

HEAT OF IONIC DISSOCIATION OF IODIDES OF RUBIDIUM AND LITHIUM AND ELECTRON AFFINITY OF IODINE.

By B. N. SRIVASTAVA, *M.Sc., Lecturer in Physics, Allahabad University.*

(Communicated by Prof. M. N. Saha, F.R.S.).

There are various methods, chiefly spectroscopic, for determining the heat of dissociation of diatomic molecules into neutral atoms. Some of these have been employed for experimentally determining the heat of dissociation of most alkali halides into their constituent atoms. From a knowledge of this the heat of dissociation of an alkali halide MX into an ionised alkali atom M^+ and a negative halogen ion X^- can be calculated if the ionization potential of the alkali and the electron affinity of the halogen atom are known. The heat of dissociation of an alkali halide into its constituent ions will be briefly termed as 'heat of ionic dissociation'. There is, however, a direct thermal method for determining this heat of ionic dissociation which has been employed by J. E. Mayer (1930) and his co-workers and in this laboratory by M. N. Saha and A. N. Tandon (1936). The principle of this method is to lead the alkali halide vapour MX into a chamber maintained at a high temperature and estimate the quantity of M^+ and X^- ions formed as a result of thermal dissociation by measuring the respective ionic currents obtained by the effusion of these ions through a narrow orifice. From such measurements the concentration of the ions can be found. The vapour pressure of the alkali halide is known from the temperature of the subsidiary furnace. We can then determine the equilibrium constant of ionic dissociation from which the heat of ionic dissociation is easily calculated with the help of the usual dissociation formula.

J. E. Mayer (1930) investigated the ionic thermal dissociation of iodides of caesium and potassium from which he derived the heat of ionic dissociation. This enabled him to calculate the electron affinity of iodine by making use of the Born cycle. J. E. Mayer later on with L. Helmholtz (1932) worked with RbBr and NaCl. M. N. Saha and A. N. Tandon (1936) studied the dissociation of KCl, NaCl and LiCl and determined the electron affinity of chlorine. A. N. Tandon (1937) worked with KBr and NaBr and KI and NaI and found the electron affinities of bromine and iodine. In the present paper the dissociation of iodides of rubidium and lithium has been investigated with an improved apparatus and the method of calculation has been freed from certain inaccuracies occurring in the previous papers. The lattice energy of the alkali halide and the electron affinity of iodine has also been deduced.

Among other interesting methods employed for experimentally determining the electron affinity of iodine may be mentioned those of P. P. Sutton and J. E. Mayer (1935) and of G. Glockler and M. Calvin (1937). The values of

this quantity from all determinations up-to-date, experimental as well as theoretical, are collected in Table 7.

On the theoretical side the most important work is that of Max Born and J. E. Mayer (1932) who have improved upon the older theory of ionic crystals by taking into account some additional factors and obtained a formula for the lattice energy which has been utilised by L. Helmholtz and J. E. Mayer (1932), Mayer and Maltbie (1932), Mayer (1933), Mayer and Levy (1933) for calculating the lattice energies of the alkali halides and some other simple salts. M. L. Huggins (1937) has recalculated the lattice energies by taking into account more recent data. From these results the heat of ionic dissociation as well as the electron affinities can be calculated.

THEORY

When the alkali iodide vapour MI enters the region of high temperatures the following reactions take place:—



where D is the heat of atomic dissociation of the alkali halide, Q the heat of ionic dissociation, I_M the ionization potential of the alkali M , E_X the electron affinity of iodine and D' the heat of dissociation of the iodine molecule. It may be emphasized that the conditions of equilibria of all the five reactions must be individually and simultaneously satisfied no matter what be the concentration of any of the components, provided only that all are present in the reaction space. Thus even if from any cause any component is present in much greater or smaller concentration the other components so adjust themselves that the dissociation formula is satisfied and the dissociation constant is always given by the usual thermodynamic formula. Hence the presence of excess of electrons due to thermionic emission from graphite does not affect the value of the dissociation constant. It can be shown from thermodynamic theory that the dissociation constant K_2 of the reaction (2) is given by the formula

$$\log K_2 = \log \frac{p_{M^+} p_{I^-}}{p_{MI}} = -\frac{Q}{2 \cdot 3RT} + \frac{3}{2} \log T + \log \left(1 - e^{-hv/kT} \right) + \log \left[\frac{k^{3/2}}{2^{3/2} \pi^{1/2} I h} \left(\frac{m_{M^+} m_{I^-}}{m_{MI}} \right)^{3/2} \right], \quad \dots \quad (6)$$

where ν is the frequency of linear vibration of the atoms in the molecule of the gaseous halide MI , I the moment of inertia of this molecule and m_{M+} , m_I , m_{MI} the masses of the ion or the molecule. The other dissociation constants are given by the following relations:—

Dissociation into atoms:

$$\log K_1 = \log \frac{p_M p_I}{p_{MI}} = -\frac{D}{2 \cdot 3RT} + \frac{3}{2} \log T + \log (1 - e^{-h\nu/kT}) + \log \left[\frac{k^{3/2}}{2^{3/2} \pi^{1/2} I h} \left(\frac{m_M m_I}{m_{MI}} \right)^{3/2} \right] + \log 8. \dots (7)$$

Ionization of the atom:

$$\log K_3 = \log \frac{p_{M+} p_e}{p_M} = -\frac{I_M}{2 \cdot 3RT} + \frac{5}{2} \log T + \log \frac{(2\pi m_e)^{3/2} k^{5/2}}{h^3}. \dots (8)$$

Formation of negative halogen ion:

$$\log K_4 = \log \frac{p_I p_e}{p_{I-}} = -\frac{E_X}{2 \cdot 3RT} + \frac{5}{2} \log T + \log \frac{(2\pi m_e)^{3/2} k^{5/2}}{h^3} + \log 8. \dots (9)$$

Dissociation of the halogen molecule into atoms:

$$\log K_5 = \log \frac{p_I^2}{p_{I_2}} = -\frac{D'}{2 \cdot 3RT} + \frac{3}{2} \log T + \log (1 - e^{-h\nu/kT}) + \log \left[\frac{m_I^{3/2} k^{3/2}}{4\pi^{1/2} I h} \right] + \log 16. \dots (10)$$

Also from considerations of Born's cycle we get

$$E_X = D + I_M - Q, \dots \dots \dots (11)$$

and the lattice energy $\phi(r_0)$ is given by

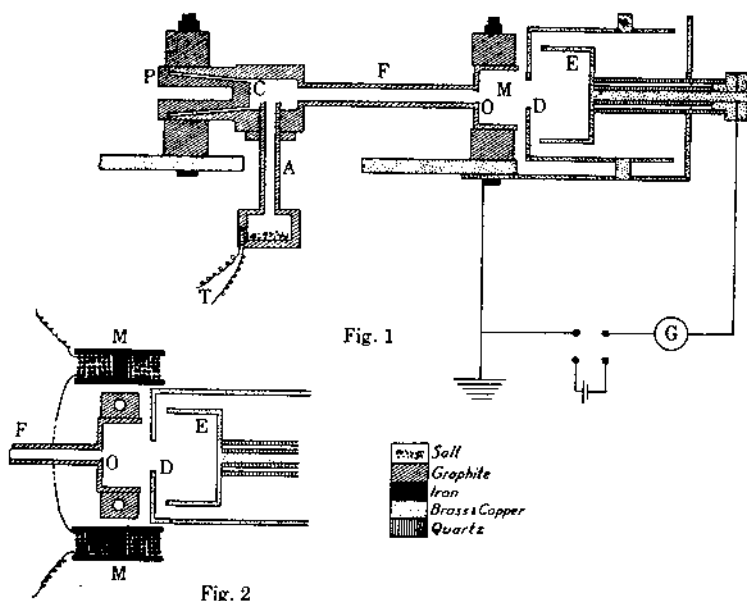
$$\phi(r_0) = Q + L_{MI}, \dots \dots \dots (12)$$

where L_{MI} is the heat of sublimation of MI at the absolute zero.

APPARATUS.

The demountable vacuum graphite furnace used in these experiments has been described in detail by M. N. Saha and A. N. Tandon (1936) but the internal arrangement followed in the present work is slightly different from theirs and is shown in Fig. 1. The improvement consists in a device for applying a magnetic field to distinguish between the negative ion current and the electron current, and in the design of the auxiliary furnace. High temperature is produced in the graphite tube F which is heated by a current of the order of a thousand amperes from a low-tension transformer. This tube has a fine

circular hole on one side while on the other side there is a conical cavity *C* in which a hollow conical plug *P* of graphite fits gas-tight. The tube was so made



that its wall near the junction of the auxiliary furnace *A* was thicker on one side of the cavity than on the other so that the auxiliary furnace could be fitted gas-tight with the help of screw and collar arrangement. This furnace was thus heated simply by conduction from the graphite furnace *F* so that by using tubes of different lengths and wall-thicknesses the desired temperatures could be obtained. These were adjusted by trial. The auxiliary furnace is made thicker at the bottom where the salt is kept so that the temperature gradient in the neighbourhood of the salt is very small, while the nickel-nichrome thermocouple is inserted in the wall. The tube was easily constructed by boring it through and closing the bottom by a tightly-fitting plug. The tube could be readily replaced by another without disturbing the graphite furnace itself. Another advantage of this form of the auxiliary tube lies in the fact that the vapour molecules first impinge on the wall of the graphite furnace and thereby lose their mass velocity and afterwards move with the thermal velocity characteristic of the temperature of the furnace. Care was taken to see that the salt vapour does not condense on the plug closing the furnace *F*. For this purpose the plug was made hollow and long enough so that it projected much beyond the clamping carbon blocks and reached up to the junction of the auxiliary tube. The wall of the graphite furnace in the middle is so thin that an actual comparison of the temperature inside *F* as measured by a platinum-platinum-rhodium thermocouple with that of the outer surface of *F* as measured

by a disappearing filament pyrometer showed no greater difference than the uncertainty in the pyrometer readings itself. Theoretical calculations from conductivity considerations also show that the difference would be negligible. It was therefore neglected.

The vapour molecules suffer dissociation inside *F* according to the equations already given and the products of dissociation effuse out through the narrow orifice after which they traverse a magnetic field produced by two electromagnets shown separately in Fig. 2. These were constructed by winding several layers of bare copper wire over iron bobbins carefully insulated by mica and two such electromagnets were arranged on opposite sides of the effusing beam. Suitable currents were passed so that the electrons were deflected and the negative ion current alone measured.

The rest of the arrangement is identical with that of Saha and Tandon. The effusion beam is limited by a diaphragm *D*. Behind this is a Faraday cylinder connected to a sensitive galvanometer. Suitable accelerating or retarding potentials can be applied between the Faraday cylinder and the limiting diaphragm in order to collect the ions of the desired charge.

Let the hole of the diaphragm be coaxial with the effusion hole. If the diaphragm subtends a cone of semi-vertical angle θ_0 , then the number of particles effusing out through the hole of area *S* and passing through the limiting diaphragm is equal to

$$S \int_{c=0}^{c=\infty} \int_{\theta=0}^{\theta=\theta_0} n_c dc \cdot \frac{1}{2} \sin \theta d\theta \cdot c \cos \theta = \frac{1}{4} n \bar{c} S \sin^2 \theta_0 = \frac{1}{4} n \bar{c} S \frac{r^2}{r^2 + d^2},$$

where *r* = radius of the diaphragm and *d* its distance from the effusion hole. The galvanometer current

$$i_g = \frac{1}{4} n \bar{c} S e \frac{r^2}{r^2 + d^2} \dots \dots \dots (13)$$

But

$$n = p/kT \quad \text{and} \quad \bar{c} = \sqrt{\frac{8kT}{m\pi}},$$

hence

$$i_g = \frac{epS}{\sqrt{2m\pi kT}} \cdot \frac{r^2}{r^2 + d^2} \dots \dots \dots (14)$$

The equilibrium constant *K*₂ is therefore given by the relation

$$K_2 = \frac{P_{M^+} P_{I^-}}{P_{MI}} = \frac{2\pi kT}{e^2 N^2} \left(\frac{r^2 + d^2}{r^2} \right)^2 \frac{i_g^+ i_g^-}{P_{MI}} \sqrt{m_{M^+} m_{I^-}} \dots (15)$$

By combining this equation with (6) and substituting the values of the other quantities *Q* is found out. The various data utilized in this paper are given in Table 1.

TABLE I.

Salt	Moment of inertia of molecule in gaseous state $\times 10^{38}$ gm. cm ²	Characteristic frequency of vibration of molecule in gaseous state in cm ⁻¹	Heat of dissociation into neutral atoms in kilocal.	Heat of ionization of alkali in kilocal.	θ (Debye)	λ_0 in kilocal.	Compressibility at 0°C. per dyne $\times 10^{12}$	Temperature coefficient of compressibility per dyne $\times 10^4$	Volume coefficient of expansion per degree $\times 10^5$	Temperature coefficient of expansion coefficient $\times 10^4$
RbI	6.64	179	76.7	96.0	113	46.4	9.58	6	12	6.5
LiI	0.401	1800.	81.6	123.8	..	38.7

EXPERIMENTAL TECHNIQUE

First the graphite tube was thoroughly degassed by heating it at a temperature much higher than that at which the experiment is to be performed. After prolonged degassing for several hours the behaviour of the tube became regular and the ion currents from the empty tube diminish to a negligible value. At the temperature of the experiments, about 1500° C., the positive ion current is extremely small, while the negative ion current, though much greater, is still much less than the current obtained when the salt is put in the furnace. The following observations (Table 2) obtained with the tube near about the final state will give an idea of the currents in the blank experiment:—

TABLE 2.

Accelerating voltage = 2 volts

Sensitivity of galvanometer = 1.13×10^{-9} amp./mm.

Temperature of graphite tube °C.	NEGATIVE DEFLECTION IN MM.		POSITIVE DEFLECTION IN MM.	
	Without magnetic field	With 3 amperes through electro-magnet	Without magnetic field	With 3 amperes through electro-magnet
1400	3	0	0	0
1455	20	4	1.5	2.5
1500	44	11	3.5	5
1540	80	16	6	8

It can be shown from theoretical considerations that the deflection of the ion beam under the influence of the magnetic field will vary as $1/\sqrt{m}$. Hence it will be greater for the lighter ion and by this means the electrons can be deflected off while the heavier positive ion will be unaffected and can be

measured. Table 3 shows the effect of the magnetic field on the ion currents and amply bears out the theoretical prediction.

TABLE 3.
Accelerating voltage = 2 volts.

Temperature of graphite tube	Current through electromagnet in amps.	Negative deflection in mm.	Positive deflection in mm.
1500°C	0	44	3.5
	1	19	5
	2	12	5
	3	11	5
	5	11	5

The observations clearly show that the negative current largely consists of electrons which are deflected off by the magnetic field and the current falls to about one-fourth of its value after which it is not further affected by the magnetic field. Evidently the remaining part is due to negative ions. The positive current at first slightly increases and thereafter remains constant. In reality the positive ion current is not affected by the magnetic field, the slight increase initially observed is simply due to the fact that some of the very fast electrons which could overcome the retarding potential of 2 volts and reach the Faraday cylinder have now been deflected off by the magnetic field and the positive current therefore increases.

It may be pointed out that the previous investigators have not used a magnetic field to distinguish between the electron and the negative ion current, and have assumed that the negative current is composed entirely of negative ions simply from the fact that the negative current in the blank experiment is comparatively negligible. It will be observed that electrons are produced in the reaction itself (see equations 3 and 4) and therefore the number of electrons produced will be roughly of the same order as the number of ions; hence if during the reaction considerable number of M^+ and I^- ions are produced, the number of electrons will also be appreciable. That this is so is evident from our experimental results which show clearly that the electron current is much greater than in the blank experiment and is approximately of the same order as the other ion currents.

The proper accelerating voltage necessary for the experiment was found out experimentally by trial. Theoretical calculations show that the ions issuing out of the hole have a mean kinetic energy of about 0.3 electron-volts. As quite a large number of ions have velocities much greater than this (in fact they obey Maxwell's distribution law and have all velocities) a retarding voltage of about 5 times this value may be sufficient. Actually in an experiment with lithium iodide the ion currents were measured with different voltages without magnetic field and the results recorded in Table 4 were obtained.

TABLE 4.

Accelerating or retarding potential in volts	Negative deflection in mm.	Positive deflection in mm.
0.4	17	35
0.5	25	55
0.66	35	98
0.8	41	106
1	59	123
1.33	84	141
1.5	97	150
2	132	180
3	140	194
4	146	204
6	158	224

By plotting the current against voltage it is seen that with increase of voltage there is first a rapid increase in current but in the neighbourhood of 2 volts the increase is very small and regular. The slight increase even after 2 volts may be due to the electric lines of force penetrating the limiting diaphragm whose effect will be to produce a virtual increase in the area of the diaphragm for larger voltages, or it may be due to the stoppage of the fastest ions of the opposite charge or both. Evidently the latter effect is desirable but not the former. Hence it is not desirable to increase the voltage beyond 2 volts. For these reasons and partly for the sake of convenience an accelerating potential of 2 volts was used in our experiments. It may be remarked that by taking observations at 2 volts the uncertainty in the measurement of the current is not more than 10% and the resulting error in Q is only about 0.5% while a much larger error is possible due to uncertainties in the value of the vapour pressure as will be seen later.

Hence in our experiments the currents were measured at 2 volts with different magnetic fields and for purposes of calculation the constant values of the negative and positive currents were utilized. It is evident from the observations that the magnetic field employed does not affect the ion currents but deflects only the electron current.

The experimental results obtained with RbI and LiI ¹ are tabulated below. The salts were supplied by Scherring-Kahlbaum and were extra pure and anhydrous. Care was taken to fill the salts quickly and proceed immediately to evacuate the system since LiI is extremely hygroscopic.

Rubidium Iodide.

Diameter of effusion hole = 1.209 mm.

Distance between effusion hole and limiting diaphragm = 1.8 cm.

Radius of the limiting diaphragm = 0.42 cm.

Accelerating voltage = 2 volts.

Current sensitivity of galvanometer = 1.13×10^{-9} amp./mm.

¹ Some observations with LiI were already taken by Dr. A. N. Tandon with the older apparatus without the magnetic field device.

TABLE 5.

Temperature of graphite furnace in °C.	Temperature of auxiliary furnace in °K.	Vapour pressure of salt in auxiliary furnace in dynes/cm ² .	Current through electromagnet in amps.	Negative deflection in mm.	Positive deflection in mm.	$K_2 \times 10^4$ in dynes/cm ² .	Q in kilocal.
1275	760	1.54	0	108	57	0.430	99.7
			1	60	"		
			2	53	"		
			3	52	"		
			5,6	50	"		
1300	773	2.60	0	258	97	0.899	99.1
			1	142	"		
			2	112	"		
			3	105	"		
			5,6	102	"		
1310	774	2.72	0	265	111	0.939	99.6
			1	149	"		
			2	131	"		
			3	123	"		
			5,6	97	"		
1340	782	3.56	0	240 × 3	88 × 3	6.96	95.2
			1	175 "	"		
			2	162 "	"		
			3	155 "	"		
			5	136 "	"		
			6	131 "	"		
			7,8	130 × 3	"		
1390	792	5.055	0	235 × 3	115 × 3	5.24	99.1
			1	136 "	"		
			2	117 "	"		
			3	111 "	"		
			5	105 "	"		
			6,7	104 × 3	"		
1410	797	5.99	0	223 × 3	104.3	4.11	101.1
			1	136 "	"		
			2	120 "	"		
			3	115 "	"		
			5	109 "	"		
			6	107 "	"		
			7,8	106 × 3	"		
1430	799	6.36	0	122 × 10	52 × 10	10.2	99.2
			1	277 × 3	"		
			2	237 "	"		
			3	212 "	"		
			5	181 "	"		
			6	174 "	"		
			7	168 "	"		
			8	167 × 3	"		
1435	807	8.45	0	117 × 10	58 × 10	9.8	99.6
			1	74 "	"		
			2	68 "	"		
			3	65 "	"		
			5	58 "	"		
			6	57 × 10	"		

Lattice energy = $99.1 + 46.4 = 145.5$ Kcal. Mean $Q = 99.1$ Kcal.
 Electron affinity of iodine = $D + I_M - Q = 76.7 + 96.0 - 99.1 = 73.6$ Kcal.

Lithium Iodide.

Accelerating potential = 2 volts.

Diameter of the effusion hole = 1.209 mm.

Distance between effusion hole and limiting diaphragm = 1.8 cm.

TABLE 6.

Temperature of graphite furnace in °C.	Temperature of auxiliary furnace in °K.	Vapour pressure of salt in auxiliary furnace in dynes/cm ² .	Current through electromagnet in amps.	Negative deflection in mm.	Positive deflection in mm.	$K_2 \times 10^7$ in dynes/cm ² .	Q in kilocal.
1350	693	3.54	0	6	27.5	0.5181	130.9
			1	5.5	..		
			2, 3, 5	5.5	..		
1365	696	3.90	0	11	49	1.355	129.0
			1	9	..		
			2, 3, 5	9	..		
1385	698	4.14	0	15.5	67	2.711	128.4
			1	14	..		
			2, 3, 5	14	..		
1415	702	4.82	0	52	113	7.877	127.2
			1	32	..		
			2	29.5	..		
			3	28	..		
			4, 5	28	..		
1430	705	5.46	0	40	103	4.720	130.1
			1	26	..		
			2	24	..		
			3	22	..		
			5, 6	21	..		
1440	707	5.79	0	68	125	9.24	128.6
			1	43	..		
			2	37	..		
			3, 4	36	..		
1470	710	6.45	0	132	180	14.27	129.4
			1	74	..		
			2	59	..		
			3	53	..		
			5	45	..		
			6, 7	43	..		

Mean $Q = 129.1$ Kcal.Lattice energy = $129.1 + 38.7 = 167.8$ Kcal.Electron affinity of iodine = $D + I_N - Q = 81.6 + 123.8 - 129.1 = 76.3$ Kcal.

For calculating K_2 we require the vapour pressure of these salts in the solid state. Unfortunately this is not known. The few available data extend over a narrow region much above the melting point of the salt and cannot be safely extrapolated to temperatures much below the melting point. Even the specific heat data for these salts are not fully known. The only available

course is to calculate the specific heat of the salt by using a Debye term and an Einstein term and then to calculate the vapour pressure of the salt with the help of the following formula:

$$\log p = -\frac{\lambda_0}{4.573T} + \frac{7}{2} \log T - \frac{1}{4.573} \int_0^{T'} \frac{dT}{T^2} \int_0^{T'} C_{p,s} dT - \log (1 - e^{-h\nu/hkT}) + 36.815 + \frac{3}{2} \log M + \log I + 6.0056. \quad \dots \quad (16)$$

This has been done for RbI by using a single Debye term. Calculation by this method gave a value for the vapour pressure differing only by about 15% with the extrapolated value as given by Helmholtz and Mayer. In case of LiI, however, there was a large difference possibly due to uncertainties in the value of λ_0 . For this reason the extrapolated value of 0.039 mm. at the melting point as given by Helmholtz and Mayer was assumed and the following empirical formula was deduced to fit in with this result:

$$\log p \text{ (dynes)} = -\frac{38700}{4.573T} + 13.4859.$$

The vapour pressure p of the salt in the graphite tube is given by $p = p' \sqrt{T/T'}$ where p' is the vapour pressure in the auxiliary tube and T' the temperature of the latter in °K. The full Knudsen effect has been assumed here.

The dissociation constant K_2 was calculated with the help of the equation

$$K_2 = \frac{2\pi kT}{e^2 S^2} \left(\frac{r^2 + d^2}{r^2} \right)^2 \frac{i^+ i^-}{p_{MI} \sqrt{T/T'}} \sqrt{m_M + m_I} \quad \dots \quad (17)$$

and the value of Q was obtained from (6). From this the lattice energy $\phi(r_0)$ and the electron affinity were calculated from equations (12) and (11). The data given by Helmholtz and Mayer have been generally utilised, the only exception being in the case of the heat of dissociation of LiI for which the value of 81.6 Kcal has been assumed which represents the mean of the three values 87.4, 82.0, 75.3 given in Landolt and Bornstein tables.

DISCUSSION OF RESULTS.

It will be observed that in the case of LiI the positive current is in general several times larger than the negative ion current which is to be expected since the Li^+ ion being 127/7 times lighter would effuse out $\sqrt{127/7} = 4.3$ times faster. The currents will however not be exactly in this ratio since the number of Li^+ and I^- ions inside the graphite tube will not be equal, being to some extent governed by the ionization potential of Li and electron affinity of I and the independent electron concentration (equations 6-9). In the case of RbI the masses of the two ions are not much different hence the two ion currents also do not much differ.

The values of the lattice energy of RbI and LiI and the electron affinity of iodine calculated therefrom are recorded in Table 7, along with the results of

† TABLE 7.

Salt.	Lattice energy in kilocal.		Electron affinity of iodine from lattice energy in kilocal.		Electron affinity of iodine by other methods.	
	Theoretical.	By direct experiment.	Theoretical.	By direct experiment.	By G. Glockler and M. Calvin.	By P. P. Sutton and J. E. Mayer.
LiI	174.1 ¹ 176.1 ²	167.8*	75.8 ¹ 73.1 ²	76.3*		
NaI	163.9 ¹ 164.3 ²	166.4*	73.9 ¹ 73.5 ²	72.0*	74.6 ± 1.5	72.4 ± 1.5
KI	150.8 ¹ 152.4 ²	153.8 ³ 150.6*	73.2 ¹ 71.6 ²	70.2 ³ 73.4 ⁴		
RbI	145.3 ¹ 148.0 ²	145.5*	73.8 ¹ 71.1 ²	73.6*		
CsI	139.1 ¹ 142.5 ²	141.5 ³	74.2 ¹ 70.8 ²	71.8 ³		

other workers. It will be seen that the values are in good agreement with other determinations. The mean of our results for the electron affinity of iodine can be put down as 74.9 Kcal. There are various sources of error in the experiment, the chief being the uncertainty in the value of the vapour pressure, the non-uniformity in the temperature of the graphite tube, the error in the determination of temperature by the optical pyrometer, etc. The error due to all these causes is not likely to exceed ± 3 kilocal. in the value of Q and the major portion is due to uncertainty in vapour pressure. When the experimental data for vapour pressure in the solid state are known, this uncertainty can be avoided.

We have remarked previously that electrons are present in the negative current and are deflected away by the magnetic field. Thus by subtracting the negative ion current at say 8 amp. through the electromagnet from the total negative current without the magnetic field, the electron current could be known. This point of view was further pursued. From the electron current the partial pressure of electrons inside the furnace was calculated. Again with the help of equation (8) using the value of $E_X = 74$ Kcal and p_i^- , the partial pressure of iodine atoms inside the furnace was found. Then using (7) we get

† In this table ¹ stands for Helmholtz and Mayer (1932), ² for Huggins (1937), ³ for Mayer (1930), ⁴ for Tandon (1937) and * denotes the values obtained in this paper.

the partial pressure p_M of the alkali atom. Thus knowing the partial pressures of the electron, M atom and M^+ ion the equilibrium constant and the ionization potential of M were calculated. The values so obtained for the various quantities in the case of RbI at 1390°C. are as follows: $p_e = 1.69 \times 10^{-4}$ dynes/cm², $p_{Rb^+} = 5.88 \times 10^{-2}$ dynes, $p_{I^-} = 6.49 \times 10^{-2}$ dynes, $p_I = 21.8$ dynes, $p_{Rb} = 1.22$ dynes and $p_{MI} = 7.32$ dynes. The ionization potential of Rb comes out to be 4.37 volts which agrees very closely with the spectroscopic value. Thus our view that a large number of electrons are present in the effusion stream has been completely justified. We have been able to calculate the concentrations or partial pressures of all quantities present inside the furnace and in fact any of the equations 6-9 can be experimentally tested by this method. Incidentally it shows that the method is quite suitable for experimentally testing the ionization formula.

In conclusion I wish to express my sincere thanks to Prof. M. N. Saha, F.R.S., for his valuable guidance throughout the work. Our thanks are also due to the Royal Society of London for giving a grant which enabled us to construct the furnace and buy its accessories.

SUMMARY.

The thermal dissociation of RbI and LiI vapours into their ions has been experimentally investigated in the temperature region 1300-1500°C. by an improved apparatus which enables separate measurements of the positive ion, negative ion and electron concentrations. From these the equilibrium constant of dissociation at different temperatures is deduced. A theoretical formula then enables us to calculate the heat of ionic dissociation of the salt, the values obtained being 99.1 Kcal for RbI and 129.1 Kcal for LiI. The lattice energies come out to be 145.5 Kcal for RbI and 167.8 Kcal. for LiI. Using Born cycle we get from these measurements the value of the electron affinity of iodine to be 73.6 and 76.3 Kcal, the mean being 74.9 Kcal. These results are in good agreement with deductions from Born and Mayer's theory and other experimental results.

REFERENCES.

- Born & Mayer, 1932, *Zs. f. Phys.*, **75**, 1.
 Glockler & Calvin, 1937, *Jour. Chem. Phys.*, **5**, 142.
 Helmholtz and Mayer, 1932, *Zs. f. Phys.*, **75**, 19.
 Helmholtz and Mayer, 1932, *Jour. Chem. Phys.*, **2**, 245.
 Huggins, 1937, *Jour. Chem. Phys.*, **5**, 142.
 Mayer, 1930, *Zs. f. Phys.*, **61**, 798.
 Mayer and Maltbie, 1932, *Zs. f. Phys.*, **75**, 748.
 Mayer, 1933, *Jour. Chem. Phys.*, **1**, 327.
 Mayer and Levy, 1933, *Jour. Chem. Phys.*, **1**, 647.
 Saha and Tandon, 1936, *Proc. Nat. Acad. Sci. India*, **6**, 212.
 —, 1937, *Proc. Nat. Inst. Sci. India*, **3**, 287.
 Sutton and Mayer, 1935, *Jour. Chem. Phys.*, **3**, 20.
 Tandon, 1937, *Ind. Jour. Phys.*, **11**, 99; *Proc. Nat. Acad. Sci.*, **7**, 102.