HEAT OF EVAPORATION OF ELECTRONS

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Abstract

On the assumption that the electrons form a space lattice like negative ions, the following expression for the heat of evaporation of electrons L_0 is derived, in terms of the grating energies V_R and V_{RX} of the metal itself and of a salt RX of this metal, and of the radii r_p and r_n of the positive and negative ions forming the crystal:

$$L_0 = V_R - V_{RX} r_n / (r_n + r_p) + a$$

where a is the energy necessary to transform the positive lattice of the metal into that of the salt. The values calculated for the alkali metals by this formula, taking $a = 0$ and computing the radii from the heat of hydration of the salt, are: for Na, 1.83 (1.82); K, 1.53 (1.55); Rb, 1.54 (1.45); Cs, 1.34 (1.36); each in volts per electron. The observed values are given in parenthesis. The values of V_R and V_{RX} are not actually known with sufficient accuracy to allow an exact calculation of L_0 but the values given above seem to support the hypothesis that the electrons in metals form a space lattice just as the negative ions in ordinary salts do.

Introduction

R ECENTLY S. C. Roy[1] published a paper in which he gives a theory of emission of electrons from hot bodies, supposing the electrons to be placed on a space lattice inside the metal. He obtained the following expression for the thermionic current per unit area per sec.

$$I = A T^2 \epsilon^{-b_0/KT}$$

where A is a universal constant, T the absolute temperature, K the gas constant per mol. and $b_0 = h\nu_0$, ν_0 being the threshold frequency and h Planck's constant.

This equation is the same as that of Dushman[2]

$$I = A T^2 \epsilon^{-L_0/KT}$$

where L_0 is the heat of evaporation of the electrons at absolute zero. In the present paper we shall calculate L_0 on the assumption that space lattices of electrons exist in the metals.

The electrical nature of the cohesion of crystals is well known and the calculations of Born[3] and others show that it gives results in fairly good agreement with the experiments. Most of the crystalline salts are con-

[1] S. C. Roy, Phil. Mag. **47**, 561 (1924)
[2] S. Dushman, Phys. Rev. **21**, 623 (1923)
[3] M. Born, Atomtheorie des festen Zustandes, Teubner 1923

stituted of positive and negative ions and the electrostatic forces acting between these ions determine many of the physical as well as chemical properties of the crystal. The grating energy of a crystal, that is to say the amount of work V necessary to convert 1 mol. of the crystal into free positive and negative ions, can be computed on purely electrostatic assumptions. On the other hand, it can be obtained from thermochemical data such as the heat of formation of the salt, etc. The two values are almost equal and this is in favor of the theory of Born.

A very interesting application of the theory has been made by Haber.[4] This author tries to explain the cohesion of a metal by the assumption that an electron is detached from each atom of the metal (monovalent). These electrons form a space lattice between the remaining positive ions. Haber is thus able to calculate a value for the grating energy of a metal which is in good agreement with the value obtained by an entirely different method.

Our purpose is to find a relation between the grating energy of the alkali metals and the energy necessary for evaporation of electrons. The experimental results of Davisson and Germer[5] have shown that this heat of evaporation is practically equal to the work done in tearing an electron from the metal.

CALCULATION OF THE HEAT OF EVAPORATION OF THE ELECTRONS

We shall consider here the alkali metals only. In the processes we shall describe below, all the energies and work units are expressed in kg-cal.

Let us use the following notation:

R = an alkali metal;

X = a halogen;

V = the grating energy;

L = heat of evaporation of 1 gram mol. of electrons at absolute zero;

M = heat of evaporation, at absolute zero, of 1 gram mol. of positive ions from the crystalline metal R;

S_R = heat of evaporation, at absolute zero, of 1 gram mol. of positive ions from the crystalline salt RX;

S_X = heat of evaporation, at absolute zero, of 1 gram mol. of negative ions of the halogen;

D = heat of sublimation, at absolute zero, of 1 gram mol. of the metal;

J = ionizing energy of 1 gram mol. of metal;

a = difference between the potential energy of the positive ions when forming the space lattice of the metal and the potential energy they have arranged in a space lattice of a salt RX;

[ ] = the solid state of a metal;

[[]] = the solid state of a salt;

( ) = the gaseous state.

[4] F. Haber, Berl. Ber. pp. 506, 990 (1919)

[5] Davisson and Germer, Phys. Rev. **20**, 300 (1922)

In the following process we have separated the evaporation of the negative and that of the positive ions in order to make our calculations clearer. We may say that for every negative ion taken from the crystal we evaporate also a positive ion.

Let us now consider the cycle shown in Fig. 1.

We start with the metal R in the crystalline state and, going to the right, evaporate the electrons. Traveling along the arrow means that we have to furnish some energy, while traveling against it means that the reaction is exothermic. Thus, in evaporating the electrons we have to furnish the energy L. We have then a gas of free electrons and the posi-
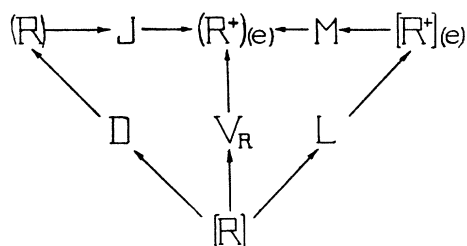
$$(R) \longrightarrow J \longrightarrow (R^+)_{(e)} \longleftarrow M \longleftarrow [R^+]_{(e)}$$

$$D \qquad V_R \qquad L$$

$$[R]$$

Fig. 1

tive ions of the metal in the solid state. Furnishing now the energy M we obtain these positive ions in the gaseous state. If we combine these ions with the electrons in order to obtain the crystal R again, the reaction gives off the grating energy V_R. Hence we have

$$V_R = L + M . \tag{1}$$

If now, we start again with the metal R but go to the left and evaporate the *atoms* of the crystal, we have to furnish the heat of evaporation D. Then, in order to ionize the gaseous atoms, we must again furnish the energy J. Hence

$$V_R = D + J . \tag{2}$$

The energy J is known accurately for the alkali metals. Unfortunately D is not as well known and an error of 2 or 3 kg-calories is very probable. However, we can consider V_R as known experimentally and its value is given in Table I for the different metals.

TABLE I

Ionizing energy and heat of sublimation in kg-cal/mol.

	J	D	V
Na	119	26	145
K	100	20	120
Rb	96	19	115
Cs	90	18	108

From Eqs. (1) and (2) we obtain

$$L = (D+J) - M. \tag{3}$$

In order to determine M we shall consider another cycle (Fig. 2). Here we start with a halide of one of the alkalis. We furnish the heat of evaporation of the negative ions S_X, which leaves the positive ions as a solid having the same crystal structure as the halide. We want now to introduce into this cycle the heat of evaporation M of the positive ions from the crystal structure of the metal itself. We have thus first to go from one space lattice to the other. Let us call a the work involved in this transformation; then we can furnish the heat of evaporation M and obtain the positive ions in the gaseous state. The energy V_{RX} will be given off if we condense the ions into the crystal RX. It is easy to see that
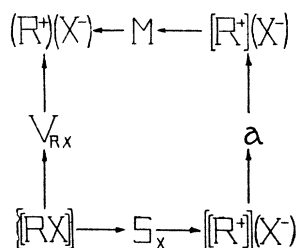
$$S_R = M + a$$

Fig. 2

and from Fig. 2 we deduce

$$V_{RX} = M + a + S_X = S_R + S_X \tag{4}$$

Both S_R and S_X are unknown, but V_{RX} has been calculated and measured. Born[6] calculated it as an electrostatic problem and his results agree within a few percent of the experimental values deduced from thermochemical data. In our calculations we used the experimental values given in Table II.

TABLE II

Grating energy of the alkali halides, in kg-cal/mol.

	Cl	Br	I
Na	183	170	159
K	165	154	144
Rb	161	151	141
Cs	156	146	137

Born[7] gave a theory of the heat of hydration of gaseous ions from which he calculated the potential energy of the ions in water and in vacuum.

[6] M. Born, Atomtheorie des Festen Zustandes, pp. 750-751; and
Grimm, Zeit. f. Phys. Chemie. **102**, 113, 504 (1922)
[7] Born, Zeit. f. Phys. **1**, 45 (1920)

The difference between these two values gives the heat of hydration, which is known experimentally. He can thus deduce the radii of the ions in the following way. The potential energy of an ion in a dielectric is given by

$$\frac{1}{8\pi\epsilon}\int E^2 dS = \frac{e^2}{2r\epsilon} \tag{5}$$

where ϵ is the dielectric constant and e the charge of the ion of radius r. The values of r calculated from (5) are given in Table III.

TABLE III

Radius of the ions[7] from heat of hydration

Ion;	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
$r\times10^8$ cm:	1.59	2.00	2.24	2.22	2.13	2.41	2.88

We can apply the same calculation to crystals. Let us call r_p and r_n the radii of the positive and negative ions respectively. We can then write

$$e^2/2r_p - e^2/2r_p\epsilon = S_R = M + a \tag{6}$$

$$e^2/2r_n - e^2/2r_p\epsilon = S . \tag{7}$$

Dividing (6) by (7) gives

$$S_R/S_X = (M + a)/S_X = r_n/r_p . \tag{8}$$

If we replace S_X in (4) by its value taken from (8) we obtain

$$M = S_R - a = V_{RX}r_n/(r_n + r_p) - a \tag{9}$$

and finally replacing M in (3) we obtain

$$L = (D + J) - V_{RX}r_n/(r_n + r_p) + a \tag{10}$$

Everything on the right hand side of (10) is known except a, but we shall see that with our present knowledge of V_R and V_{RX} the omission of a is not of any importance.

The values of S_R calculated from (9) are given in Table IV.

TABLE IV

Heat of evaporation of positive ions in kg-cal/mol.

	Cl	Br	I	Average	Volts/ion
Na	104	102	102	102.6	= 4.44
K	85	84	85	84.6	= 3.67
Rb	78	78	79	78.3	= 3.39
Cs	79	76	77	77.3	= 3.34

It can be seen that the different values obtained for a given metal and various halogens do not differ greatly and that the variations do not seem to follow any regular law. (This may be due to our inaccurate knowledge of the constants involved.) On the other hand, a must be of the order of

magnitude of the difference between the values of S_R for two different halogens. We thus see that the omission of a does not affect the results.

The values of L (calculated on the assumption that $a = 0$) are given in Table V.

TABLE V

Values of L in kg-cal/mol.

	Cl	Br	I	Average		Calc. (Volts/electron)	Obs.
Na	41	43	43	42.3	=	1.83	1.82
K	35	36	35	35.3	=	1.53	1.55
Rb	37	37	36	35.6	=	1.54	(1.45)
Cs	29	32	31	30.6	=	1.34	1.36

The last column gives the value of L in equivalent volts/electron as measured experimentally by thermionic emission or by the photo-electric effect.

CONCLUSIONS

The calculated values of L in Table V check with the observed values within 3 percent except for Rb. The heat of evaporation of electrons has not been measured for this metal but we have good reasons to believe it to be 1.45 volts. However, a small error on the sublimation heat of Rb can explain the rather large error occurring in the calculated value of L for Rb.

It seems thus that the assumption of space lattices for electrons in metals gives us a good explanation of various properties of the metal even if it does not allow actual solution of every problem in this field.