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THE THERMAL IONIZATION OF GASEOUS ELEMENTS AT HIGH TEMPERATURES

BY ARTHUR A. NOYES AND H. A. WILSON

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Introduction

In a recent article Eggert¹ suggested 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, could 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. Saha² has shown that the theoretical evaluation of one of the factors in Eggert's formulation can be eliminated by introducing the ionization-potential of the element. He then calculated by this method the dissociation of the first electron from the atoms of many important elements, and thus the extent to which such reactions as $\text{Na} = \text{Na}^+ + \text{E}^-$ take place, where E^- represents electron gas. He has tabulated the values of this percentage ionization at various temperatures and pressures, and has 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 astronomers, 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 the calcium ions which produce the H and K lines; and also to convert the neutral sodium atoms, to which the D lines are due, completely 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

¹ Eggert, *Physik. Z.*, **20**, 570 (1919).

² Saha, *Phil. Mag.*, **40**, 478, 809 (1920); **41**, 267 (1921).

³ Russell, *Astrophys. J.*, **55**, 129 (1922).

at the lower temperature prevailing in sun spots this conversion might well be only a partial one.

The Thermodynamic Expressions

The equilibrium constant K of a reaction $M = M^+ + E^-$ at any definite temperature in terms of the partial pressures p_M , p_{M^+} , p_{E^-} , of the three substances, regarded as perfect gases, is expressed by the following equations.

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

The second equation, in which x represents the fraction ionized, 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 the following equations for the change of this equilibrium constant 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; thus, by the formula, $\Delta H = \Delta H_0 + T \Delta C_p$, where ΔC_p is the increase in the heat-capacity C_p at constant pressure that results from the occurrence of the reaction; namely:

$$d \ln K = \frac{\Delta H_0 + T \Delta C_p}{RT^2} dT \quad (3)$$

$$\ln K = -\frac{\Delta H_0}{RT} + \frac{\Delta C_p}{R} \ln T + \frac{I}{R} \quad (4)$$

In this equation, I is the integration constant resulting from the integration of Equation 3.

Now Saha employs the following assumptions as to the quantities occurring in this equation. Of these the second and third were introduced by Eggert,¹ adopting the conclusion of Richardson that the heat capacity of electron gas is the same as for ordinary monatomic gases,⁴ and the conclusion of Laue that the entropy constant is the same as for other monatomic gases, which has since been confirmed by Tolman's calculations on the emission of electrons from hot filaments.⁵

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

⁴ Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green and Co., London, 1916.

⁵ Laue, *Jahrb. Radioakt. Elektronik*, 15, 257 (1918). Tolman, *THIS JOURNAL*, 43, 1592 (1921).

(3) The constant I , which is the sum, $I_{M^+} + I_{E^-} - I_M$ of constants characteristic of the 3 separate substances, can be evaluated by assuming $I_{M^+} = I_M$, and calculating I_{E^-} , the constant for electron gas, from a relation apparently applicable to ordinary monatomic gases in the way indicated in the following paragraphs. (It may be noted that these constants I are 2.303 R times greater than the "chemical constants" employed by Nernst.⁶)

It follows, then, from the general principles relating to entropy, and from the fact that the molal heat capacity at constant pressure of perfect monatomic gases at all temperatures is $\frac{5}{2}R$, that the entropy S of one mole of any such gas at any temperature and pressure is given by the following equation, in which S_1 is a constant characteristic of the gas:

$$S = S_1 + \frac{5}{2} R \ln T - R \ln p.$$

Now the considerations of Sackur,⁷ Tetrode,⁸ Stern,⁹ Tolman,¹⁰ and Lewis¹¹ have led to the conclusions that the quantity S_1 is a function only of the molecular weight M of the gas, and that the constants occurring in the functional relation can be evaluated with fairly concordant results by certain methods that need not be here described. Adopting the value obtained by Lewis from the theory of ultimate rational units,¹² and shown by him to be concordant within 0.5 to 2% with the experimentally determined entropies of the four best studied monatomic gases (helium, argon, cadmium and mercury)¹³ we find, in calories per degree and for the pressure in atmospheres

$$S_1 = -2.63 + R \ln M \quad (5)$$

Substituting for M the value 5.4×10^{-4} , we find for electron gas $S_1 = -25.02$. Finally, it can be shown thermodynamically that the integration constant I considered above is less than the entropy constant S_1 for a monatomic gas by its molal heat-capacity C ; that is, $I = S_1 - C = S_1 - 4.96$. There is thus obtained for I/R the value -15.10 .

These considerations lead then 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 have finally,

$$\log K = -\frac{5048 V}{T} + 2.5 \log T - 6.56 \quad (6)$$

⁶ Nernst, "Theoretische Chemie," 7th ed., p. 472.

⁷ Sackur, *Ann. Phys.*, **36**, 598 (1911); **40**, 67 (1913).

⁸ Tetrode, *ibid.*, **38**, 434; **39**, 255 (1912).

⁹ Stern, *Z. Elektrochem.*, **25**, 66 (1919).

¹⁰ Tolman, *THIS JOURNAL*, **42**, 1185 (1920); **43**, 1593 (1921).

¹¹ Lewis, *Phys. Rev.*, **18**, 121 (1921).

¹² Lewis and Adams, *ibid.*, **3**, 92 (1914).

¹³ Lewis, Gibson and Latimer, *THIS JOURNAL*, **44**, 1009 (1922).

The Electrical Conductivity of Flames and Its Interpretation

It will now be shown that the investigations of H. A. Wilson on the conductivity of flames containing salts have led to results which clearly indicate that the conductivity arises from ionization reactions of the type considered in the previous section of this article.

The final experiments of Wilson¹⁴ were made by spraying solutions of various salts of known concentrations into a mixture of air and gasoline, which then passed through a burner consisting of a series of parallel quartz tubes, whereby a large flame was produced. Near the sides of this flame were introduced two vertical strips of platinum, by means of which a steady current was passed through the flame. Between these electrodes were inserted in the heart of the flame 2 horizontal platinum wires; and the potential difference between these 2 wires (as measured with a quadrant electrometer) for a given current was taken to be proportional to the resistance of the flame between them. By employing the potential difference at these wire electrodes, instead of that between the plate electrodes where the current entered the flame, the effect of the large potential gradient around these latter electrodes was eliminated. Two such flames were always operated in series with the same current passing through them, and their conductances were compared by measuring the potential differences between the wires in the two flames. By varying the concentration of the solution sprayed into one of the flames and keeping the other concentration unchanged, the variation of the conductance with the concentration and with the nature of the salt was obtained. The temperature in the heart of the flame, as measured with a thermocouple, registered about 1650°. Since the couple is considerably cooler than the flame itself, we will assume the temperature to be 2000° A.

The general conclusions originally drawn from his measurements by Wilson, so far as they have a bearing on the present considerations, are summarized in the following paragraphs.

1. The conductance is independent of the acidic constituent of the salt, as was first shown by Arrhenius¹⁵ in 1891. Thus the conductance was found by Wilson¹⁶ to be identical when equivalent quantities of sodium chloride and carbonate, or of potassium chloride and carbonate, were sprayed into the flame. These facts show that the basic and acidic constituents of the salts must be completely separated in the flame, and thus that both sodium chloride and sodium carbonate are completely dissociated, with the help of the water present, into Na₂O and HCl or Na₂O and CO₂, or into Na, HCl, and O₂, or Na, CO₂, and O₂. The latter conclusion is the one to which the considerations presented below lead.

¹⁴ Wilson, *Phil. Trans. Roy. Soc.*, **216A**, 63-90 (1915).

¹⁵ Arrhenius, *Wied. Ann. Phys.*, **43**, 18 (1891).

¹⁶ Ref. 14, pp. 76, 81.

Chemical equilibrium data are not available for determining whether the oxides of the alkali elements are dissociated into their elements at the temperature and partial pressure prevailing in the flame; but this conclusion is made *a priori* probable by the facts that the partial pressure of the salt is extremely small (of the order of 10^{-8} atmospheres), and that in the heart of the flame, where the combustion is still incomplete, reducing gases such as carbon monoxide and hydrogen are probably present and the partial pressure of free oxygen is relatively small.

2. The conductance of a flame containing a salt of any alkali element was shown by Arrhenius to be roughly proportional to the square root of the concentration of the salt solution sprayed into it. As seen from Equation 2 above, this is to be expected if the ions are produced by a uni-bimolecular reaction (one by which 2 molecules are produced from a single one), and if the fraction of the salt ionized is small.

Wilson¹⁷ found that the relation between the conductance L and the concentration c can be expressed over the whole range of concentration by the equation

$$10^4 c = \frac{L^2 - 1}{L} (b + aL) \quad (7)$$

In this equation b and a are constants, the values of which were determined for a number of alkali salts. When the conductance is large this equation becomes approximately $10^4 c = aL^2$, so that the conductance then varies as the square root of the concentration, as found by Arrhenius.

Equation 7 was obtained in the following way, under the assumptions that both the salt and some constituent of the flame are ionized with formation of electrons and positive ions, and that equilibrium prevails between these and the un-ionized parts of the 2 ionizing substances.

Let p_{E^-} denote the partial pressure due to the electrons in the flame, p_{M^+} that due to the positive ions of the salt, p_M that due to the neutral atoms of the salt, p_{F^+} that due to the positive ions of the ionizing flame substance F, and p_F that due to the un-ionized atoms of this substance; also let K be the ionization constant of the element of the salt sprayed into the flame, and K_F that of the ionizing flame substance. The mass-action expressions are then as follows.

$$K = \frac{p_{M^+} p_{E^-}}{p_M} \quad (8) \qquad K_F = \frac{p_{F^+} p_{E^-}}{p_F} \quad (9)$$

Since the conductance L is proportional to the number of electrons present, the conductance of the positive ions being negligible because their mobilities are small compared with that of the electrons, we have

$$AL = p_{E^-} = p_{M^+} + p_{F^+} \quad (10)$$

where A is a constant for all substances, equal to the ratio of the partial pressure of the electrons to the conductance of the flame.

¹⁷ Ref. 14, pp. 78-80.

Furthermore, the concentration c of the salt solution sprayed into the flame (when expressed in equivalents per liter) is proportional to the sum of the partial pressures of the neutral atoms and positive ions, since the conditions of spraying were always the same. Hence, denoting by B a constant that has the same value for all the substances, we have

$$B c = p_M + p_{M^+} \quad (11)$$

Combining Equations 8, 9, 10 and 11, we find

$$A L = \frac{K B c}{A L + K} + \frac{K_F p_F}{A L}$$

Placing, as Wilson did in recording his results, the conductance of the salt-free flame equal to unity, that is, placing $L = 1$ when $c = 0$, we have $K_F p_F = A^2$ and, therefore, assuming p_{F^+} small compared with p_F so that p_F is a constant.

$$c = \left(\frac{L^2 - 1}{L} \right) \left(\frac{A}{B} + \frac{A^2 L}{K B} \right) \quad (12)$$

Comparing this equation with Equation 7 used by Wilson, we see that they become identical if we place

$$\frac{A}{B} = \frac{b}{10^4} \quad \text{and} \quad \frac{A^2}{K B} = \frac{a}{10^4}$$

From these equations there follows for the ionization constant K the relation

$$K = A \frac{b}{a} = \frac{p_{E^+} b}{L a} \quad (13)$$

As an example of the satisfactory way in which Equations 7 and 12 represent the variation of the conductance with the concentration, the observed conductances of cesium chloride¹⁸ are shown in the following table, beside those obtained by plotting the curve corresponding to Equation 7 when the constants b and a are taken equal to 10 and 1, respectively, and c is in grams per liter.

TABLE I
VALIDITY OF THE MASS-ACTION RELATION

Grams per liter	Conductance observed	Conductance calculated	Grams per liter	Conductance observed	Conductance calculated
0.00	1.00	1.0	0.08	22.7	23.8
0.0032	2.88	2.9	0.16	32.8	35.4
0.008	5.72	5.5	0.8	85.2	84.5
0.016	8.9	8.7	8.0	282	278
0.032	13.5	13.7	80.0	883	890

Further evidence that the reaction which gives rise to the flame conductivity is essentially a uni-bimolecular one is afforded by the fact that the conductance of flames fed with mixtures of 2 different alkali elements is found to be that predicted by the mass-action law. This law requires that the ionization of each element, and especially that of the less ionized

¹⁸ Ref. 14, p. 78.

one, be reduced by the electrons arising from the other; and this was shown to be the case by Arrhenius, H. A. Wilson,¹⁹ and A. B. Bryan.²⁰ Thus without entering into the details of the calculation, it may be mentioned that a solution 0.171 *N* in sodium carbonate and 0.00238 *N* in potassium carbonate (which salts when used separately gave conductances of 21.3 and 23.3, respectively, the sum being 44.6), produced a conductance of 32.2, while the conductance calculated was 31.55.

3. The conductivity of the flame arises from the presence of positive ions and electrons; but the mobility of the positive ions is so much less that their conductance can be neglected in comparison with that of the electrons. Thus Wilson²¹ found the mobility of the positive ions produced from the various alkali salts to be about 1 cm. per second for a potential-gradient of 1 volt per centimeter, while he had previously found,²² by measuring the Hall effect, the mobility of the negative ions to be 2450 cm. per second. These last measurements were made with flames containing different alkali salts and the mobility was found to be very nearly the same for all salts, as it should be if the negative ions are always electrons. The fact that the negative ions have a much greater velocity than the positive ions can only be explained by supposing the negative ions to be electrons, and the positive ions to be atoms or molecules.

These various facts make it fairly certain that the conductance arises from a uni-bimolecular reaction by which a positive ion and an electron are produced directly from a substance whose partial pressure is proportional to the concentration of the un-ionized part of the salt sprayed into the flame. As there seems to be no substance other than the neutral element which could ionize in accordance with these conditions, we may conclude that the flame conductance arises from complete conversion of the chloride or carbonate into hydrogen chloride or carbon dioxide, oxygen, and the alkali element, and partial ionization of the latter in accordance with equations such as $\text{Na} = \text{Na}^+ + \text{E}^-$, where E^- represents the electron.

Correspondence between the Ionization Values Derived from the Flame Conductivities and from the Thermodynamic Equation

The thermodynamic equation (Equation 6) applied to 2 different elements, whose equilibrium constants are K_1 and K_2 and ionization potentials V_1 and V_2 , leads to the following expression:

$$\log \frac{K_2}{K_1} = \frac{5048 (V_1 - V_2)}{T} \quad (14)$$

Now the values of the ratio b/a of the constants of Wilson's equation are shown by Equation 13 to be proportional to the ionization constants

¹⁹ Ref. 14, p. 87.

²⁰ Bryan, *Phys. Rev.*, **18**, 285 (1921).

²¹ Ref. 14, p. 71.

²² Wilson, *Phys. Rev.*, **3**, 375 (1914).

K of the respective elements. Hence, if we assume the value of the ionization potential for one alkali element, we can calculate it for the others by Equation 14 from Wilson's values²³ of b/a . These are given in the second column of the following table. Taking the ionization potential of sodium to be 5.111 volts and the temperature of the flame to be 2000° A., the other ionization potentials are calculated to have the values given in the third column of the table. Beside them, in the fourth column under the heading "observed," are placed the values tabulated by Hughes,²⁴ as calculated from the frequencies of the spectral lines according to the quantum theory, which values agree closely for the most part with those derived from the direct measurements by Mohler, Foote, and their collaborators.

TABLE II
OBSERVED IONIZATION POTENTIALS COMPARED WITH THOSE CALCULATED FROM FLAME CONDUCTANCES BY THE THERMODYNAMIC EQUATION

	Values of b/a	Ionization potential V	
		Calc.	Obs.
Cesium.....	10.00	4.00	3.873
Rubidium.....	2.25	4.26	4.154
Potassium.....	1.38	4.35	4.317
Sodium.....	0.0160	..	5.111
Lithium ²⁵	0.0023	5.46	5.362

It will be seen that the calculated and observed ionization potentials not only change in the same order, but that the values are of the same general magnitude. 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.

Instead of calculating the values of the ionization potential by assuming its value for sodium, we may calculate relative values of all the ionization constants by Equation 14, by using the known values of the ionization potential. The values of K so obtained should be proportional to the values of the constant b/a obtained from the flame conductivities, or the product Ka/b should be constant for the various elements. Placing the value of K for lithium equal to unity we have the following results. The values of the product Ka/b are seen to vary to the extent of about 40% from the mean value.

²³ Ref. 14, p. 82.

²⁴ Hughes, *Nat. Research Council Bull.*, 2, 168 (1921).

²⁵ The value of b/a for lithium was obtained by using the results on the conductivity of flames containing lithium salts given by Smithells, Dawson, and Wilson [*Phil. Trans. Roy. Soc.*, A193, 108 (1899)], which show that lithium salts give nearly the same conductance as sodium salts when the concentration of the lithium is about 7 times that of the sodium. Hence the value of b/a for lithium is $1/7$ as great as that for sodium, since the constant a is proportional to the (large) concentrations which give equal conductances.

These results confirm the validity of the term containing the ionization potential in the Saha equation; but they do not confirm the heat capacity and integration constant terms, since these are eliminated in the calculations. It will now be shown that the conductivity data lead also to ab-

TABLE III
COMPARISON OF IONIZATION CONSTANTS DERIVED FROM THE IONIZATION POTENTIALS BY THE THERMODYNAMIC EQUATION WITH THOSE DERIVED FROM THE FLAME CONDUCTANCES

	V	b/a from L	K from V	Ka/b
Cesium.....	3.873	10.00	5731	573
Rubidium.....	4.154	2.25	1119	497
Potassium.....	4.317	1.38	434	315
Sodium.....	5.111	0.0160	4.3	269
Lithium.....	5.362	0.0023	1.0	435
				Mean 418

solute values of the ionization constants which are at least of the same order of magnitude as those calculated by the thermodynamic equation.

Equation 13 shows that the ionization constant K of an element is equal to $p_{E^-} b / La$ in terms of the conductances L and the constants a and b derived from them. For a flame free from salt L was taken equal to unity, so that $K = p'_{E^-} b / a$, where p'_{E^-} denotes the pressure of the electrons in a flame free from salt. Now it was found²⁶ that a flame into which no salt was sprayed, such as was used in the above described experiments, has a specific conductance of 5×10^{-7} reciprocal ohms, and that the mobility of the electrons, as estimated from the Hall effect, is 2450 cm. per second for 1 volt per centimeter. The specific conductance \bar{L} is, however, substantially equal (since the positive ions have only negligible conductance) to the product of the electron mobility U_E times the charge F on one equivalent of electrons times their concentration c_E (in mols per cc.); that is

$$\bar{L} = U_E F c_E; \text{ or } \bar{L} = \frac{U_E F p'_{E^-}}{R T}, \text{ since } p'_{E^-} = c R T$$

whence

$$p'_{E^-} = \frac{R T \bar{L}}{U_E F} = \frac{82.07 \times 2000 \times 5 \times 10^{-7}}{2450 \times 96500} = 3.5 \times 10^{-10} \text{ atm.}$$

An independent estimate of the partial pressure of the electrons in flames not fed with salt is afforded by the work of Wilson and Gold,²⁷ who from the apparent specific inductive capacity for high-frequency currents found the number n_E of electrons per cc. to be 1.1×10^9 . Their partial pressure at 2000°A. is, therefore, given by the following equation in which N denotes the number of molecules in 1 mole.

$$p'_{E^-} = \frac{n_E}{N} R T = \frac{1.1 \times 10^9 \times 82.07 \times 2000}{6.06 \times 10^{23}} = 3.0 \times 10^{-10} \text{ atm.}$$

²⁶ Wilson, *Phil. Mag.*, [6] 10, 475 (1905).

²⁷ Wilson and Gold, *Phil. Mag.*, [6] 11, 484 (1906); also Wilson's "Electrical Properties of Flames," p. 110.

Using the first of these values of this partial pressure the ionization constants given in the following table were obtained by the equation $K = p'_E - b/a$, derived from Equation 13 by placing $L = 1$. The values of K derived from the ionization potentials by the thermodynamic equation (Equation 6) for a temperature of 2000°A . are also given for comparison.

TABLE IV

VALUES AT 2000° ABSOLUTE OF THE IONIZATION CONSTANT K MULTIPLIED BY 10^{12}

	Cs	Rb	K	Na	Li
From flame conductances.....	3500	780	430	5.6	0.8
From the thermodynamic equation....	8200	1600	620	6.2	1.4

It will be seen that these two sets of values do not differ by a factor of more than 2 or 3. Since the value of the partial pressure of the electrons was derived from measurements of a flame different from that used in the conductivity measurements, the agreement is as good as could be expected. The results, 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.

Summary

In this article the thermodynamic equation used by Saha for calculating the thermal ionization of the neutral atoms of gaseous elements into positive ions and electrons from their ionization potentials is first reviewed, especially with reference to the assumptions involved in the calculation.

It is then shown that the recent measurements of H. A. Wilson, as well as the earlier ones of Arrhenius, on the conductivity of flames into which salt solutions are sprayed clearly indicate that the conduction arises from an ionization process of the type under consideration, and that they make possible a computation of the relative magnitudes of the ionization constants.

It is next demonstrated that the relative ionization constants of the 5 alkali elements, calculated on the one hand from the flame conductances and on the other hand from the ionization potentials by the thermodynamic equation, form two series of values which run closely parallel to each other (see Table III). Thus, though in passing from lithium to cesium the ionization constant increases 5700 fold, the ratio of the constants derived by the two methods for any one element does not differ from the mean value of that ratio for all 5 elements by more than 40%.

Finally, absolute values of the ionization constants are derived from the flame conductances with the aid of previous rough determinations of the mobility of the electrons and of the number of them per cc. in similar flames. Although this could afford an estimate only of the order of magnitude of the constants, yet they were found to correspond well with the values calculated by the thermodynamic equation, these last being only from 1.1 to 2.3 fold larger (see Table IV).