

which, up to this time, was attributed to neutral nitrogen. But in my paper (*Phil. Mag.*, **44**, 1138, 1922) I pointed out that since these groups of lines do not occur in classes cooler than Ao, they are most probably due to N⁺.

This prediction has been verified by Fowler's² recent work on the spectrum of ionised nitrogen, and he has now definitely assigned $\lambda=3995$ and other associated lines to N⁺. The I.P. of neutral nitrogen is still unknown, but recent work by Kiess³ indicates that it is in the neighbourhood

of 12 volts. The I.P. of N⁺ is also unknown, but Fowler estimates it to be about 24 volts, so that the excitation potential for the line $\lambda=3995$ is $12+24-8.5=27.5$ volts, while the corresponding quantity for the C⁺ line $\lambda=4267$ is $7+24-6.1=24.9$ volts. Thus the nitrogen lines present not only no difficulty to the theory of steric factor, but they probably justify the theory. We must, however, wait till the I.P. of C, N, and N⁺ are accurately determined.

*Physics Department,
Allahabad University:
1925 August 14.*

² Fowler, *Proc. Roy. Soc. Lond.*, **107** (1925).

³ Kiess, *Journ. Am. Optical Society*, 1925 June.

28. INFLUENCE OF RADIATION ON IONISATION EQUILIBRIUM

MEGHNAD SAHA AND RAMANI KANTA SUR

(*Nature*, **115**, 377, 1925)

In considering ionisation equilibrium of the type $M \rightleftharpoons M^+ + e - U$, the usual method adopted is to write down the entropies of M, M⁺, and e from the quantum theory, and then the law of reaction isochore is obtained from the equation $S+S'-s=U/T$. In this way we obtain the law of ionisation equilibrium

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots (1)$$

The system is regarded as unary (one-component), *i.e.* all the reacting electrons as well as M are derived from the ionisation of M, but when there is excess of electrons, the system is binary and the equilibrium is expressed by the form first given by H. N. Russell, namely,

$$\log \frac{x}{1-x} \cdot \frac{x'}{1+x'} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad (2)$$

The process is regarded as an abrupt one, M-atoms passing directly under the influence of heat to the M⁺-stage, without going through the intervening metastable states. Darwin and Fowler have attempted to include these intervening states by adding to the right-hand side of equation (1) a function $B(T)$. Prof. Russell has pointed out that neither equation (1) nor (2) can be regarded as final, because it fails to take account of the possible influence of radiation and excitation of higher states. We may introduce the matter in the following way. Suppose we have a mass of sodium-vapour in the solar chromosphere. Then the ionisation of sodium atoms is determined not only by the temperature of the chromosphere (say 5000°C), but also by the intensity of photospheric radiation of wave-length λ less than the wavelength

of the limit of the P series, passing through these sodium atoms. This radiation has a higher temperature than the local temperature; hence, as was first pointed out by Milne, we have no thermodynamic equilibrium in the solar chromosphere. The excited states are produced under the joint influence of temperature of the chromosphere and of the photospheric radiation passing through the chromosphere. To the same class belongs the absorption experiments of Wood and others, in which a column of sodium or other vapour is acted on by light of much greater intensity than what would be produced at the temperature of the absorbing gas. Here all the excited atoms, or ionised atoms, are produced by light only, and almost none are due to temperature.

The general problem has been thus attacked. In all photochemical reactions the equilibrium is determined by the intensity of light, and in treating these cases from the point of view of the phase rule, Smits expressed the opinion, without however giving his reason, that the ordinary Gibbs formula, $F=C+2-P$, must be replaced by $F=C+3-P$. We, however, arrive at the same result by assuming that the number of components has increased by one, the photochemically active light being regarded as a new and independent component. In other words, when a normal sodium-atom passes to the 2p-stage by absorbing the $h\nu$ -pulse of D-radiation, then either the excited atom of sodium or the pulse of light may be regarded as a new component, except when the D-light is derived from the effect of temperature prevailing in the gas. In the latter case, the system is a system of one component, as in the corresponding case⁴ of free electrons in equation (1).

We thus regard excited sodium-atoms as a compound, in a special sense, of normal sodium-atoms and D-pulse. It has been possible to deduce the equilibrium conditions in such cases by combining the methods given by S. N. Bose (*Zs. f. Physik*, vol. 27, p. 384) and P. Ehrenfest. We give only the final results. If ρ_ν be the density of radiation which is absorbed, and if n_1 and n_2 be the concentration of atoms in the normal and excited states,

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{\rho_\nu}{8\pi(h\nu^3/c^3) + \rho_\nu} \quad \dots\dots\dots(3)$$

When the light is derived from the temperature of the system we can put

$$\rho_\nu = 8\pi \frac{h\nu^2}{c^3} \frac{1}{e^{h\nu/kT} - 1},$$

and we have

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-h\nu/kT}, \quad \dots\dots\dots(3a)$$

as is usually obtained from direct application of Maxwell's law, and g_1, g_2 are the weights of the two states. If ρ_ν is very large

$$\frac{n_2}{n_1} = \frac{g_2}{g_1}, \quad \dots\dots\dots(3b)$$

as we can expect from the definition of g_1 and g_2 .

In the case of ionisation, let ν be the frequency of ionising radiation (supposed monochromatic). Then the law of ionisation is given by

$$\log \frac{x^2}{1-x^2} P = -\frac{(U-Nh\nu)}{2.3RT} + \log \left(\frac{\rho_\nu}{8\pi(h\nu^3/c^3) + \rho_\nu} \right) + \frac{5}{2} \log T - 6.5, \quad (4)$$

where $N=R/k$.

If

$$\rho_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1},$$

i.e. radiation is due to the temperature of the system, (4) reduces to

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5, \quad (4a)$$

as is obtained directly from thermodynamical theories.

Equation (4) expresses equilibrium in a two-component system, equation (4a) in a one-component system.

Of course the ionising power is not limited to one single radiation, nor are all pulses of frequency $\nu > \nu_0$ (ν_0 =convergence frequency of the principal series) equally effective in causing ionisation. But these facts can be taken into consideration in the method used above.

Allahabad, India,

January 21.

29. THE PHASE RULE AND ITS APPLICATION TO PROBLEMS OF LUMINESCENCE AND IONISATION OF GASES

(*Journ. Ind. Chem. Soc.*, 2, 49, 1925.)

The phase rule was discovered by the great American physicist, Willard Gibbs, in the year 1877, but was first popularised by W. Ostwald in the year 1894, in his *Wissenschaftliche Klassiker*. Since this date, it has formed one of the corner-stones of the science of physical chemistry, and has served as an invaluable guide for the study of problems of gaseous equilibrium, and changes of state.

The present author has shown¹ about four years ago that a thermal stimulus alone can excite atoms to luminescence and ionisation, and how these problems can be treated thermodynamically. A serious defect of these theories is that radiation which plays an essential part in determining the equilibrium cannot be taken into account. The theory has been extended by Russell in America²,

Darwin, Fowler and Milne^{3,4}, in England and by Enskog⁵ and Becker⁶ in Germany. But though many essential improvements have been made, none of the attempts to include radiation as a factor in determining the equilibrium can be said to have met with success.

The object of the present paper is to present the ionisation theory from the standpoint of the phase rule. The phase rule states that if in a gaseous system C=number of independent components, P=number of phases, F=number of degrees of freedom, then

$$F = C + 2 - P \quad \dots(1)$$

³ C. G. Darwin and R. H. Fowler, *The Philosophical Magazine*, Vol. 45, Page 1, 1924.

⁴ R. H. Fowler and E. A. Milne, *Proc. Phys. Soc., London*, Vol. 35, p. 94.

⁵ Enskog, *Annalen der Physik*, Band 72.

⁶ R. Becker, *Zeitschrift für Physik*, Bd. 18, 325, Vol. 28, p. 258.

¹ M. N. Saha, *On a Physical Theory of Stellar Spectra*, *Proc. Roy. Soc., Lond.* (1921), Vol 99, p. 135.

² H. N. Russell, *The Astrophysical Journal*, Vol. 55, pp. 119-144.