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,

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

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

$$\rho\nu = 8\pi \frac{h\nu^2}{c^3} \frac{1}{e^{h\nu/k^T} - 1},$$

and we have

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-h\nu/k^T}, \qquad \cdots\cdots\cdots (3a)$$

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

$$\frac{n_2}{n_1} = \frac{g_2}{g_1}, \qquad \cdots\cdots\cdots (3b)$$

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

$$\log \frac{x^2}{1-x^2} P = -\frac{(U - Nh\nu)}{2\cdot3RT} + \log\left(\frac{\rho_\nu}{8\pi(h\nu^3/c^3) + \rho_\nu}\right) + \tfrac{5}{2}\log T - 6\cdot5, \qquad (4)$$

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

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2\cdot3RT} + \tfrac{5}{2}\log T - 6\cdot5, \qquad (4a)$$

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

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 shown[1] 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 America[2],

Darwin, Fowler and Milne[3,4], in England and by Enskog[5] and Becker[6] 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

$$F = C + 2 - P \qquad \cdots (1)$$

[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.
[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.

Case 1. Take Ca-metal which is heated in a closed vessel. We neglect the intermediate stages, and consider simply the equilibrium

$$Ca \underset{\leftarrow}{\rightarrow} Ca^+ + e \qquad \ldots (2)$$

the neutral atoms directly dissociating into the positively charged atom and the electron. We suppose that the vessel emits no electrons.

Here we have $C=1$, because the concentration of electrons is determined by the fraction x of original Ca-atoms ionised. $P=1$ (all are in the gaseous phase). Variables —T, p, and x (fraction ionised). From the phase rule,

$$F = 1 + 2 - 1 = 2,$$

i.e., when 2 variables are given, say T and p, the third, x, is automatically determined. The equation connecting x, T and P is the well known law of ionisation.

$$\log \frac{x^2}{1-x^2} P' = -\frac{U}{2 \cdot 3RT} + \frac{5}{2} \log T - 6 \cdot 5 \quad \ldots (3)$$

Case 2. Ionisation of calcium gas in an atmosphere containing an excess of electrons.

This is a two component system, the independent components being Ca^+ (concentration y), e (concentration x), Ca-atoms may be regarded as a compound of Ca^+ and e. The variables are now T, p, x and y.

Consequently, $F = C + 2 - p = 3$.

Now we have four variables, and the number of degrees of freedom 3. Hence there must be one equation connecting the variables T, p, x and y. This is the equation first given by Russell.[7]

$$\log \frac{P_{Ca^+} P_e}{P_{Ca}} = K \qquad \ldots (4)$$

$P_{Ca^+}=$partial pressure due to Ca^+ atoms,
$P_e=$partial pressure of electrons, etc.,
Now,

$$P_{Ca^+} = yRT, \ P_e = xRT, \ P_{Ca} = (1-y)RT$$
$$P = P_{Ca^+} + P_e + P_{Ca} = (1+x)RT.$$

Hence

$$P_{Ca^+} = \frac{y}{1+x}P, \ P_e = \frac{x}{1+x}P, \ P_{Ca^+} = \frac{1-y}{1+x} \cdot P.$$
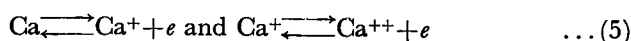
Thus

$$\log \frac{x}{1+x}, \frac{y}{1-y}p = -\frac{U}{2 \cdot 3 RT} + \frac{5}{2} \log T - 6.5 \quad \ldots (4')$$

where U=heat of ionisation.

Case 3. Double Ionisation.

Let us now treat the case when calcium vapour is heated within an enclosure to such a temperature, that not only is calcium ionised to Ca^+ and e but some fraction of Ca^+ is also ionised to Ca^{++} and e.

The reactions are now

$$Ca \underset{\leftarrow}{\rightarrow} Ca^+ + e \text{ and } Ca^+ \underset{\leftarrow}{\rightarrow} Ca^{++} + e \qquad \ldots (5)$$

[7] H. N. Russell, *loc. cit.*, p. 144.

taking place simultaneously from Ca-vapour alone. This is a one component system, because the products, if all reduced to absolute zero, would yield only Ca-atoms leaving no excess of electrons.

The variables are T, p, x and y, where x, fraction of atoms ionised to Ca^+ and y, fraction ionised to Ca^{++}. There is only one phase. From the phase rule,

$$F = 1 + 2 - 1 = 2.$$

There are four variables, but the number of degrees of freedom is two. Hence we must have two independent equations. These are the equations of mass action representing the two reactions

$$Ca \underset{\leftarrow}{\rightarrow} Ca^+ + e \qquad Ca^+ \underset{\leftarrow}{\rightarrow} Ca^{++} + e$$
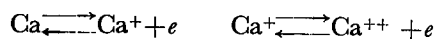
We have

$$\log \frac{P_{Ca^+} \ P_e}{P_{Ca}} = K, \ \log \frac{P_{Ca^{++}} \ P_e}{P_{Ca}} = K' \qquad \ldots (6)$$

Now

$$P_{Ca} = (1-x-y)RT. \ P_{Ca^+} = xRT, \ P_{Ca^{++}} = yRT$$
$$P_e = (x+2y)RT \text{ and hence } P = (1+x-2y)RT.$$

Hence

$$\log \frac{x(x+2y)}{(1+x+2y)(1-x-y)} P = -\frac{U_1}{2 \cdot 3RT}$$
$$+ \frac{5}{2} \log T - 6 \cdot 5 \qquad \ldots (6')$$

$$\log \frac{y(x+2y)}{x(1+x+2y)} P = \frac{-U_2}{2 \cdot 3RT} + \frac{5}{2} \log T - 6 \cdot 5 \qquad \ldots (6'')$$

since p and T are given, x and y are perfectly determinate.

Case 4. Double ionisation, but concentration of electrons is now arbitrary.

The variables are now T, p, x, y and f, where

$x=$fraction of Ca atoms ionised to Ca^+

$y=$ „   „   „ Ca^{++}

$f = \dfrac{\text{concentration of electrons}}{\text{concentration of original Ca atoms.}}$

The number of independent components is now two, for if the system be reduced to absolute zero, we shall be left with Ca atoms and an excess of electrons.

Phase=1 (gaseous).

Hence from the phase rule

$$F = C + 2 - P = 3.$$

We have five variables, but the number of degrees of freedom is 3. Hence we must have two independent equations. These are the equations of mass action representing the reactions

$$Ca \underset{\leftarrow}{\rightarrow} Ca^+ + e, \qquad Ca^+ \underset{\leftarrow}{\rightarrow} Ca^{++} + e.$$

The equations now take the forms:

$$\log \frac{x}{1-x-y}, \frac{f}{1+f} = K = -\frac{U_1}{2\cdot 3RT} + \frac{5}{2} \log T - 6\cdot 5$$

$$\log \frac{y}{x} + \frac{f}{1+f} = K' = -\frac{U_2}{2\cdot 3RT} + \frac{5}{2} \log T - 6\cdot 5 \quad \ldots(7)$$

U_1 and U_2=heats of first stage and second stage ionisation respectively.

From these two equations, it will appear that x and y cannot be determined unless f is known. This fact may have an interesting application in the problem of successive disappearance of lines of Si, Si⁺, Si⁺⁺ and Si⁺⁺⁺ in stars, because in high temperature stars, f must be abnormally high, and we may put

$$\frac{f}{1+f} = 1$$

For treble ionisation in an atmosphere of excess of electrons, the equations will take the form

$$\log \frac{x}{1-x-y-z} \cdot \frac{f}{1+f} = K_1$$

$$\log \frac{y}{x} \cdot \frac{f}{1-f} = K_2 \quad \ldots(8)$$

$$\log \frac{z}{y} \cdot \frac{f}{1+f} = K_3$$

If we change the notation a little, we can express the formula in a symmetrical form. Let $x_0, x_1, x_2, x_3 \ldots x_n$ denote the fraction of Ca atoms which are respectively neutral, singly ionised, doubly ionised, etc.

then $x_0 + x_1 + x_2 + x_3 + \ldots \ldots \ldots x_n = 1$
and let f denote the ratio concentration of electrons to the original number of Ca atoms.

then we have

$$\log \frac{x_1}{x_0} \cdot \frac{f}{1+f} = K_1$$

$$\log \frac{x_2}{x_1} \cdot \frac{f}{1+f} = K_2 \quad \Bigg\} \ldots(8')$$

$$\log \frac{x_3}{x_2} \cdot \frac{f}{1+f} = K_3$$

It is clear that the method might be extended to cover such cases as the reaction of any positively charged particle with any negatively charged particle which need not necessarily be an electron. We have been assuming so far that an ionised metal ion, say Ca⁺, can only combine with an electron, but there is no reason why Ca⁺ will not combine with a negatively charged atom like Cl or O, giving us a Ca⁺ Cl⁻ or Ca⁺O⁻ molecule having its

characteristic band spectrum. The Cl ion will be as likely to combine with a positively charged particle as a free electron. But as we know nothing about the spectroscopy of such processes, no purpose will be served by putting down the equations. The suggestion is thrown here simply to account for the non-recurrence of the lines of electronegative gases like Cl, Br and I in the solar spectrum, and for the occurrence of a large number of lines showing a band structure, e.g., the bands ascribed to CN.

Radiation as a factor in determining the equilibrium

As has been pointed out on several previous occasions, radiation must play a very essential role in determining the equilibrium. For there are an infinite number of metastable quantum orbits between the normal state and the ionised state. In passing from the normal to the ionised state, the atom may pass through these states. As radiation pours through the normal atom, the pulses belonging to the principal series are absorbed, and the atom passes to the metastable state. It is easier to ionise the metastable states, e.g., in the case of a sodium atom in the $2p$ stage, the ionisation potential is 2·6 volts. The percentage of ionised Na atoms will therefore be materially affected by the density of radiant energy in the space corresponding to the characteristic lines of Na.

It is evident from the above that in addition to considering reactions of the type

$$M = M^+ + e$$
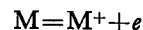
we have also to consider such reactions as

$$Na_{1s} \underset{\longleftarrow}{\overset{\longrightarrow}{}} Na_{2p} - h\nu_{1s-2p} \quad \ldots(9)$$

i.e., radiation ν_{1s-2p} enters into the equilibrium. These are quite new types, and I have yet no clear idea how to tackle these problems. Yet a few casual remarks may be made.

Smit[9] expresses the opinon that in the analogous case of photo-chemical equilibrium, besides T and p, the intensity of light will also appear as a new variable. The phase rule must then be modified from the form

$$F = C + 2 - P \text{ to the form } F = C + 3 - P$$

But no theoretical argument is given. We may regard Na_{2p} as a new component, if excess of ν_{1s-2p} pulses be present. There is no objection in calling Na_{2p} or any other excited state of Na as a new component, because the ionisation potential, consequently the chemical properties of the excited atom are widely different from those of the normal atom. We have then from $F = C + 2 - P$, since $C = 2$ and $P = 1$, $F = 3$ or the number of degrees of freedom is three, T, p, and the intensity of light. The cases can now be subdivided into two broad categories:—(1) Cases

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8 Pringsheim, Physik der Sonne, p. 116.
9 Smit, The Theory of Allotropy, Chap. VII, p. 177.

in which we start with Na atoms only, and the proportion Na_{2p}, or the hv_{1s-2p} pulses is determined by the value T and p only. We may say that in such cases, the radiation is in equilibrium with matter at this temperature. (2) Cases in which Na atoms, otherwise all in the (1s) orbit, are illuminated by (1s-2p) pulses. The proportion of Na_{2p} atoms will now be completely determined by the intensity of (1s-2p) pulses. To this class belong the various absorption experiments performed by Wood, Bevan and others. (3) Classes intermediate between the two, e.g., the solar chromosphere, where T is sufficiently high to convert Na_{1s} atoms to Na_{2p} states, but in addition, there are the 1s-2p pulses pouring from the photosphere. Here the equilibrium will depend upon T, p and the intensity of light. That the chromosphere is not in a state of thermodynamic equilibrium was first pointed out by E. A. Milne in a recent letter to *Nature*.

It is evident that instead of Na_{2p} atoms, the reacting pulse of light $v = 1s - 2p$ may be looked upon as a new component.

The range within which a particular state may occur.

In this connection it is necessary to add a few words regarding the thermodynamical range within which a particular metastable state may occur. To introduce the matter we may begin with a general examination of the effect of heat on matter. The states succeeding each other may be visualized in the following scheme given by me a few years ago.

HYDROGEN

State	Phenomena
Solid	
$\downarrow$	Fusion
Liquid	
$\downarrow$	Vaporisation
Gas (molecular)	
$\downarrow$	Dissociation
Atomic state	
$\downarrow$	Luminescence
Excited states of atoms	
$\downarrow$	Ionisation
Positively charged atom	

It does not always follow that the succeeding stages occur in the order given above. Thus, to take a familiar

example, camphor vaporises directly without melting at all. Water can be obtained in the liquid form between 0°C and 100°C under the conditions prevailing in this globe of ours, but if the experimenter is transported to the moon, where the pressure is, say only 2 mms. of mercury ice would behave just like camphor and vaporise without melting at all. The experimenter on the moon would have to increase the pressure artificially to get the liquid stage. A similar case is that of carbon which vaporises without previously melting but Lummer and others[10] claim that they have obtained the liquid stage by heating carbon under great pressure.

The analogy may be extended further. In the cases of tungsten, platinum and other metals, the metal emits electrons even in the solid state.

The problem we are discussing here is the range of experimental conditions in temperature and pressure, within which a metastable state, say 2p or 3d of sodium or any other element may occur. It has been recorded by several observers that it is very difficult to obtain the exact experimental conditions at which the 2p or 3d orbits would occur in sufficient proportion to give us the diffuse and the sharp lines in absorption. At low temperatures the stimulus is not sufficient to produce an appreciable number of Na_{2p} atoms. If the temperature be sufficiently raised, they pass directly into ionised condition. The intermediate states may be obtained by combining high temperature with high pressure, or using a very long column of vapour at comparatively low temperature and low pressure. A similar phenomenon is well known to spectroscopists in the case of the spectra of C and Si. The ionised spectra of these elements have been studied in great detail, but it is very difficult to get lines of the neutral atoms. Only a few lines are recorded[11]. Probably when carbon and silicon vaporise directly from the solid state, a large percentage of them are ionised or there is not much range for the metastable states of C or Si to be developed. Even when the spectra are obtained from vacuum discharge through their volatile compounds, they split more readily into C^+, or C^{++} than into the neutral form. Attempts are being made to study these phenomena experimentally.

The author had many opportunities of discussing the subject-matter (from the standpoint of the physical chemist) with his friend Dr. N. R. Dhar, and wishes to record here his sincere thanks.

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[10] Kohn—Zeitschrift für Physik, Vol. 27 (1924), p. 305.
[11] T. R. Merton and R. C. Johnson, Proc. Roy. Soc., London, Vol. 103, p. 394.