they have not so far interpreted, at 1.5 cm of N_2 at N.T.P. It appears, therefore, that at 35 km (oxygen=200 cm), part of the solar spectrum which does not coincide with the O_2 bands may leak through. But the absorption of O_2 below 1000 to 650 is according to these authors very heavy, and nothing can be expected between these limits at 35 km. Below 650 Angstroms no prediction is possible, as laboratory data are not available, but one or two strips of continuous spectrum may be transmitted.

We conclude from the above discussion that a spectro-photogram of the sun, taken at a height of 40 km, will extend the spectrum to $\lambda 2000$, and probably no atmospheric bands will appear between $\lambda\lambda 2900$ and 2000. Between $\lambda\lambda 2000$ and 1700 the Runge-Schumann bands of O_2 may appear in absorption. The region $\lambda\lambda 1700—1250$ will probably be completely cut off. A strip between $\lambda\lambda 1250$ and 1000 may be expected to be transmitted. Below $\lambda 1000$ no prediction can be made, as laboratory data are not available.

But access even to these limited regions will result in invaluable additions to our knowledge, for they will afford information about the behavior of the resonance lines of most of the elements which occur in the Fraunhofer spectrum and thus ease our way for the final solution of the mysteries of solar physics; e.g., we expect to get information (a) about La $\lambda 1216$ of H; (b) about $\lambda 1640$ $\left(=4 \text{ R} \left(\frac{1}{2^2}-\frac{1}{3^2}\right)\right)$, $\lambda 1215$ $\left(=4 \text{ R} \left(\frac{1}{2^2}-\frac{1}{4^2}\right)\right)$ of He$^+$; (c) about the existence or otherwise of the Li- continuum at about $\lambda 2300$; (d) about the resonance lines of elements from Be to O $(4{\to}8)$; we shall not probably obtain any information about F and Ne, but we may obtain the Na-continuum. (e) As regards Mg, we shall obtain much desired information about the resonance lines of Mg and Mg$^+$ which are just beyond $\lambda 2900$; (f) the same is true of the resonance lines of the elements Al to S. (g) We hope also to obtain very valuable information regarding transitional elements, particularly Fe$^+$.

The above short account will indicate how much we should gain from a "Stratosphere Observatory".

65. EXPERIMENTAL DETERMINATION OF THE ELECTRON AFFINITY OF CHLORINE

M. N. Saha and A. N. Tandon

It is well known that halogens have an affinity for electrons and many methods have been proposed for calculating this quantity. Let us take a halide atom X. The affinity E is given by the relation:—

$$X+e=X^-+E.$$

E can be expressed in calories, volts or wave-length units. The following table gives the values in Kilo calories obtained by different workers:—

	F	Cl	Br	I
Mayer and Helmholtz[1] (Theoretical)	95·3	86·5	81·5	74·2
J. E. Mayer[8] (Experimental)	..	..	..	72·6±2
P. P. Sutton and J. E. Mayer[9] (Experimental)	..	..	..	72·4±1·5
Angerer and Müller[4] (Spectroscopic)	94	86·6} 89·6}	79·1} 81·3}	71·3
E. Lederle[5] (Spectroscopic)	95±2	90	82	73
Saha and Sharma[3] (Theoretical)	163·3			

There are several methods for calculating the electron affinity of the halogens. Theoretical calculations have been made by E. Mayer and L. Helmholtz[1] from the crystal energies of the alkali halides. They used the formula for the grating energy of these salts derived by Max Born and E. Mayer[2]. Saha and Sharma[3] used an extrapolation method for calculating the electron affinities. They showed that the value of the ionisation potentials of Ne-like atoms Ne, Na$^+$, Mg^{++} is given by the formula:—

$$E=(Z-6{\cdot}745)^2+1{\cdot}917-\frac{42{\cdot}8}{(Z-6{\cdot}745)}+\frac{70{\cdot}165}{(Z-6{\cdot}745)^2}.$$

If now Z is put equal to 9, we get the electron affinity for fluorine. The value so obtained is 7·1 volts; though this value is high and is rather in violent disagreement with values calculated by other workers, it is in agreement with the value calculated by Mulliken.

On the experimental side, this subject has not been much investigated and the few data that are available have been obtained indirectly from spectroscopic methods. Only in a few cases direct experimental determination has been made. An attempt was made by Angerer and Müller[4] to calculate the electron affinity from spectroscopic
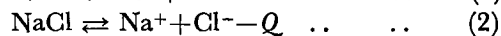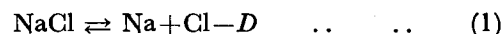
evidence. They observed the absorption spectra of the vapours of alkali halides KF, NaCl, CsCl, KBr, CsBr and KI and found that these begin to absorb continuously at high temperatures from a long wave-length limit. The continuous absorption was attributed to absorption by Cl⁻ or other halogen ions which was supposed to arise from thermal decomposition of the salts. The electron affinity was determined according to the quantum relation $eV = h\nu$. E. Lederle[5] calculated the electron affinities of halogens from the data of Angerer and Müller by an application of the Born-Heisenberg method, but later on H. Kuhn[6] showed that the calculation was based upon a wrong interpretation of the experimental results. Attempts have also been made to observe the emission spectra due to the capture of electrons by neutral halogen atoms, but so far nothing indicative of the actual occurrence of such a process has been observed. Oldenberg[7] tried to observe the electron-affinity spectrum with improved experimental technique, but failed to observe any new spectrum. He gave a theoretical explanation of his negative result. It amounted to showing that the probability of capture of electrons by neutral halogen atoms is very small compared to that of capture of electrons by positive ions like Na⁺ leading to the formation of neutral atoms.

At the suggestion of Born and Franck, a direct method was used by J. E. Mayer[8] to determine experimentally the electron affinity of iodine. He studied the thermal ionisation of the iodides of caesium and potassium at temperatures of the order of 1160°K. and calculated the equilibrium constant; from this, by an application of the dissociation formula and thermochemical data, he could calculate the electron affinity. Recently P. P. Sutton and J. E. Mayer[9] have described another general method for the determination of electron affinity and applied it to determine that of iodine. In Mayer and Sutton's method a tungsten filament was heated in an evacuated globe in which iodine vapour could be introduced. The iodine vapour molecules on coming into contact with the strongly heated filament suffer dissociation into atoms, some of which attract electrons and become negatively charged. These negatively charged atoms and electrons are collected by a concentric anode cylinder. By means of a magnetic field, the electrons are switched off and the current due to the negatively charged iodine atoms can be measured. The value obtained for the electron affinity of iodine was found to be 72·4±1·5 Kilo cals. But so far no direct experimental determination on these lines of the electron affinity of the other halogens has been carried out.

The method described in this paper is also of very general application and is based on the study of the thermal ionisation of alkali halide vapours at high temperatures. The principle involved is of the same nature as that used by J. E. Mayer[8], but the experimental technique has been much improved and is altogether different.

The method essentially consists in vaporising the alkali halide in an electric furnace and then bringing it to a region of higher temperature where the vapour molecules suffer thermal dissociation into atoms as well as into ions. The products of dissociation are made to pass through a narrow circular opening, and then through a circular diaphragm into a Faraday cylinder where they are collected and the current measured by a galvanometer.

The process of dissociation inside the high temperature region, where free electrons are also present, is given by the following set of equations. Taking sodium chloride as a typical example the possible processes of dissociation can be written as follows:—

$$NaCl \rightleftarrows Na + Cl - D \quad \quad \quad (1)$$
$$NaCl \rightleftarrows Na^+ + Cl^- - Q \quad \quad (2)$$
$$Na \rightleftarrows Na^+ + e - I \quad \quad \quad (3)$$
$$Cl^- \rightleftarrows Cl + e - E_x \quad \quad \quad (4)$$
$$Cl_2 \rightleftarrows 2Cl - D' \quad \quad \quad (5)$$

where D is the heat of dissociation of NaCl, Q the heat of dissociation into a sodium and a chlorine ion, I the ionisation potential of sodium and E the electron affinity of chlorine. D' is the heat of dissociation of chlorine into atoms. The dissociation of diatomic molecules has been studied in detail and the formula has been worked out by Gibson and Heitler[10] (see also *Treatise on Heat*, by Saha and Srivastava, p. 703, 1935) with the aid of quantum mechanics. They have taken into account the translational, rotational and vibrational states of the molecules and also the effect of nuclear spin, and given the expression for the entropy and other thermodynamical functions of diatomic molecules. If ψ be the thermodynamical potential given by the relation

$$\psi = S - \frac{U + pV}{T},$$

where U is the internal energy, S the entropy, T the absolute temperature, p the pressure and V the volume, then the expression for ψ is given by

$$\psi = -\frac{U_o}{RT} + \frac{7}{2} \ln T - \ln p + \ln \left[\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} \frac{8\pi^2 Ik}{h^2} \left\{ \frac{3}{2} + \frac{1}{2} \right\} \right] - \ln \left(1 - e^{-h\nu/kT} \right) + \ln g_n$$

according as the nuclei have got a spin or not. m is the mass of the molecule, I its moment of inertia and g is the weight factor.

Hence, we have

$$\psi_{NaCl} = -\frac{U_{0NaCl}}{RT} + \frac{7}{2} \ln T - \ln p_{NaCl} - \ln \left(1 - e^{-h\nu/kT} \right)$$
$$+ \ln \left[\frac{(2\pi m_{NaCl})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} \frac{8\pi^2 Ik}{h^2} \right] + \ln g_{NaCl}$$

$$\psi_{Na} = -\frac{U_{0Na}}{RT} + \frac{5}{2} \ln T - \ln p_{Na} + \ln \frac{(2\pi m_{Na})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} + \ln g_{Na}$$

$$\psi_{Cl} = -\frac{U_{0Cl}}{RT} + \frac{5}{2} \ln T - \ln p_{Cl} + \ln \frac{(2\pi m_{Cl})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} + \ln g_{Cl}$$

Hence $ln\dfrac{p_{Na}p_{Cl}}{p_{NaCl}} = -\dfrac{D}{RT} + \dfrac{3}{2}ln\,T + ln\left(1 - e^{-h\nu/kT}\right) + ln\dfrac{g_{Na}g_{Cl}}{g_{NaCl}}$

$$-ln\left[\dfrac{k^{\frac{3}{2}}}{2^{\frac{3}{2}}\pi^{\frac{1}{2}}Ih}\left(\dfrac{m_{NaCl}}{m_{Na}m_{Cl}}\right)^{\frac{3}{2}}\right].$$

Since $\psi_{NaCl} = \psi_{Na} + \psi_{Cl}$.

In this case $g_{Na} = 2$, $g_{Cl} = 4$, $g_{NaCl} = 1$ therefore, we have

$ln\,k_1 = ln\,\dfrac{p_{Na}p_{Cl}}{p_{NaCl}} = -\dfrac{D}{RT} + \dfrac{3}{2}ln\,T + ln\left(1 - e^{-h\nu/kT}\right)$

$$+ ln\left[\dfrac{2^{\frac{3}{2}}\,k^{\frac{3}{2}}}{\pi^{\frac{1}{2}}Ih}\left(\dfrac{m_{NaCl}}{m_{Na}m_{Cl}}\right)^{\frac{3}{2}}\right].$$

Similarly we have

$ln\,k_2 = ln\,\dfrac{p_{Na}p_{Cl}}{p_{NaCl}} = -\dfrac{Q}{RT} + \dfrac{3}{2}ln\,T + ln\left(1 - e^{-h\nu/kT}\right)$

$$+ ln\left[\dfrac{k^{\frac{3}{2}}}{2^{\frac{3}{2}}\pi^{\frac{3}{2}}Ih}\left(\dfrac{m_{NaCl}}{m_{Na}\,m_{Cl}}\right)^{\frac{3}{2}}\right].$$

Since $g_{Na}^+ = 1$, $g_{Cl}^- = 1$,

$ln\,k_3 = ln\,\dfrac{p_{Na}p_e}{p_{Na}} = -\dfrac{I_0}{RT} + \dfrac{5}{2}ln\,T + \dfrac{(2\pi m_e)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}$

$ln\,k_4 = ln\,\dfrac{p_{Cl}p_e}{p_{Cl}^-} = -\dfrac{E}{RT} + \dfrac{5}{2}ln\,T + ln\left[\dfrac{(2\pi m_e)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3}\right] + ln\,8.$

It is easy to verify that these constants are not independent, but we have

$$k_4 = \dfrac{k_1 k_3}{k_2},$$

and $$Q = D + I - E.$$

k_2 is determined experimentally from which we can calculate the value of Q. We obtain E from the relation

$$E = D + I - Q.$$

Apparatus.—The demountable vacuum graphite furnace used in these experiments has been described in detail in a previous paper by M. N. Saha and A. N. Tandon[11]. It will suffice here only to mention the internal connections inside the furnace. These are illustrated in the adjoining diagram (Fig. 1). The high temperature is produced in the graphite tube F which is heated by passing a current of about a thousand amperes from a low tension transformer. The graphite tube has only a small hole A on one side and female cone C on the other. Into the female cone is inserted another wire-wound furnace whose male cone exactly fits C, so that the salt vapour can only pass through the hole A. The wire-wound furnace F' is so designed that the temperature of the salt vapour can be determined without much error, and the salt vapour does not condense in any part between this and the graphite tube. An iron rod is bored from both the ends and a very thin iron partition is left. One end of this tube is then made conical so as to fit exactly into the cone of the graphite tube. The tube is then bent into the shape as shown in figure (1), so that the molten salt may not run down

the graphite tube. The thermocouple T is placed on the other side of the diaphragm as shown in the figure. Over the iron tube some mica is put and then the furnace is made by winding nichrome wire on it. The cone C is pushed inside the graphite tube, into a temperature region which is greater than the temperature at which the salt vaporises. This ensures that the salt vapour does not condense between the furnace and the high temperature region.
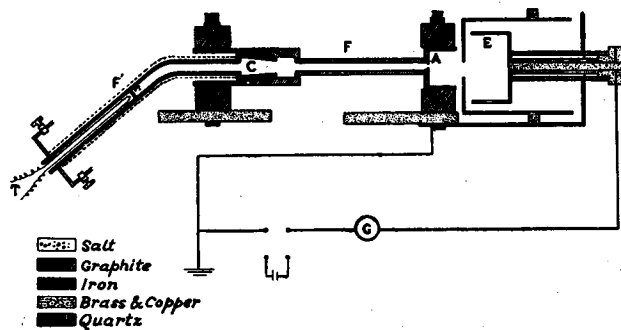

Salt
Graphite
Iron
Brass & Copper
Quartz

Fig. 1

The salt to be investigated is put inside this furnace and the temperature is measured by means of a thermocouple.

At a distance d from the small hole in the graphite is put a diaphragm D of radius r, behind which is placed a Faraday cylinder E. The cylinder is connected to a sensitive galvanometer. If S denotes the area of the circular orifice, the number of particles coming out of the hole per second is given by $\dfrac{S}{4}n\bar{c}$, where n is the number of particles per cubic centimeter inside the graphite tube and $\bar{c}$ the mean velocity at the temperature of the graphite tube.

Now the pressure $p = nkT$ or $n = p/kT$ where p is the pressure of the particles inside the tube.

If p_M^+ be the partial pressure of the positive ions inside the tube, then the number of positive particles coming out per second is equal to $\dfrac{S}{4}\dfrac{p}{kT}\bar{c}$ and therefore the positive ion current i_M^+ is given by

$$i_M^+ = \dfrac{S}{4}\dfrac{p_M^+}{kT}e\sqrt{\dfrac{8kT}{m\pi}}.$$

If i_g is the current indicated by the galvanometer

$$i_M^+ = \dfrac{2d^2}{r^2}i_g,$$

therefore $$p_M^+ = \dfrac{i_M^+}{eS}\sqrt{2\pi m_M kT}.$$

Similarly $$p_X^- = \dfrac{i_X^-}{eS}\sqrt{2\pi m_M kT}.$$

If p_{MX} denotes the vapour pressure of the salt MX, then

the dissociation constant K_2 is equal to $\dfrac{p_{M^+} \cdot p_{X^-}}{p_{MX}}$ and is therefore given by the expression

$$K_2 = \frac{i_{M^+} l_{X^-}}{e^2 S^2} \, (2\pi k T) \sqrt{\frac{m_M m_X}{p_{MX}}}.$$

The magnitude of the currents is measured experimentally by the galvanometer. The diameter of the effusion hole is determined by means of a travelling microscope, from which S is calculated.

Experimental technique.—It is first of all necessary to study the emissions from the graphite tube when no salt is put inside the subsidiary furnace. For this reason the furnace tube is heated for an hour at a temperature of about 2000°C. in a vacuum of about 10^{-4} mms. The process is continued till the vacuum remains undisturbed by the heating of the graphite tube.

The Faraday cylinder is then given a small positive or negative voltage with respect to the graphite tube from a potential divider and the current due to electrons and positive ions is measured at different temperatures with different applied voltages. The positive current is found to be negligible in comparison to the negative current, which must be due to electrons emitted from the graphite tube.

The furnace is then opened and the salt is introduced into the subsidiary furnace. After proper degassing of the graphite tube the current in the subsidiary furnace is switched on. The temperature takes a steady value in about 15 minutes. The currents due to the positive and negative ions is measured again in the manner described above by giving the Faraday cylinder a small negative or positive potential with respect to the graphite tube, which is always kept at earth potential. The retarding potential is usually kept two volts but in the case of lithium chloride, the order of the electron current is comparable with the current due to the chlorine ions and so while measuring the chlorine ion current the retarding potential is kept very low. If the potential is kept high the electrons are accelerated and an unusually high current is recorded.

The temperature of the graphite tube is recorded by means of a disappearing filament type of pyrometer having two ranges. A nickel nichrome thermocouple is used to indicate the temperature at which the salt vaporises. It is very necessary that during the experiment the temperatures remain steady. There is no difficulty in maintaining steadiness of temperature in the case of the subsidiary furnace, but the temperature of the graphite tube sometimes fluctuates by small amounts due to the fluctuations in the voltage of the supply mains. For this reason, it becomes necessary to record the temperature of the graphite tube at very short intervals.

The experiments have been performed with three salts, KCl, NaCl and LiCl. The results obtained with each salt are given below and discussed separately.

Potassium Chloride

The heat of ionisation of potassium is well known to be 99·5 Kilo calories. The heat of dissociation of potassium chloride into a potassium and chlorine atom is known to be 101·4 Kcal. The order of ion currents obtained in this case is of much greater order than the electron current (obtained from a blank experiment) and therefore the presence of the latter does not disturb the equilibrium represented by equation (2). Theoretically the positive ion current and the current due to chlorine ions should vary inversely as the square root of their atomic weights, and the effect of the extra electrons due to the graphite should increase the proportion of chlorine ions, but on the contrary it was found in many cases that the positive ion current was slightly larger than the chlorine ion current at low temperatures. This is probably due to the formation of molecular chlorine, according to equation (5), which diminishes the pressure of chlorine atoms, and hence the chlorine ion concentration decreases according to the equation (4). At higher temperatures the formation of molecular chlorine diminishes and more electrons are given out by the graphite tube, hence the current due to the chlorine ions increases in proportion. Table 1 gives the results of observations. The vapour pressure of KCl was directly extrapolated from the empirical formula of Fiöch and Rodebush.[12]

$$\log p_{mm} = \frac{9115}{T} + 8 \cdot 3526.$$

TABLE 1

Diameter of the effusion hole (mms.)	Vapour pressure (dynes/cm²)	Temperature of the graphite tube (°C)	$i_{K^+} \times 10^6$ (amps.)	$i_{Cl^-} \times 10^6$ (amps.)	$K \times 10^5$	Q (Kilo cals.)
1·17	90·95	1620	583·4	583·4	127·6	114·7
,,	84·48	1560	37·04	34·61	52·72	114
,,	27·66	1530	24·5	21·78	41·6	113·6
,,	15·2	1380	4·668	4·279	3·909	111
·4955	28·3	1625	11·97	17·96	114	114·8
,,	15·55	1625	16·16	15·19	276·2	112
,,	17·33	1550	8·079	5·171	40·51	114·2
,,	111·1	1540	25·22	12·93	49·03	112·9
,,	17·33	1520	5·819	3·555	19·72	114·8

Taking the mean of the above values of Q we get 113·5 Kilo calories, and hence from the formula $E = D + I - Q$ we get $\{99 \cdot 5 + 101 \cdot 4 - 113 \cdot 5\} = 87 \cdot 4$ Kilo calories for the value of the electron affinity of chlorine.

Sodium Chloride

The results obtained with sodium chloride vapour are given in table 2. It will be found that the positive ion current is much larger than the current due to the negatively

charged chlorine ions, specially at low temperatures and pressures. The atomic weight of sodium (23) is smaller than that of chlorine (35·5) and so the effusion current due to Na^+ should be larger by 1.243 times, but it will be seen that the current is sometimes twice or even more. The cause is again due to the formation of molecular chlorine as explained in the case of potassium chloride. At high temperatures the proportion of chlorine ions increases. The vapour pressure of sodium chloride has been calculated from the empirical formula of Fiöch and Rodebush[12].

$$\log_{10} p_{mm} = -\frac{9419}{T} + 8.3297.$$

TABLE 2

Diameter of the effusion hole	Vapour pressure (dynes/cm²)	Temperature of the graphite tube (°C)	$i_{Na^+} \times 10^7$ (amps.)	$i_{Cl^-} \times 10^7$ (amps.)	$K \times 10^7$	Q (Kilo cals.)
1·17 mm.	82·59	1625	70·37	57·57	128·5	132·4
,,	11·71	1620	27·52	25·6	180·3	131·7
,,	61·37	1600	103·7	64·82	283·2	127·7
,,	41·49	1560	74·54	45·37	206·3	126
,,	15·81	1505	21·34	5·762	19	130·5
,,	11·71	1500	14·41	5·403	16·26	130·7
,,	76·9	1470	30·4	14·99	14·24	128·7
,,	15·81	1450	11·89	3·60	6·439	130
,,	11·71	1450	7·565	2·881	4·422	131·3
,,	31·11	1440	10·87	4·478	3·701	131·1
,,	76·9	1400	21·07	9·317	5·895	126·3

The average of Q from the above comes out to be 129.7 Kilo calories. The heat of dissociation of sodium chloride into sodium and chlorine is known to be 97.7 Kilo calories and the ionisation potential of sodium is 117.9 Kilo calories. The electron affinity of chlorine is therefore (97·7 + 117.9 − 129·7) = 85·9 Kilo calories.

Lithium Chloride

It has been seen in the ionisation of KCl and NaCl that the current due to chlorine ions is diminished due to the formation of molecular chlorine. It is therefore to be expected that in the case of lithium chloride the proportion of chlorine ions would be much smaller. On the contrary it was found that the number of chlorine ions was much larger than the number of lithium ions. Lithium has a high ionisation potential of 123·8 Kilo calories and the heat of dissociation of LiCl is also very large (114·4 Kilo calories). The order of currents obtained at the temperatures used (1400°C.—1625) is therefore of much smaller magnitudes than the corresponding currents for KCl and NaCl. The electron current due to the emission from the graphite tube was negligible in the latter cases, but in this case it is of the same order as the current due to the ions.

The effect of a large percentage of free electrons will naturally be to retard the ionisation of lithium and to accelerate the formation of chlorine ions. It is for this reason that chlorine ions are present in such a large proportion.

As no arrangement has yet been made to distinguish between the negative ion and electron currents, it has been supposed here the negative current is all due to the chlorine ions. This may introduce an error in this case. Attempt was made to carry out the experiments at low temperatures in the absence of free electrons but then the currents were so small that the galvanometer could not detect them. One extra precaution has however been taken in this case. The retarding potential, while measuring the chlorine ion current, was kept very low (0·5 volt) because of the presence of electrons. A large voltage accelerates the electrons and an unusually high current is obtained.

The results obtained are tabulated in table 3. The vapour pressure has been extrapolated from the formula given by Wartenburg and Schulz[13]

$$\log p_{atm} = -\frac{37200}{4·57 T} + 4·923.$$

TABLE 3

Diameter of the effusion hole	Vapour pressure (dynes/cm²)	Temperature of the graphite tube (°C)	$i_{Li^+} \times 10^8$ (amps.)	$i_{Cl^-} \times 10^8$ (amps.)	$K \times 10^{10}$	Q (Kilo cals.)
1·17 mm.	139	1660	98·54	262·8	2743	148·7
,,	360·6	1640	102·2	240·8	979·7	151·1
,,	139	1625	73	175·2	1330	148·8
,,	203·7	1620	43·8	153·3	475·2	152·4
,,	77·27	1610	37·35	79·41	550·9	150·9
,,	77·27	1575	32·79	42·05	250·4	150·9
,,	307·6	1420	9·344	9·344	3·659	152

CONCLUSION

In this paper is described an experimental method for finding out the electron affinity of the halogens. The method has for the present been applied to chlorine only. The value of this quantity, from the two sets of most reliable determinations, comes out to be 86·6 Kilo cals, and the theoretical value given by Börn, Mayer and Helmholtz[1] is also 86·5. The results are therefore in perfect agreement with the theory. Further experiments are in progress for finding out, according to this method, the electron affinity of the other halogens.

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66. MOLECULES IN INTERSTELLAR SPACE ?

In a recent note in NATURE[1], and more in detail elsewhere,[2] Dr. T. Dunham, jun., has described his discovery of more interstellar lines due to K ($\lambda 7699 \cdot 03$), Ca ($\lambda 4227$), Ti$^+$($\lambda 3242 \cdot 6$ and others) and a number of other lines the origin of which has not yet been traced ($\lambda 3957 \cdot 7$, $\lambda 4300 \cdot 3$, $\lambda 4232 \cdot 6$). We have to add to these Merrill's interstellar lines[3] ($\lambda 5780$, $\lambda 6284$).

Dunham's work and his discussion of the occurrence of Ti$^+$-lines forms a landmark in the story of interstellar investigations, as it throws clear light on the mechanism of excitation, and removes a good deal of misconception arising out of the former idea that only Ca$^+$-lines, and the sodium D-lines occur in interstellar space.

Dunham's discovery that only such Ti$^+$-lines which arise from absorption in the lowest orbit of Ti$^+$($3d^2$. $4s$. $^4F_{3/2}$) occur as interstellar lines and that no Ti$^+$ atom in the next excited state Ti$^+$($3d^2$. $4s$. $^4F_{5/2}$ excitation potential $0 \cdot 012$ volt) occur in interstellar space, shows that the reaction between matter and radiation in interstellar space is of a kind which cannot be described in terms of any interspace temperature. The temperature in interspace is very nearly absolute zero, and ionization is produced only by the photochemical action of quanta meeting atoms or ions after long intervals of time in space. The recombination between ions and electrons also take place at very long intervals. The result is that only such states of atoms and ions occur in interstellar space as have infinitely long life.

The argument raises the question: Why should not molecules also occur in interstellar space ? In fact, the above arguments, if forced to their logical conclusion, lead us to the view that we should have molecules in interstellar space. Merrill in fact notes that the lines $\lambda 5780 \cdot 4$, and $\lambda 6284 \cdot 0$ discovered by him are diffuse, and in course of a conversation told me that they might be molecular in origin. In fact, the line $\lambda 6283 \cdot 0$ appears decidedly to be due to *molecular sodium*, Na$_2$, due to the transition (Na$_2$: $^2S^2S$ A $^1\Sigma \rightarrow {}^2S$. ^2P B $^1\Sigma$, $n''=0$, $n'=8$). This band is obtained in absorption in molecular sodium, and according to the Franck-Condon principle, the transition is strong as r'' (internuclear distance at the lowest state) is $3 \cdot 07 \times 10^{-8}$ cm., and r' (internuclear distance at the excited state) in $3 \cdot 66 \times 10^{-8}$ cm., so the transition $n''=0$ to $n'=8$ is the most probable. According to the arguments presented here, no other line (or band) of Na$_2$ is likely to occur among the interstellar lines.

Merril's other line ($\lambda 5780$) may be provisionally identified with a line of NaK ($n''=0$, $n'=5$), though in this case the identification is less sure.

The molecule which is likely to be most abundant in interstellar space is H$_2$, but as it gives absorption lines only in the Lyman region, there is no possibility of our being able to prove its existence, but lines due to hydrides may be found amongst interstellar lines.

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April 6.

[1] NATURE, **139**, 247 (1937).

[2] *Pub. Ast. Soc. Pac.*, **49**, 26 (1937).

[3] *Pub. Ast. Soc. Pac.*, **48**, 179 (1936).