line ratio of helium II 4686 to helium I 5876 on the erroneous assumption of LTE.

The practical problem that we are now faced with is that of setting up some sort of criterion based on observable quantities that will establish whether or not the atomic relaxation time of the particles of the plasma is sufficiently rapid that the equations of LTE provide an adequate description of the plasma at all instants of time. Since normally there is no information about the plasma electron temperature independent of the assumption of LTE it is not possible to make use of such information in determining the criterion. Information on the electron density is usually available on such independent evidence as the Stark width of some line. It is now necessary to make some estimate of the ionization recombination coefficients appropriate to the ions of the plasma that are observed. These values depend upon the electron temperature and for ionization the dependence is very strong, but for recombination is less so. Nevertheless by some method of iteration it may be possible to come to reasonable estimates for these coefficients. The product of the electron density with the coefficient gives the reciprocal of the time constant for the plasma either to recombine or ionize. It has been shown above how important it is for the recombination coefficient to include effects to radiation trapping. The time constants thus estimated may now be compared with the rates of variation of the spectral lines observed. For the three LTE equations to represent the plasma adequately the calculated relaxation times should be very much shorter than, say a tenth of, the time required for

a spectral line to change in its intensity by a factor 3. It is clear that this is a very difficult criterion to apply in practice.

4. DEPARTURES DUE TO INHOMOGENEITIES IN THE PLASMA

Real plasmas are never highly homogeneous because the heating and cooling rates are never completely uniform. Typically this results in the outer layers of the plasma being cooler than the central core. Nevertheless, in principle at least, one may still expect to apply the equations of LTE to different regions of plasma and expect them to provide adequate descriptions. There are, however, mechanisms of which we have not taken account so far that can disturb the distribution of populations of plasmas having different temperatures and densities and in close proximity to each other. For simplicity we shall consider that there are two regions of plasma in contact with each other but having different temperatures and densities. Particles from one region can diffuse into the other and carry their own particular population distributions into the second region. If the rate of diffusion of particles is greater than the rate at which their populations are redistributed in the second region by collisions with local particles then important departures from the local LTE distribution can take place. Griem⁽⁵⁾ has given a formula by which the conditions may be recognised where diffusion causes departures from LTE in inhomogeneous plasmas.

If the regions of plasma in close proximity to each other, and having different conditions are also optically thick then there is the possibility that resonance radiation from one region will modify the population distribution in the other. Suppose the first region is optically thick in its resonance radiation so that it emits radiation at the wavelength of the core of the resonance lines close to the intensity of a black body at the electron temperature of the first region. The second region having the lower electron temperature, is then bathed in the resonance radiation corresponding to a higher temperature and hence of higher intensity than the local black body temperature. Under these circumstances the resonance radiation will be strongly reabsorbed and, unless the collision rate is sufficiently great to overcome it, the population distributions modified from the locally determined values. It is this phenomenon which gives rise to the well known self-reversal of resonance line radiation.

It is not possible to write down clear generally applicable criteria by which one can recognize the circumstances under which these departures due to inhomogeneities are important. It seems that individual cases must be treated on their merits. Of the two processes, that is diffusion of particles and trapping of resonance radiation, probably the latter is the more important in practice.

5. DEPARTURES CAUSED BY THE POSITIVE IONS HAVING A DIFFERENT KINETIC TEMPERATURE FROM THE ELECTRON

For levels lying close in energy to their neighbours, collisions by positive ions can be more effective than electron collisions in causing transitions. This is essentially because the cross-sections for collision by an impinging electron fall at high electron velocities, and allow the positive ions a chance to participate. Thus transitions between closely lying levels at the region of the ionization limit for example will tend to be

dominated by positive ions. If the ions have a different kinetic temperature from the electrons then the distribution that they will set up will not be the same as would be established by the electrons in LTE conditions. Such circumstances are most likely to arise in plasmas having rather a low degree of ionization where the atoms are considerably cooler than the electrons and are in close association (in terms of their kinetic energy) with the positive ions.

6. CIRCUMSTANCES WHERE THE SAHA AND BOLTZMANN EQUATIONS MAY BE APPLIED IN A RESTRICTED SENSE

The general conclusion to be drawn so far from the discussion is that there are few circumstances where one can safely say that a plasma is in local thermodynamic equilibrium. This means to say that the three very convenient equations set out at the beginning of this paper can seldom be applied in their entirety. However, it may be shown that in circumstances where the density is not sufficiently high for LTE to hold according to the criteria given above and where there is not sufficient time for the plasma to have reached a steady population distribution, it is nevertheless possible to apply the Saha-Boltzmann eq.(4) and obtain a good description of the population distribution for the upper levels of the ions. The level above which the Saha equation may be applied has been called the collision limit and also the thermal limit. The method of calculating the value of the thermal limit is set out by Bates, McWhirter et al.⁽³⁾. Their calculations are also used to illustrate the way in which the dominant population mechanisms change from radiative processes for the lower levels of an atom to collision processes above the thermal limit. This is shown in Fig.5 for hydrogen-like ions.

It is worth pointing out that the departure of only one level from the population that it would be calculated to have under LTE is sufficient to throw out the whole scheme by which the population distribution among all the particles of the plasma could be calculated. The failure of this one level means that it is not possible to relate through the Saha equation the populations of ions of different charge.

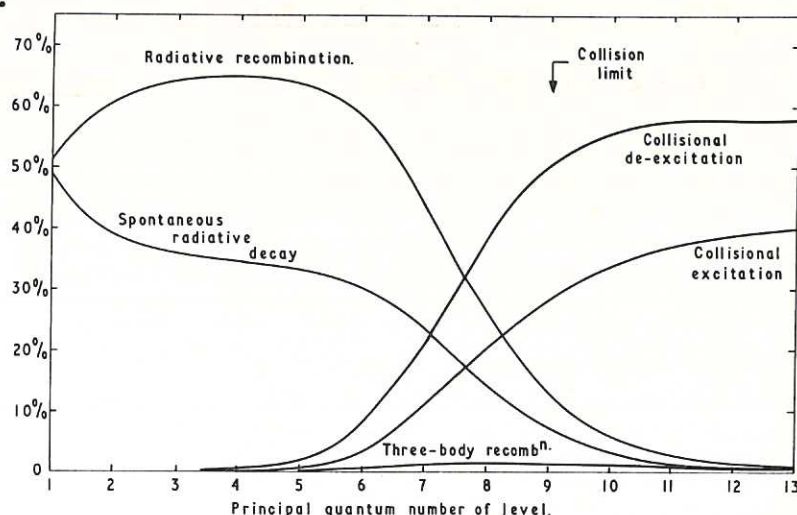


Fig. 5 (CLM-P 150)
The relative magnitudes of the five processes populating the first thirteen principal quantum levels of hydrogen for a plasma with $T_e = 64,000^\circ\text{K}$ and $n_e = 10^{10} \text{ cm}^{-3}$

7. CONCLUSION

This paper started with the definition of local thermodynamic equilibrium as a situation where equations (2), (3) and (4) applied. Following this, hypothetical situations have been discussed where for the following reasons departures from the LTE distributions may be expected: (a) plasma density may be too low, (b) plasma conditions may be changing so rapidly that the plasma distribution population does not have time to

catch up, (c) energy exchange between different regions of an inhomogeneous plasma may upset LTE distributions, (d) positive ion collisions where their kinetic temperature is different from that of the electrons may disrupt the LTE distribution in the proximity of the ionization limit, and (e) the effect of the trapping of resonance radiation was discussed for some of the above situations. Finally it was remarked that although they may not be fully applicable in certain circumstances the Saha and Boltzmann equations may still be used to describe populations particularly of upper levels.

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