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THE THERMAL IONIZATION OF GASEOUS ELEMENTS AT HIGH TEMPERATURES

A CONFIRMATION OF THE SAHA THEORY

BY ARTHUR A. NOYES AND H. A. WILSON

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND PHYSICS LABORATORY OF THE RICE INSTITUTE

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In a recent article Eggert[1] has shown that the ordinary thermodynamic expression for the effect of temperature on the equilibrium of chemical reactions, when supplemented by assumptions as to the values of the special constants occurring in it, can be applied to the calculation of the extent to which under different conditions neutral atoms of the gaseous elements are converted into positive ions and free electrons. Saha[2] has shown that the most uncertain factor in Eggert's formulation can be eliminated by introducing the ionization-potential of the element. He has then calculated the dissociation of the first electron from the atoms of many important elements, thus, the extent to which such reactions as $Na = Na^+ + E^-$ take place, where E^- represents electron gas. He has tabulated the values of this percentage ionization at various temperatures and pressures; and he has especially pointed out the great significance which these considerations may have for the interpretation of the spectra of elements under solar and stellar conditions.

These principles are of great interest to astrophysicists, as may be illustrated by the following applications. It has long been known that the solar prominences show strongly the hydrogen and helium lines and the enhanced (H and K) lines of calcium, but not the blue line of calcium nor the familiar lines of sodium or of other alkali elements. The remarkable absence of these lines had not been explained; but the thermodynamic relations now show that the extremely small pressure combined with the high temperature of the prominences must greatly promote the

ionization of all elements, and may well suffice to convert the neutral calcium atoms into calcium ions, which produce the H and K lines; and also to convert completely the neutral sodium atoms, to which the D lines are due, into sodium ions, which do not yield strong lines in the visible spectrum. A second interesting application of Saha's equations has been made by Russell,[3] who was led to the discovery of rubidium in sun spots by the considerations that the absence of its lines in the general solar spectrum is probably due to the complete conversion by the high temperature there prevailing of the neutral rubidium atoms (which produce the characteristic lines of the element) into rubidium ions (Rb^+), and that at the lower temperature prevailing in sun spots this conversion might well be only partial.

The thermodynamic expressions may first be presented which are applicable to a reaction of the type under consideration, by which the neutral atoms of a gaseous elementary substance M are converted into positive ions and electrons in accordance with the chemical equation $M = M^+ + E^-$. At any definite temperature the equilibrium-constant K of such a reaction is expressed in terms of the partial pressures, p_M, p_{M^+}, p_{E^-}, of the three substances, regarded as perfect gases, by the following equations:

$$\frac{p_{M^+} p_{E^-}}{p_M} = K \qquad (1) \qquad\qquad \frac{x^2 p}{1 - x} = K. \qquad (2)$$

Unlike the first equation, which is general, the second equation, in which x represents the fraction ionized and p the sum of the pressures p_M and p_{M^+}, is valid only when $p_{M^+} = p_{E^-}$; that is, only when electrons do not originate from any other source, as from the presence of another ionizing element or from thermionic causes.

The second law of thermodynamics leads to a simple expression for the change of this ionization constant K with the temperature, in the case where the heat-content-increase ΔH attending the reaction can be expressed as a linear function of the absolute temperature T, thus by the formula $\Delta H = \Delta H_o + T \Delta C_p$, where ΔH_o is an empirical constant and ΔC_p is the increase in the heat-capacity at constant pressure that results from the occurrence of the reaction. The second law leads, namely, to the following equations, in which R is the gas-constant (1.985 calories per degree), and I is the integration-constant resulting from the integration of equation (3).

$$d \ln K = \frac{\Delta H_o + T \Delta C_p}{RT^2} dT. \qquad (3)$$

$$\ln K = -\frac{\Delta H_o}{RT} + \frac{\Delta C_p}{R} \ln T + \frac{I}{R}. \qquad (4)$$

Now Saha introduces the following assumptions as to the quantities occurring in this equation:

(1) That the energy increase attending the ionization of a single molecule is equal to the electrical work Ve that must be expended in order to give to an electron a kinetic energy which just suffices to ionize an atom of the element with which it collides; e being the charge on the electron and V the ionization-potential, which last may be determined by direct measurement or computed from the spectral series of the element.

(2) That the heat-capacities of the neutral atom M and its ion M^+ are equal, and that the heat-capacity of electron gas is the same as that of any other monatomic gas, namely, $2.5\,R$ per mol of the gas.

(3) That the constant I, which is the sum $I_{M^+} + I_{E^-} - I_M$, of constants characteristic of the three substances (the positive ion, the electron, and the neutral atom), can be evaluated by assuming $I_{M^+} = I_M$ and by calculating I_{E^-}, the constant for electron gas, by a theoretical principle that has been shown applicable to ordinary monatomic gases,[4] which need not be here described.

These considerations lead to the following values of the constants occurring in equation (4):

$$\frac{\Delta H_0}{R} = \frac{N\,e\,V}{R} = \frac{96500\ V}{8.316} = 11625\ V; \quad \frac{\Delta C}{R} = 2.5; \quad \frac{I}{R} = -15.10.$$

Substituting these values in equation (4) and changing from natural to ordinary logarithms, we get

$$\log K = -\frac{5048\ V}{T} + 2.5 \log T - 6.56. \qquad (5)$$

By this equation the ionization-constant K of an element at any absolute temperature T can evidently be calculated from its ionization-potential V (in volts); and from this ionization-constant its actual ionization can then be found by equation (1) or (2).

The main purpose now of this paper (of which a much more complete form will soon appear in the *Journal of the American Chemical Society* and the *Astrophysical Journal*) is to point out that the earlier investigation of Arrhenius,[5] and especially the more recent researches of H. A. Wilson,[6] on the electrical conductivity of flames into which salt solutions are sprayed clearly indicate that the conduction arises from an ionization process of the type here considered, and that these measurements make possible a computation of the relative magnitudes of the ionization-constants. Thus the experiments of these investigators have established the following facts.

1. The conductance of the flame is independent of the acidic constituent

of the salt; thus it is the same for the chloride and carbonate of any given alkali element.   This is in accord with the assumption that these salts are completely decomposed in the way expressed by the chemical equations $2 MCl = 2 M + Cl_2$, or $M_2CO_3 = 2 M + CO_2 + \frac{1}{2} O_2$, and that the conductance is due to ionization of the metallic element M which is common to its various salts.

2. The conductance changes with the concentration of any given salt and in mixtures of salts in the way required by equations (1) and (2), showing that the ions result from an ionization process in which one molecule dissociates into two others, as is the case in the reaction $M = M^+ + E^-$, where E^- denotes electron gas.

3. There is present in the flames both positive and negative carriers, but the mobility of the latter has been shown to be roughly 2500 times as great as that of the former, clearly indicating that the negative carriers are electrons and that substantially the whole conductance is due to them.

From the way in which the conductance changes with the concentration it was found possible by a mathematical process that need not be here described to calculate under the above stated assumptions relative values of the ionization constants K of the five alkali elements whose salts were investigated by H. A. Wilson.   These relative values could then be compared with the absolute values calculated from the ionization-potentials by the thermodynamic equation (equation 5 given above).   The results are reproduced in the following table.

TABLE 1

VALUES OF THE IONIZATION-CONSTANT $(10^{12} K)$ AT 2000° ABSOLUTE

	Cs	Rb	K	Na	Li
From flame conductances....................	3500	780	430	5.6	0.8
From ionization-potentials..................	8200	1600	620	6.2	1.4

It will be seen that the ratios of the values for the successive elements run closely parallel to each other in the two series.   Especially noteworthy is the very large change in both series in passing from sodium to potassium, and the much smaller differences between the other elements.

As stated above, the flame conductance data lead only to relative values of the ionization-constants; and the values given in the preceding table would contain an arbitrary multiplying factor if they were based on those data alone.   It was found possible, however, by combining with the conductance data the results of previous rough determinations of the mobility of the electrons[7] and of the number of them per cubic centimeter[8] in entirely similar flames free from salt, to obtain absolute values of the ionization constants; and these are the numbers that are recorded in the first row of the above table.   Although they afford an estimate only of the order

of magnitude of the constants, yet they are seen to correspond well with the values calculated by the thermodynamic equation.

The results here presented therefore afford a striking confirmation of the general validity of the calculation of the ionization of elements from their ionization-potentials by the thermodynamic equation employed by Saha.

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AN ELECTRON THEORY OF ELECTRIC CONDUCTION IN METALS

By EDWIN H. HALL

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

This is a modification and extension of the dual conception of conduction which I set forth in a paper[1] printed several years ago and to which I have referred in more recent publications. The theory in its present shape, like every other theory of metallic conduction with which I am acquainted, involves propositions that may well be questioned, but it contains certain features not present, so far as I know, in other theories, and I hope these will be found worthy of consideration, even if they are finally to be rejected.

I shall endeavor to state this theory, without extended argument, in the form of certain propositions, some of which are or involve outright assumptions. Any helpful hypothesis, not in conflict with well established facts or principles, I have considered justifiable, in view of the difficulties of the problem with which I am dealing.

Behavior of the Ions in Conduction

1. Complete metal atoms are of such hardness and symmetry that they are not subject to appreciable polarization or orientation in impressed electric fields of ordinary strength.

2. An ion is formed from an atom by loss of an electron from the outer shell and is, accordingly, unsymmetrical, essentially polarized, and therefor subject to orientation in a uniform electric field such as may be ap-