The state of polarization of these resolved echoes were studied by Roy and Verma with the help of a radio polarimeter following Eckersley's method of echo-selection. The O– and X–waves always come as tilted ellipses and with an axis ratio of approximately 2 to 4, and the sum of their tilt angles is 270°. It is difficult to obtain the polarization patterns of scattered waves. They come sometime as circles, sometime as tilted lines and sometime as ellipses. Not much study has been made of them yet.

To elucidate how N and ν are determined from the polarization date, the results of a typical observation for the F2-layer echoes are given in (Plate II).

O– ellipse: $x = \cdot 2,\ \psi_o = 119°$

X– ellipse: $x = \cdot 32,\ \psi_x = 150°$

So $\psi_o + \psi_x = 269° \simeq 270°$ as theoretically expected. We obtain by the use of the formulae:

$R = \cdot 5856,\ \alpha = 26°3'$ for the O– wave.

$\tan \nu = 4{\cdot}182,\ \xi^2 + \eta^2 = \cdot 891,\ \eta = \cdot 2196.\ \xi = \cdot 9183$

from which we get $r = \cdot 98$, $\nu = 3{\cdot}07 \times 10^6$, and for the x-wave similarly r is found to be $\cdot 95$ and $\nu = 3{\cdot}55 \times 10^6$. Polarization patterns of the echoes from the E-layer show that they correspond to a value $r = 1$, and $\nu = 1{\cdot}72 \times 10^6$. It is to be noted that the limiting polarization of the waves correspond to the reflection level which leads to the conclusion that after reflection the waves are propagated without any change of phase velocity.

The experiments are still in the preliminary stage, but sufficient results have been obtained which convince us of the great potentialities of the method.

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88. ON ELECTRON-CHEMISTRY AND ITS APPLICATION TO PROBLEMS OF RADIATION AND ASTROPHYSICS*

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Both classical and modern Thermodynamics have hitherto been confined to the treatment of the influence of heat on material substances up to the stage of chemical decomposition and vaporisation (or atomisation). The successive stages which come up for treatment can be thus schematically written:-

Phase	Phenomenon	Example
Solid		Ice
	Liquefaction	
Liquid		Water
	Vaporisation	
Gas (Consisting of molecules)		H_2O (Steam)
	Decomposition	
Gas (Consisting of constituent atoms).		H_2O_2
	Atomisation	
Gas (Elementary)		H, O

What happens when the gaseous mass consisting purely of atoms is further heated ? The problem has not merely an academic interest, for though the temperatures we are considering may not be commanded in the Laboratory, such is usually the case in the Stellar universes with which we are acquainted through their spectra.

The answer to the problem raised easily follows from considerations of the Rutherford-Bohr theory of the atom viz., further heating of the gaseous mass will cause ionization *i.e.* some of the atoms will lose one electron, and under particular conditions of temperature and pressure, a definite chemical equilibrium will be established between the neutral atoms, the atoms which have lost one electron and the electrons split of, according to the scheme

$$Ca \rightleftarrows Ca^{+} + e \qquad (1)$$

That this will be the case may be seen from the fact that at high temperatures, many metals throw off copious quantities of electrons in these substances (Tungsten for example), ionization precedes liquefaction, just as in camphor, carbon and other volatile substances, vaporization (sublimation) precedes liquefaction.

These problems were foreshadowed by Nernst in his book

* An introduction and synopsis of the following four papers communicated to the Phil. Mag.
Paper A. Ionisation in the Solar Chromosphere.
B. On the Problems of Temperature-Radiation of Gases.
C. On Elements in the Sun.
D. On the Harvard Classification of Stellar Spectra.

"Das Neue Warmesatz", for in page 154, we come across the following passage:-

"Die thermische Dissoziation eines Atoms in das positive Ion und das negative Electron ist also eindeutig bestimmt wenn Wir die Dissoziationwärme kennen. Letzere ist in gewissen Fällen durch das Bohrsche Atommodell gegebea, wenn freilich dieser Weg zurzeit auch noch einigermassen hypothetisch ist".

The equation of chemical equilibrium of the process (1) is given by Nernst's law of Reaction-isochore,

$$\log K = \log \frac{x^2}{1-x^2} P = -\frac{U}{2{\cdot}3RT} + \log T \frac{\Sigma\gamma Cp}{R} + \frac{\Sigma\gamma C}{R}$$

Where x is the fraction of the total number of atoms dissociated,

U=heat of ionisation, in the energy-relation $Ca = Ca^+ + E - U$,

$\Sigma\gamma Cp$=Sum of the atomic specific heats of the reacting atoms including the electron,

$\Sigma\gamma C$ =Sum of the chemical constants of the reacting atoms including the electron.

As suggested by Nernst, the specific heat at constant pressure of the electron is $\frac{5}{2}$ R (assuming the electron to be a monatomic gas) and its chemical constant can be calculated from the Tetrode-Sackur formula

$$C = -1{\cdot}6 + \tfrac{3}{2} \log M,$$

if we put M, the atomic weight of the electron$=\frac{1}{1836}$. Eggert assumes the chemical constant of Ca and Ca^+ to be equal.

The formula finally stands as

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2{\cdot}3RT} + \tfrac{5}{2} \log T - 6{\cdot}5.$$

The value of U still remains undetermined. At this place, Nernst's suggestion is entirely misleading, for the ionisation-potential of elements as determined by Franck and Hertz, Mackenan and others gives us the most exact data for the calculation of U, and it is unnecessary* to introduce any artificial hypothesis for calculating U, as Eggert has done.

The ionization-potential gives us the amount of energy which is required for tearing the outer-most electron from an atomic system to infinity. The quantity U (heat of ionisation for a gm-atom) can therefore be calculated from the relation,

$$U = \frac{eVN}{300\,J}, \quad \begin{array}{l} N = \text{Avogadro Number}, \\ J = \text{Mechanical Equivalent of Heat.} \end{array}$$

In cases where the ionisation-potential is not known, its value can be calculated from spectroscopic data from the value of (1, s) which is the convergence-frequency of the Principal series of the element, according to the quantum-relation,

$$V = \frac{h\,(1, s)}{e} \times 300$$

With the aid of equation (1), we can calculate and tabulate the degree of ionisation of the following elements at definite temperatures and pressures:—

Mg, Ca, Sr, Ba, Na, K, Rb, Cs—H, He. For other elements we have no satisfactory data.

Tables of percentage ionisation have been prepared from formula, and successfully applied to the following astrophysical problems.

(1) Occurrence of Elements in the sun and stars.

It has been shown that the alkali metals Rb, Cs are almost completely ionised in the sun, and hence cannot be detected by their ordinary lines. The lines of their ionized atoms lie in the ultra violet. K (I. P=4·32 Volt) is 80% ionized, and hence is only feebly represented. Na (I. P=5·12 Volt) is 60% ionized on the photosphere, but the ionization becomes complete when the pressure falls to 10^{-3} to 10^{-4} Atms and hence the D-lines are confined to the lower layers of the chromosphere. In the sunspots, temperature being diminished to about 5000°K, the ionisation falls down to 5% and hence the D-lines are greatly intensified.

(2) The occurrence of Enhanced lines in the chromosphere.

Of the alkaline earths, Ca is 30% ionized, while Sr and Ba are 50% and 60% ionized respectively. Hence on the photospheric level, we get not only the lines of Ca, Sr, and Ba, also of Ca^+, Sr^+, Sr^+, Ba^+, but at greater heights, owing to the fall of pressure, ionization becomes almost complete. This explains the disappearance of the g-line of Ca, and of the corresponding lines of Sr and Ba, and exclusive occurrence of the enhanced lines in the high-level chromosphere. The case of the Mg-lines is also successfully treated. (With the aid of the following formula which represents the degree of dissociation for diatomic molecule.)

$$\log \frac{x^2}{1-x^2}, P = -\frac{U}{2{\cdot}3\ RT} + \tfrac{3}{2} \log T + \Sigma\gamma C$$

it is shown, that H_2 and O_2 are completely dissociated into atoms not only in the sun, but also in sunspots, and are represented by their atomic spectra only. N_2 may remain partly undissociated and hence show its molecular spectrum (the so-called cyanogen band).

A method for dealing with the spectra of chemical compounds is also fore-shadowed.

(3) It is shown from considerations of the Bohr-Sommerfeld theory of spectral emission that the transition of an atom from a neutral state to the ionized state is not abrupt, but is marked by successive states of equilibrium of the atomic system. In the normal state, the system has the energy A—h (hs) (1/s), corresponding to the possession of

* Eggert's object was to verify Eddington's hypothesis of ionisation in the interior of stars.

one quanta of angular momentum by the outermost vibrating electron. The next stable states of the atom are marked by the energy-contents A-h(2,p), A-h(3,d) etc... corresponding to the possession of 2, 3-m quanta of radial angular momentum by the vibrating electron. Ionisation corresponds to $m=\infty$.

It therefore follows that radiation of normal lines will precede ionisation, and the order in which the lines will come out is as follows:—

$$(1, s)-(m, p), (2, p)-(m, d), (3, d)-(4, b) \text{ etc}$$
$$(2, s)-(m, p), \text{ etc}$$

The temperature of emission of a certain group of lines therefore bears a relation to the temperature of ionisation of the atom, the general rule being that the higher the temperature of complete ionisation, the higher is the temperature at which the gas can be made to glow. It was shown that the existing data on radiation of elements under a purely thermal stimulus can best be explained on the above hypothesis. Thus while elements like Ca possessing a low ionisation potential can be excited even in the flame, even the highest temperatures fail to excite H_2, O_2, N_2, A, which have very high ionisation-potentials varying from (13·6 to 25·6 volts). In the case of hydrogen, the temperature of complete ionisation is about 22000°K, and the temperature of emission for the Balmer lines is not less than 4500°K. The corresponding figures for Helium are 35000°K and 12000°K.

(4) The second stage ionisation of elements.

If P=1 Atms, Ca becomes completely ionised when T=13000°K. Beyond this stage, we have only Ca^+ atoms. But this now begins to get further ionised. A theory of this second-step ionisation is also worked out. The formula is approximately

$$\log \frac{x^2}{(2+x)(1-x)} = -\frac{U}{2{\cdot}3RT} + \tfrac{5}{2} \log T - 6{\cdot}5$$

With the aid of this formula, the second-step ionisation of Ca, Sr, Ba, Mg, He have been calculated.

Phenomena	Temp.	Press	Remarks	Stellar-class
Appearance of K	5000°	1 Atm	Beginning of the Ionisation of Ca	Ma
Disappearance of G	13000°	,,	Ca completely ionised	B 8
Appearance of Mg (4481)	7500°	,,	Beginning of the Ionisation of Mg	G *o*
Disappearance of K	19000°	,,	Ca^+ completely ionised	O*d*
,, of 4481	23000°	,,	Mg^+ ,,	O*a*
Appearance of He	16000°	,,	Beginning of the Ionisation of He	B_3A
Disappearance of He	30000°	10^{-5}	He completely ionised	Pc
Luminescence of H begins at	4500°	1 Atm.	Appearance of (2, p) orbit	M*b*
Luminescence of He begins at	12000°	,,	,, (2,p)	Ao
Maximum Luminescence of H	12000°	,,		Ao
Maximum Luminescence of He	17000°	,,		B_2A

The table contains the results of the applicatio of the above formulæ to problems of stellar spectra. A physical basis is thus provided for the Harvard classificatio of stars according to the nature of their spectra. Colum 5 shows the stellar-class at which the phenomena describe under column 1 take place. This has been compiled from the Harvard Annals. The temperature under colu has been calculated from the formulæ given in the pape

The conclusion is therefore made "The contin variation of stellar spectral types, as observed by th Harvard Astrophysicists, can mainly be ascribed to th varying value of the temperature of emission of the stella atmospheres".

We can now furnish a complete scheme of the train o physical phenomena which we come across when the temperature is gradually enhanced.

Phase	Phenomena	Example	Temp.
Solid		Ice	
	Liquefaction		
Liquid		Water	
	Vaporization		
Gas		Steam	
Gas (molecules of the constituents)	Decomposition attended with the emission of H_2O-spectrum	H_2, O_2	
Gas (Atoms with (1, *s*) orbits)	Atomisation (Emission of the molecular Spectrum)	H, O,	
Gas (Atoms with (2, *p*) orbits)	Emission of (1, *s*) − (*m*, *p*) lines.		
Gas (Atoms with (3, *d*) orbits)	Emission of (2, *p*)−(*m*, *d*) lines		
⋮	Ionisation (First Step)		
Gas (Positively charged atom and the electron).	Ionisation (Second Step)	H^+, e	
		Ca^+, e	
Gas (Atom with 2 plus charges & electron)		Ca^{++}, e	

etc. till in the interior of stars, the whole mass consists of positive nucleii, and electrons.

The theory probably also provides us with the long-sought for source of stellar energy. It is well-known that neither the energy of gravitational contraction nor the energy of radioactive disintegration suffice for this purpose. All observational data point out that the source is of the nature of latent heat, and it is only one step to conclude this heat is provided when, owing to a fall of temperature, a fraction of ionised atoms combines with electrons producing the neutral atom, or the ionised atom with one plus charge less, with the liberation of the latent heat of ionisation. The general trend of this source of heat will be to retard the progress of cooling, and it can come to action only at about 4000°.