21. ON THE TEMPERATURE IONIZATION OF ELEMENTS OF THE HIGHER GROUPS IN THE PERIODIC CLASSIFICATION

The theory of the temperature ionization of gases and its application to problems of radiation and astrophysics was given by the present writer in a number of papers published during last year. In these papers the theory was limited to the ionization of gas consisting of atoms of a single kind. Recently E. A. Milne and Henry Norris Russell[1] have extended the theory to mixtures of elements. By a comparison of the sun-spot and the solar spectrum, Russell finds that the predictions of the theory with reference to the relative intensity in the hotter and the cooler spectrum of lines associated with ionized and non-ionized atoms are found to be in general agreement with the facts. Russell has also shown that the temperature of the sun and the sunspot comes out to be much more in accord with the figures obtained from general intensity measurements when mixtures of different elements are considered instead of one single element.

But discrepancies have also been pointed out by Russell, which suggests the need of some modification. The nature of these discrepancies may be grasped from the following.

Let I_1 and I_2 be the ionization-potentials of elements A and B. Then at a definite temperature and pressure the ratio of the degrees of ionization of A and B is given by the equation

$$\log \frac{K_1}{K_2} = \log \left(\frac{x_1}{1-x_1}\right) - \log \left(\frac{x_2}{1-x_2}\right) = 5036 \frac{I_1 - I_2}{T}$$

where x_1, x_2 are the fractions ionized, I_1, I_2 are expressed in volts.

If $I_1 = I_2$, x_1 should equal x_2.

That this is not the case is shown from the fact that sodium and barium have got practically the same ionization potential (5·11 and 5·12 volts respectively), yet both in the sun and in the sun-spot, barium is a good deal more ionized than sodium. The resonance line of Ba, $\lambda = 5535 \cdot 93$, is absent or very faint both in the solar and the spot spectrum, and it is represented only by the enhanced lines (Ba+, $\lambda = 4934 \cdot 07$, $4554 \cdot 04$), which shows that barium is completely ionized not only in the sun but also in the spot. The resonance lines of sodium, $\lambda = 5889 \cdot 97$, $5895 \cdot 94$, on the other hand, are very prominent in the

solar spectrum, and are greatly intensified in the spot, which shows that in the sun a large percentage of sodium is unionized, and in the spot the percentage increases owing to a lowering of temperature.

What has been said of sodium and barium admits of a widegoing generalisation, viz. the alkaline earths are, as a rule, much more strongly ionized than their ionization potential would indicate. The behaviour of the alkalies is normal, and we shall see later on that, as a rule, *elements belonging to the higher groups are more easily ionized than elements of the preceding group, and the successive steps of ionization follow each other in rather quick succession.*

First of all, let us consider the relative intensities of the lines of alkalies and the alkaline earths in the sun and the spot spectra.

	Alkalies				Alkaline Earths.		
	I.P. volts.	Intensity Sun	Spot		I.P. volts.	Intensity Sun	Spot
Na	5·11	30	60	Mg	7·65	30	30[a]
K	4·32	6	15	Ca	6·08	20	25
R	4·16	—	1	Sr	5·67	1	3
Cs	3·81	—	?	Ba	5·12	—	—

The table shows that Ba is at least as highly ionized as Rb, though $I_1 - I_2 = 0.96$ volt. Sr is only slightly less ionized than Rb, both in the sun and the spot. Calcium is less ionized than potassium. When we compare the intensity of the lines of Ca, and Na, we find that in the sun they are almost equally ionized (calcium a bit more), but in the spot the recombination between Ca+ and (e) is much less marked than between Na+ and e.

Prof. Russell suggests that if the effect of radiation could be taken into account, the theory would be more improved, and the discrepancies could be explained. (See Russell, The Astro. Journ., May 1922).

II

It cannot be denied that the theory is always to be regarded as incomplete until the effect of the general field

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[1] Milne, The Observatory, Sept. 1921; Russell, The Astrophysical Journal, March 1922.

[a] Russell, loc. cit. p. 130; the intensity given against Mg is that due to the $2p$-$3s$ line; the resonance line of Mg, $\lambda = 2852$, is beyond the range.

of radiation can be taken into account. But it is doubtful if this alone will explain all the discrepancies. Another factor, the consideration of which is presented below, seems to play a rather important part.

It is now well accepted that elements of the first group, Li, Na, K, Rb, Cs, have only one electron in the outermost ring, while metals of the second group, Mg, Ca, Ba, Sr, have two electrons in the outer ring. Besides, these two electrons are equally situated—in other words, whenever a Ca-atom is subjected to the action of any physical agency tending to tear off the electrons, it will act equally on both of the valency electrons. In the case of the alkalies, it will act on one electron[3] only. Let us take the case of electrolytic solutions. Here the electrical forces act *equally strongly from all directions*, and a calcium atom loses both electrons. The inner electrons being more solidly fixed to the nucleus do not get detached. A sodium atom, on the other hand, loses under the same conditions only one electron, because there is only one electron which can be torn off by the same agency from a Na-atom.

This proves that in the normal case both the valency electrons in Ca occupy nearly identical positions in the atomic system—they are contained in the same part of the atomic volume, and are fixed to the system with forces which are either identical or very nearly identical.

Let us now consider what will take place when a Na-atom and a Ca-atom are subjected to the same ionizing agencies, say bombarding electrons, light pulses, or thermal collisions. For the sake of simplicity we consider the first case only. We shoot at a Ca- and at a Na-atom with the same number of electrons, which are possessed of such energy that they can tear off just one outer electron when it hits at the right place in the atom. Now, assuming the atomic volumes to be the same and the I.P. to be the same, it is clear that the number of successful hits on a Ca-atom will be twice as great as the number of successful hits on a Na-atom for in the outer volume calcium has two electrons, while sodium has only one. In other words, for the same strength of the ionizing agent, Ca-gas will be, roughly speaking, twice as highly ionized as Na-gas.

These considerations may be extended to all cases where ionization takes place by encounter, either with a light pulse or another atom.

In support of this view, an interesting observation by Millikan[4] may be cited here. Helium has two electrons which, according to Bohr and Lande[5], are both in the same part of the atomic volume. Millikan finds that when helium gas is bombarded by α- particles, then in one case out of seven, both electrons are simultaneously carried off by the α-particle. This could not take place if one electron

was much nearer the nucleus than the other, and was attached to the nucleus with a greater force. If they are contained in the same part of the atomic volume, then according to the laws of probability, in one case out of eight both electrons would come simultaneously in the same octant, and both would be carried by an α-particle which chanced to pass close to them.

The alkaline earths resemble helium is so far that they have two valency electrons in the same part of the atomic volume in the outermost region of the atom[6].

In solutions we have always Ca^{++}-atoms and never Ca^{+}-atoms, because the electric forces act equally strongly from all directions. In the cases considered by us, Ca^{+}-atoms are more probable than Ca^{++}-atoms, because the ionizing agencies act from one side only.

The cases of recombination of Ca^{+} and e, Na^{+} and e may be considered in the same light, and we find that in the case of Ca^{+} and e, recombination is more difficult than between Na^{+} and e. If we consider an Na^{+} atom, we find that there are no electrons in the outermost ring, and the positive lines of force proceeding from the nucleus act equally strongly within the 4π solid angles about the atom. From whichever side the electron may approach the Na^{+}-atom, provided other things (energy, distance) are of the right order, the electron will be captured by Na^{+}. Not so in the case of Ca^{+}. It has still got a valency electron in the outermost rings; lines of force proceeding from the nucleus are strongly concentrated on it. In other words, to use the language of Stark, there is a negative patch on one side. An electron cannot be captured if it approaches Ca^{+} from this side. It can be captured only when it approaches the Ca^{+}-atom within only a definite fraction $4\pi/n$ of the total solid angle about the Ca-atom, where n is a number > 1. We may call 'n' the "steric factor".

These considerations show that for an atom like Ca, ionization is easier, and recombination of Ca^{+} and e is more difficult than recombination of Na^{+} and e. For trivalent and tetravalent elements like Sc and Si these considerations will apply with even stronger force.

III

It is a more difficult task to take account of the above facts in a statistical theory. To Boltzmann we owe the idea that when two atomic species A and B associate, every case of approach of A and B does not result in a combination, but only when A and B present to each other certain definite parts, $\dfrac{1}{n_a}, \dfrac{1}{n_b}$, of their respective surfaces. Boltzmann was of opinion that for the formation of diatomic molecules 'n' varies directly as the maximum valency of the element (viz. 2 for Ca, 7 for I, and so on)[7].

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[3] The strength of the ionizing agent is assumed to be not so large as to be able to tear off any one of the inner electrons.
[4] Millikan and Wilkins, Phys. Rev., March 1922.
[5] *Zeitschrift fur Physik*, Bd. ix. p. 33.

[6] It may be pointed out that Langmuir places helium at the head of the alkaline earths (see Loring, "Atomic Theories").
[7] Boltzmann, *Gastheorie*, Band ii, pp. 175-177; Jeans, "The Dynamical Theory of Gases," pp. 209-217, 2nd edition.

In recent years the "steric factor" has been introduced into thermodynamics by Stern[8] in a new theory of the dissociation of I_2 vapour.

Stern considered the case from the standpoint of both thermodynamics and the kinetic theory, and came to the conclusion that 'n' lay between 6 and 7 in case of combination of two I-atoms to form an I_2-molecule, thus lending colour to Boltzmann's belief. The kinetic theory is not very convincing, for the following reasons. According to dynamical principles, two particles A and B approaching each other from infinity cannot form a closed system until and unless they lose a certain fraction of their energy, presumably by radiation. Similarly, a molecule AB cannot be dissociated into A and B if the system does not absorb energy from the outside.

Thus a complete theory of ionization is incomplete without a consideration of the mutual action between radiation and matter, and we are beset with the same difficulties which have confronted all investigators on the subject since the days of Boltzmann.

Proceeding to the thermodynamical theory, the fundamental equation was derived from the equation

$$S_a + S_b - S_{ab} = U/T \qquad \qquad .. \quad (A)$$

where U=heat evolved, S_a, S_b, S_{ab} were calculated from the quantum theory involving certain assumptions. (Here 'a' is Ca^+, b is 'e', S_{ab} is Ca). The above equations are derived on the assumption that the steric factor $n=1$. Taking the "steric factor" into account, the probability that a and b would simultaneously present the definite portions, $\frac{1}{n_a}$, $\frac{1}{n_b}$, of their surfaces to each other is given by

$$W = \left(\frac{1}{n_a} \cdot \frac{1}{n_b} \right)^N,$$

where N=total number of particles of each species.

The diminution in entropy
$$S_0 = k \ln W = -R \ln (n_a n_b),$$
so that instead of equation (A) we shall have

$$S_a + S_b - S_{ab} - S_0 = \frac{U}{T};$$

hence the equation of ionization takes the form, assuming that only one species of atom is present,

$$\log \frac{x^2}{1-x^2} P = - \frac{U_1}{2 \cdot 3RT} + \frac{5}{2} \log T - 6 \cdot 5 + \log (n_a n_b).$$

The *effective ionization potential* I_e now becomes
$$U - 2 \cdot 3RT \log (n_a n_b)$$

$$\text{or } I_e = I - \frac{2 \cdot 3RT \log (n_a n_b)}{23000} \text{ volts.}$$

For the electron and the alkalies we can take $n_b=1$. For alkaline earths, if we follow Boltzmann, $n_b=2$, but this evidently does not suffice in the present case. It may be pointed out that the present case is entirely different from that considered by Boltzmann, for we are considering the combination between an ionized atom and an electron, whereas Boltzmann considered the combination of two atoms. There is no reason why the steric factor should have the same value in both cases.

IV

On the basis of the above formula, let us consider the effective I.P. of helium and the alkaline earths at different temperatures.

Taking $n=2, 4, 6, 8$ respectively, we have for

$$\begin{aligned} n &= 2, \ I_e = I - \cdot 060m, \\ &= 4, \ I_e = I - \cdot 119m, \\ &= 6, \ I_e = I - \cdot 158m, \\ &= 8, \ I_e = I - \cdot 180m, \end{aligned} \quad \begin{array}{l} \text{the temperature being} \\ \text{m-thousands.} \end{array}$$

Russell is inclined to take the temperature of the spot $=4000°K$ and that of photospheric emission$=6000°K$. If this view be correct, the temperature of the spot is only slightly above that of the arc. But we find that in the arc the Ba $\lambda=5535$ is quite strong, while it is entirely absent from the spot. The discrepancy can, of course, be explained by assuming that the temperature of the arc is not uniform; the absorption of $\lambda=5535$ is due to the cooler mantle of gaseous barium next to the air. But more extended research is required to test this point.

Taking the temperature of the spot and the sun to be $5000°K$. and $7000°K$. respectively, and $n=8$, we find that for Ba, $Ie=4 \cdot 22$ and $3 \cdot 86$ respectively, i.e. in the sun barium is ionized like Cs, in the spot like Rb. This very nearly explains the complete ionization of Ba in the sun, as well as in the spot.

For Ca, $Ie=5 \cdot 18$ and $4 \cdot 82$ respectively. Thus in the sun, calcium is more ionized than sodium, while in the spot it ought to be a bit less ionized than sodium. This satisfactorily explains the behaviour of the Ca-lines in the sun and spot.

If we turn to the stellar spectra, we find that calcium 'g' disappears from the B8-stage. By using the original equation of ionization it was found that the temperature could not be less than $13000°K$. But according to Wilsing and Scheiner's intensity measurements, the temperature is only slightly above $10000°K$. Taking $n=8$, the effective I.P. becomes $4 \cdot 21$ volts, the ionization is complete at $10000°K.$[9] Thus the introduction of the "steric factor" seems to bring down the temperature of different spectral classes in a line with the temperature obtained from intensity measurements.

In my original calculation of the ionization of the helium, the I.P. was taken to be $20 \cdot 4$ volts. This is now known to be

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[8] Stern, *Ann. der. Physik*, vol. xliv.

[9] Vide M. N. Saha, "Elements in the Sun", Phil. Mag., Dec. 1920.

wrong, for numerous workers have established definitely that real ionization begins at 25·4 volts. The former figures are therefore to be revised. Taking the steric factor =8, the effective I.P. at 25000°K. becomes 21 volts, and ionisation is 74 per cent, under concentrations corresponding to one atmosphere pressure. If $P = 10^{-1}$ atm., the ionization becomes complete. Thus the temperature of the Oa stars given in my former paper (Proc. Roy. Soc. Lond, May 1921, p. 151) remains unaltered.

Manganese—Let us next consider the element Manganese, because the constitution of its series spectrum has been recently elucidated by Catalan (Phil. Trans. vol. 223). He finds the 1s term of $Mn = 59937$, the I.P. $= 7·41$ volts. The resonance lines of Mn are the triplet $\lambda = 4030·92$, $4033·21$, $4034·62$, so that, as far as the variation in intensity of its lines in stellar spectra is concerned manganese is an ideal element. According to Lockyer, they occur as faint lines in the spectra of Ao-stars (intensity 1 on a scale $1-10$, the Ca-line 4227 being of intensity 2). Thus, in spite of the fact that the I.P. of M_1 is 1·23 volts higher than that of calcium, it is more highly ionized at $T = 10000°K$ than calcium. Manganese has got 7 electrons in the outermost shell; its steric factor is therefore expected to be much higher than that of calcium, which probably accounts for its comparatively high degree of ionization.

According to Lockyer, Mn^+ is represented in stellar spectra by $\lambda = 4344·19$. It does not occur in King's furnace spectra[10], though groups of lines due to Mn^+ occur about $\lambda = 3442-3497$, $2914-2940$. $4344·19$ is certainly not a resonance line of Mn^+. Probably it is of the same type as He^+ 4686. According to Lockyer, this line vanishes from the stage δ Tauri or β Persei. Thus in stellar ranges we have not only Mn and Mn^+, but Mn^{++} as well. None of the lines of Mn^{++} seems to be known.

Let us now treat some of the other elements in the order in which they occur in the periodic tables. For elements of the thrid group, e.g. Al, Sc, Y, La neither the series classification nor the variation in intensity of lines in stellar spectra is satisfactorily known. We pass to the next group.

Group IV. Carbon, Silicon, Titanium.

These elements are extremely interesting, because they have got 4-valency electrons, and the steric factor is expected to be unusually large not only for the neutral, but also for the singly-and doubly-charged atoms. As a result, the successive stages of ionization will follow each other in rather quick succession. Unfortunately, the knowledge of the spectra of these elements, as well as of the variation of their intensity in stellar classes, is not so well known.

Carbon—The spectrum of this important element is one of the least known. The line $\lambda = 4267$ is supposed to

be due to C^+; Lockyer, Baxandall, and Butler[11] treat the lines 4650·8, 4647·4 as specially enhanced: we can assume that they are due to C^{++}. One wonders what lines are to be attributed to carbon itself. There are two strong lines, $\lambda = 6583·0$, 6577·5 which may be due to carbon. The variation in intensity of the lines of C^+ and C^{++} in stellar spectra is given below:

	A	B9	B6	B5	B3	B2	B1	Bo	Oe5	Oe
$\lambda = 4267$ (C^+)	—	—	2	3	5	5	3	2	—	—
$\lambda = 4650·8$ $4647·6$ (C^{++})	—	—	—	—	1	4	10	25	15	‡

‡ Present, but intensity not exactly measured.

The pair 4550·8 and 4647·6 are very prominent in the spectra of Novae simultaneously with strong enhanced nitrogen lines *4634·34, 4640·82*. If the above considerations be correct, carbon occurs in stellar spectra as C^+ and C^{++}, and the two stages follow each other in rather quick succession. This is to be expected of an element having a large "steric factor".

Silicon—Lockyer[12] classified the lines of silicon in four groups, according to their mode of production, and has shown that each group is represented with the greatest intensity in stars at different stages of development. The following is compiled from the Harvard Annals:

Stellar Class.	Group I $\lambda = 3905$ (Si)	Group II $\lambda = 4131$ (Si^+) 4128	Group III $\lambda = 4359$ (Si^{++}) 4553	Group IV $\lambda = 4089$ 5740
K	?	—	—	—
G	12*	Absent	—	—
F	Present	Present	—	—
A	—	Present	—	—
B9	—	3	—	—
B6	—	3	—	—
B5	—	3	—	—
B3	—	2	1	—
B2	—	1	2	2
B1	—	—	4	5
Bo	—	—	5	15
Oe5	—	—	?	12
Oe	—	—	?	6

* Intensity in the solar spectrum on Rowland's scale.

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[10] King, Astro. Journal. vol. liii. (1921).

[11] Lockyer, Baxandall, and Butler, Proc. Roy. Soc. Lond. vol. lxxxii p. 352. Fowler, Report on Series in Line Spectra, p. 163.
[12] The Si^+—pair is present in the stary γ Cygni (F8A) and is as strong as in α Cygni (A2F) (Lockyer, Month. Not. R. A. S. 1921). In F5A stars they are weakened, and entirely absent from the solar spectrum. Additional lines of Group IV at $\lambda = 5740·2$, 4829·1, 4820·1, 4813·7, have been identified by Fowler in the spectra of β Crucis type B_1, Monthly Notices, vol lxxvi, p. 196.

It is not quite certain if lines belonging to Group III and Group IV can be regarded as due to Si^{++} and Si^{+++} respectively. If Sommerfeld and Kossel's spectral displacement law[13] be true, the spectrum of Si^{++} ought to have the same constitution as the spectrum of neutral magnesium, i.e. ought to consist of triplets and singlets. Group III and Group IV may be both regarded as due to Si^{++}, Group III belonging to combinations like $1s$-mp_2, Group IV to stronger combinations like $1s$-mp. This is of course only a suggestion. But there appears to be but little doubt that in the stellar range available for us, silicon occurs not only as a neutral and a singly-ionized atom, but also at least as a doubly-ionized element, and the stages follow each other in rather quick succession.

Titanium—The spectrum of Ti is very well studied, though the series classification is not yet known. In their general behaviour the lines of Ti, Ti^+, and Ti^{++} resemble the corresponding lines of Si, Si^+, Si^{++}, but titanium becomes ionized at a much earlier stage than Si, which is in accordance with the general rule that for elements belonging to the same group, heavier elements have got the smaller I.P. Lines of Ti^+ ($\lambda=3759{\cdot}47$, $3761{\cdot}47$, $4578{\cdot}19$) are quite strong in the solar spectrum, and according to W. J. S. Lockyer[14], they are more intense in F5G stars (ϕ Cassiopoeiae) than in A2F stars (αCygni). The ionization of Ti commences much earlier than that of Si.

Group V. Nitrogen, Phosphorous, Vanadium.

The enhanced lines in the spectrum of Nitrogen and their occurrence in stellar spectra were first noted by Lockyer, Baxandall, and Butler[15]. The subject has been subsequently treated by Lunt, Fowler, and Wright.

According to these workers, the spectral lines of nitrogen can be divided into 2 or 3 groups according to the stimulus necessary for exciting them. The chief lines of Group I are $\lambda=3995{\cdot}15$, $4447{\cdot}20$, $4630{\cdot}73$, and the chief lines of Group II are $\lambda=4097{\cdot}48$, $4103{\cdot}54$, $4640{\cdot}82$, $4634{\cdot}34$. There is, besides, another line at $4379{\cdot}26$ which seems to belong to an enhanced group of still more pronounced type. Since lines of Group I do not occur in the low-temperature spectral classes like G, F, and even at Ao[16], I am inclined to think that they are due to N^+, or belong to some remote combination of the neutral nitrogen series. In the former case, Group II would correspond to N^{++}. They first come out in the B2 classes (intensity 1), and

gradually increase in intensity as we go to the still hotter stars, as the following shows-:

	29 Canis Majoris (Oe)	Can. Maj. (Oe5)	ε Orionis (B1)	β Centauri	γ Orionis
N^{++} (4097·45)	18	6	4	2	1

The lines of N^{++} are very prominent in the spectrum of Novae in their later stages simultaneously with He^+ 4686 and C^{++} 4650·8, 4647·6.

Nitrogen, having 5 electrons in the outer shell, would have a large "steric factor" for not only the neutral atom, but also for N^+ and N^{++} which probably accounts for the quick succession of the different stages of ionization.

According to Lockyer[17], Protovanadium or V^+, as represented by the line $\lambda=4053{\cdot}9$, is strongly developed in F5A stars, but shows a weakening in Ao-stars, and disappears somewhere about the B8-stage. In the stellar ranges we have, therefore, V, V^+, and V^{++} in rather quick succession.

It will be seen that the above discussion mainly centres round the life-work of the late Sir Norman Lockyer. To him is due not only the idea, but also extended and elaborate studies of the enhanced and super-enhanced lines of elements, and their application to the study of the ordered sequences in stellar spectra. In this connexion, attention may be drawn to the views which he presented in his 'Inorganic Evolution of Elements'. He tried to impress the idea that the enhanced lines are due to some proto-form or fractional part of chemical atoms. But in those days the atom was an 'elastic solid sphere", and his ideas did not find many adherents. The real significance of his works is being realized in these days of the Rutherford-Bohr theory of atomic constitution.

The present paper probably brings out the great importance of these studies to problems of atomic physics. Lockyer's studies have been continued by American and English workers, but the data hitherto available are not sufficient for the purpose. The above discussion, though scrappy, probably points out the direction in which these studies ought to be extended and amplified.

Note added during correction: Since the paper was written, Russell has published a paper in the Astro. Journal, May 1922, where he has modified the view that Ba is absent from the sun. The $1s$-$3p$ line of Ba ($\lambda=3071{\cdot}59$) has been identified with a line of intensity 00, the resonance line $\lambda=5535$ being probably masked by an iron-line at $\lambda=5535.68$.

[13] Sommerfeld, *Atombau.*
[14] W. J. S. Lockyer, *loc. cit.*
[15] Lockyer and others, Proc. Roy. Soc. Lond. A. vol. clxxxii, p. 532; Lunt, Monthly Notices, lxxx, p. 534 (1920); Fowler, Monthly Notices, lxxx. p. 693.
[16] Of this last I am not quite sure.

[17] Proc. Roy. Soc. Lond. vol. lxiv. p. 396; Phil. Trans. "On the spectrum of α Cygnus," 1903.