THE RECOMBINATION SPECTRA OF THE ALKALI ATOMS AND THE HALOGEN ATOMS.

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ABSTRACTS.

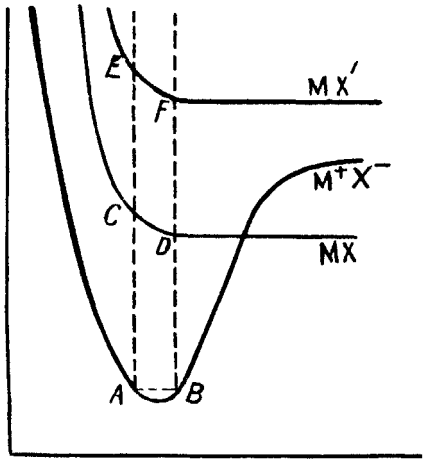
The large volume of experimental facts proving that a diatomic molecule, on the absorption of light, dissociates in the first stage into two normal atoms when the molecule is polar, and into one normal atom and one excited atom in the case of non-polar molecules, points to another possibility that two normal atoms may combine to form a polar molecule and emit radiation, and one normal atom and one excited atom may combine to form a non-polar molecule with the emission of radiation. Such recombinations giving rise to non-polar molecules are known. The possibility of this type of recombination in the cases of Na and Cl, and K and Cl has been studied here. Though the probability of this type of recombination by two-body collisions is small, yet by burning sodium and potassium in an atmosphere of chlorine, the authors have succeeded in photographing spectra, which can be understood only by attributing them to the recombination of Na and Cl and K and Cl by two-body collisions. The relevant features of the spectra are explained on the Franck-Condon Principle. From the most intense part of the spectra, an estimate is made of the temperature of the reaction zone.

INTRODUCTION.

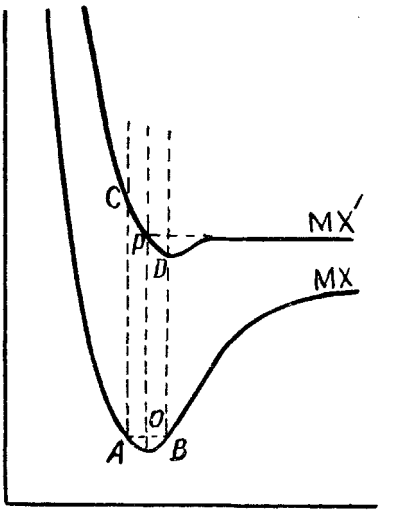
The absorption spectra of a large number of diatomic polar molecules have been studied by Franck, Kuhn and Rollefson (1927) and others; the general feature of all such spectra is that there is a continuous absorption extending towards short wavelength and beginning (in some cases sharply, in others diffusely) with a certain wavelength. In a number of cases there is a region of retransmission also, followed by a second or third region of continuous absorption. These features are well explained on the Franck-Condon Principle. This principle states that when a molecule absorbs light, the primary action is that the molecule is excited to the higher electronic states, the excitation taking place, according to the classical picture, at the two end-points of the vibration states of the ground state. In the transitions the internuclear distance and the kinetic energy of the molecules remain constant. Text-fig. 1 represents the potential energy curves of a typical polar molecule where the ground state is the ionic state and the next higher state is due to two normal atoms of the elements M and X. At the room temperature, most of the molecules are in the vibration state $v'' = 0$ corresponding to AB in the text-fig. 1. On the absorption of light, the molecule goes to C or D where it dissociates into a normal M and a normal X. Since the upper state is repulsive, the energy is absorbed continuously, the long wavelength beginning of the continuous spectrum corresponds to BD. If the molecule goes to E or F, it dissociates into M and X′, where X′ is an excited atom; this gives rise to the second continuum in the absorption spectrum. The wave-number separation of the long wavelength limits of the absorption continua is equal to the term value difference of X and X′.

In the case of the non-polar molecules, for which the potential energy curves are given in text-fig. 2, the ground state of the molecule arises from two normal atoms M and X, and the next higher states correspond to a normal M and an excited X′ or a normal X and an excited atom M′. Usually the higher states are also stable. In case the equilibrium distance in the upper state is not very much larger than that in the ground state, the transition from B to D gives rise to discrete bands, which gradually converge joining on to a continuous spectrum, starting with the wavelength corresponding to OP. The transition at A takes the molecule to C where it dissociates into M and X′.

These experimental facts and their explanation on the Franck-Condon Principle prove that a polar molecule, on the absorption of light, dissociates in the first stage into



TEXT-FIG. 1.



TEXT-FIG. 2.

two normal atoms and a non-polar molecule dissociates in similar circumstances into one normal and one excited atom. It should, therefore, be expected that the reverse process of radiative combination of two atoms leading to the formation of a stable molecule may also take place, i.e. two normal atoms or one normal atom and one excited atom may combine to form a polar molecule with the emission of radiation; and one normal atom and one excited atom may combine to form a non-polar molecule with the emission of radiation. Under suitable conditions this emitted radiation should be observed. This has been called the recombination spectrum. The present work was undertaken to study this possibility in the case of the combination of the alkali atoms with the halogens.

THE MECHANISMS OF SIMPLE CHEMICAL COMBINATIONS.

The simple chemical combinations between alkali atoms represented by M and halogens by X can take place in two ways: by (1) three-body collisions, and (2) two-body collisions. A mechanism involving three-body collisions in the case of the alkali atoms and the halogen atoms has been suggested by Polanyi and co-workers (1928) which is given below:

$$
\begin{aligned}
&(1)\ \mathrm{M}+\mathrm{X}_2 \rightarrow \mathrm{MX}+\mathrm{X}\\
&(2)\ \mathrm{M}+\mathrm{X} \rightarrow \mathrm{MX}\\
&(3)\ \mathrm{M}_2+\mathrm{X} \rightarrow (\mathrm{MX})'+\mathrm{M}\\
&(4)\ (\mathrm{MX})'+\mathrm{M} \rightarrow \mathrm{MX}+\mathrm{M}'\\
&(5)\ \mathrm{M}' \rightarrow \mathrm{M}+h\nu
\end{aligned}
$$

This mechanism was suggested to explain the fact that in the chemiluminescent spectra, only those lines of the principal series of the alkali atoms are observed which have their energy of excitation less than $Q+J-E$, where Q is the heat of formation of the molecule MX, and J the heat of ionisation of M, and I the electron affinity of the halogens X. The reaction (1) occurs at every collision; and the reaction (3) occurs at every collision also.

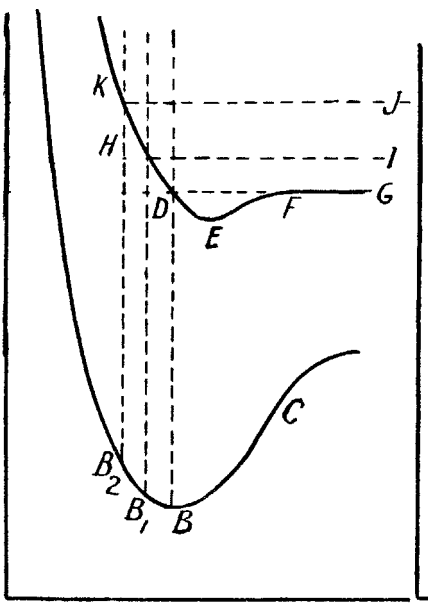
The mechanism of recombination by two-body collisions can be outlined as follows with the help of the potential energy curves:—

Let us first consider the formation of non-polar molecules by two-body central collisions between a normal atom and an excited atom. Taking the relative kinetic energy of the

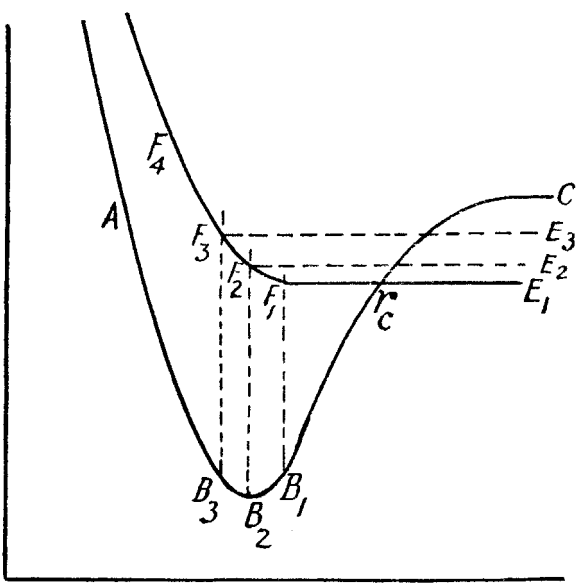
atoms to be zero, the potential energy of the colliding system may be represented by the straight line *GFD* in text-fig. 3, the vertical distance of the straight line above the potential energy curve *GFED* represents the relative kinetic energy at those points. At *D* all energy is potential, and this represents the classical turning point of the atoms. The atoms stay the longest at the internuclear distance represented by *D* (10^{-13} sec., of the order of the time period of vibration). Here three incidents may occur: (*a*) the system may collide with a third particle and lose all its potential energy, and return to the ground state *B* (three-body collisions); (*b*) the energy *BD* may be radiated as light of frequency corresponding in energy to *BD* (recombination by two-body collisions); (*c*) the atoms may fly apart. If the relative kinetic energy of the colliding atoms be larger, the total energy will be represented by *IH* or *JK*: the classical turning points will be *H* and *K*, the points of intersection of the potential energy curve and the straight lines *IH* and *JK*. The transition can take place at *H* and *K* giving rise to radiation of energy HB_1 and KB_2. Since the atoms can have all possible kinetic energy, the turning points (*D*, *H*, *K*, etc.) at which transitions will take place, will be contiguous giving rise to continuous radiation. The longest wavelength will correspond to *BD*. The long wavelength beginning of the continuous absorption spectrum also corresponds to *BD*.

In the case of the non-central collisions, the minimum distance of approach, where the probability of transition is the largest, is greater than the distance represented by *D*. The transition, in such cases, takes place at distances represented by *E*, *F*, etc. resulting in the radiation of light of wavelength usually larger than that corresponding to *BD*. As the atoms remain at the minimum distance for shorter time in the case of a non-central collision than in the case of a central one, the probability of transition in the former case will be much smaller. Even then, it should be expected that some light of wavelength longer than that corresponding to *BD* will be emitted.

Let us consider the formation of a polar molecule by collision between two normal atoms. In this case, when the relative kinetic energy is zero, their mutual potential energy is given by the curve $E_1F_1F_2F_3$ in text-fig. 4, but they cannot approach nearer to



TEXT-FIG. 3.



TEXT-FIG. 4.

each other than F_1, where the repulsive force starts operating. Here again the system may lose energy by collision with a third body and return to the stable state; or it may give away its potential energy B_1F_1 in the form of radiation and return to B_1 in the

ground state, vertically below F_1. If the two colliding atoms have some relative kinetic energy represented by the height E_1E_2, they approach each other up to a distance represented by F_2, the classical turning point, where all energy will become potential; and here transition to B_2 in the ground state vertically below F_2 may occur, giving away the energy B_2F_2 in the form of radiation. As all relative kinetic energies are possible, the recombination spectra emitted will be continuous with the long wavelength beginning corresponding to B_1F_1.

The probability of the formation of non-polar molecules by two-body collisions can be estimated as follows: since the time of stay of the colliding atoms at the classical turning points is of the order of 10^{-13} sec. and since the life-period of an atom in the excited states is of the order of 10^{-8} sec. the probability of transition from D to B in fig. 3 with the emission of radiation is 1 in 10^5. The probability of such a recombination is still less, due to the fact that one of the colliding atoms forming a non-polar molecule by a two-body collision must be in an excited state. In the case of the two-body collisions giving rise to polar molecules the probability of recombination is larger, as in this case it is not necessary that one of the colliding atoms should be in an excited state. Even though the two-body collisions will not lead to recombination with the emission of radiation in more than 1 in about 10^5 cases, there are instances where recombination spectra have been observed.

Historical review.

Kondratjew and Leipunsky (1929) studied the spectra emitted by the halogens when heated to a temperature of about 1000°C. in a fused quartz tube. The spectra they photographed correspond most completely with the absorption spectra of the corresponding halogens. They interpret the spectra as arising from the recombination of the halogen atoms X and X′ which proceeds according to the following scheme:

$$X + X' \rightarrow X_2 + h\nu$$

Urey and Bates (1929) have observed the recombination spectra of halogens in flames.

If Te_2 is subjected to electric discharge, a strong dissociation of vapour occurs. Rompe (1936) found a continuum in the spectra of the light emitted by the discharge and attributes it to the formation of Te_2 by two-body collisions.

T. H. Hori (1933) observed a continuum with a maximum and a minimum of intensity in the spectra of the light emitted by the potassium arc in hydrogen atmosphere. He explains this result on the assumption that a normal H atom and an excited K atom, on collision, form an unstable KH molecule in $^1\pi$ state. The continuum is emitted by the transition of the molecule from this state to the ground $^1\Sigma$ state.

Stenvinkel (1939) has observed that AlH at the oven temperature of 2400°C. and a hydrogen pressure of 45 cm. emits a continuum with the maximum of intensity in the centre of the 1-1 band. This has been explained as the consequence of the formation of AlH molecule in $^1\pi$ state, by collision between Al and H atoms, and the transition from this state to the various vibration states of the ground state. A similar continuum with a maximum and a minimum of intensities is observed for NaH also, but the intensity is much smaller.

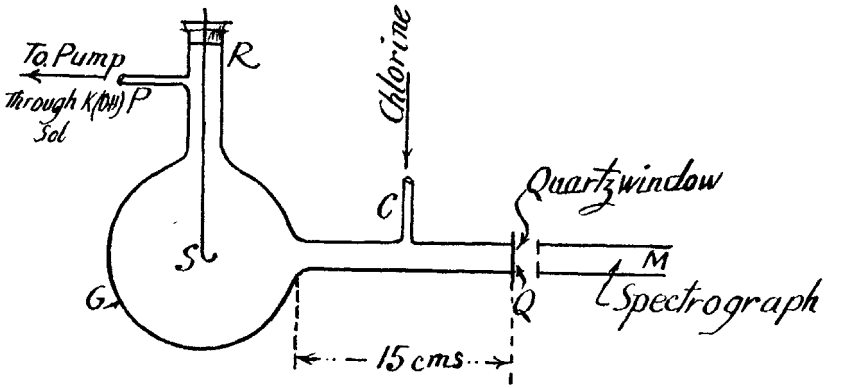
Kondratjew (1928) tried to photograph the recombination spectra of the sodium and the chlorine atoms but failed. He concluded, therefore, that when an alkali atom and a chlorine atom, approaching towards each other, come to a distance r_c in fig. 4 where the ion-ion and the atom-atom potential energy curves intersect, the valence electron is transferred adiabatically from the alkali atom to the halogen atom; and the ions start vibrating in the ionic ground state. The probability of the radiation of the vibration energy is small, and therefore, the system, on colliding with an alkali atom, gives its potential energy to the latter, exciting it to the higher atomic energy state, and itself returns to the ground state. We have been able to photograph[1] the spectra of the light

[1] The recombination spectra of sodium and chlorine, and potassium and chlorine were photographed in November 1942, but due to unavoidable reasons the authors' results were not published.

emitted in the incandescent reaction between Na and Cl, and K and Cl. These spectra can be understood as due to the recombination by two-body collisions between Na and Cl, and K and Cl. The experimental arrangement for photographing them and the explanation of their relevant features are given below.

The experimental arrangement.

The arrangement set up for photographing the recombination spectra of the alkalies and halogens was as shown in text-fig. 5. A glass vessel G of the type shown in the figure



Text-fig. 5.

was prepared. Q is a quartz window. S is an iron spoon, attached to the rubber cork R. Chlorine, prepared by dropping Conc. HCl on $KMnO_4$ crystals, was passed into the vessel G through the inlet C. Pieces of sodium and potassium were first washed in ether, as suggested by Ditchburn (1928) to purify them and then were placed in the spoon. The alkali pieces in the spoon were heated over a gas burner till they started glowing: then the spoon was introduced into the vessel G and placed in the position as shown in the figure; and the pump was started. A vigorous reaction started. The spectrum of the light emitted was photographed by a small quartz spectrograph M. At the spot of photographic plate 25 to 30 exposures were given, each lasting about a quarter of a minute depending on the size of the alkali piece. The slit of the spectrograph was kept about 1 mm. wide. This was enough to give a good photograph. The gas in the vessel was always contaminated with air. In order to see which part of the spectrum was due to the reaction between the alkalies and air, a photograph of the light emitted by alkali burning in air also was taken.

Attempts to prepare an apparatus, wherein the temperature and the pressure of the reacting substances could be regulated and oxygen could be entirely eliminated, did not succeed for want of suitable materials.

Attempts were made to photograph the recombination spectra of sodium and potassium, with bromine and iodine; as the reactions in these cases were less vigorous, the result was not conclusive. On account of the war conditions, suitable apparatus could not be made.

The description of the plate (Plate XXII).

The fig. 1_b is the spectrum of the light emitted in the reaction between sodium and chlorine. 1_a and 1_c are the copper arc spectra. In 1_b there is a continuum up to $\lambda 3600$ and then there is another continuum from $\lambda 3036$ to $\lambda 2300$. The most intense part of the spectrum lies at $\lambda 2766$. The fig. 2_b is the spectrum of the light emitted by the reaction between potassium and chlorine. 2_a and 2_c are copper arc spectra. In 2_b there is a continuum from the beginning up to $\lambda 3600$ and another continuum from $\lambda 2961$ to $\lambda 2300$. The region at 2740 has the greatest intensity in the second continuum. The

fig. 3_b is the spectrum of the light emitted by the reaction between sodium and air, with copper lines for comparison above and below. The spectrum is continuous here also, terminating at λ3500. The time of exposure in this case was the same as in 1_b and 2_b.

Discussion of the results.

The first continuum in 1_b and 2_b (Plate XXII) was due mainly to the reaction of the alkali with the oxygen of the air: this fact is proved by the experiment carried in the air. In this part some lines are usually observed; for instance, D_1 and D_2 lines observed by Haber and Zisch (1922), and the arc and the enhanced lines of potassium as observed by Ramdas (1927); but they are not distinguishable in the plate given herewith, because the slit was very wide and the exposure long. The appearance of the second continuum, as described above, can be understood on the hypothesis of the radiative combination by two-body collisions. It would be clear from the discussion of the mechanism of the simple chemical combinations that the mechanism suggested by Polanyi and his co-workers does not predict the emission of continuous radiation in course of the chemical reaction; they predict the emission of certain spectral lines, characteristic of the combining atoms, whereas the recombination by two-body collisions should give rise to continuous spectrum of essentially the same nature as the continuous absorption spectrum of those very molecules, i.e. a certain long wavelength beginning, extending towards the shorter wavelength; a region of the strongest intensity, with fading off of intensity on both the sides. The figs. 1_b and 2_b (Plate XXII) and the table I show that the spectra that we have photographed,

Table I.

Experimental results.

Elements.	The short wavelength limits of the first continuum.	The long wavelength limit of the second continuum.	The short wavelength limit of the second continuum.	The most intense part of the second continuum estimated visually.	The long wavelength limit in absorption.
Na+Cl ..	λ3600	λ3036	λ2300	λ2766	λ2925 (Thermochemical data.)
K+Cl ..	λ3600	λ2961	λ2300	λ2740	λ2800 (Direct absorption spectra data).[1]
Na+Br	The results obtained are not conclusive.				λ3100 (Direct absorption spectra data).[1]
K+Br					λ3100 (Direct absorption spectra data).[1]
Na+I					λ3900 (Direct absorption spectra data).[1]
K+I					λ3800 (Direct absorption spectra data).[1]

[1] Franck, Kuhn and Rollefson (1927).

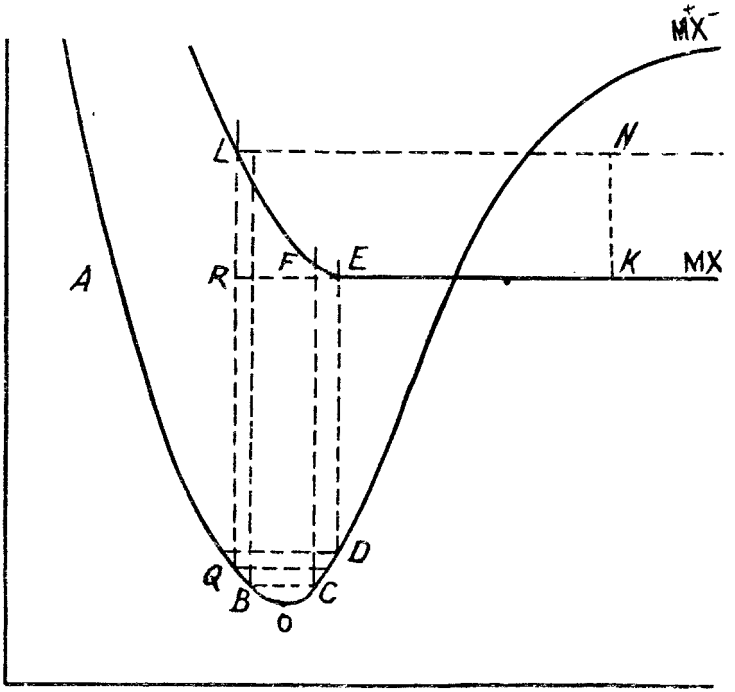
have the characteristics of radiations emitted by the recombination by two-body collisions. The fact that the formation of NaCl and KCl by three-body collision is a more frequent process is proved by the great intensity of the atomic lines. The long exposure necessary to photograph the recombination continuum proves that the radiative combination by two-body collision is a rarer process—a fact already pointed out on theoretical considerations. The appearance of the second continuum proves that Kondratjew's conclusions are not correct. A certain fraction of NaCl and KCl molecules are certainly formed by 'a direct recombination of the alkali and of the halogen atoms in a salt molecule, followed by a continuous light emission'.

It may be mentioned here that this is the first instance when the recombination spectra in the case of the formation of the polar molecules have been observed: so far such spectra had been observed only in the case of non-polar molecules.

It will be noticed from table I that the recombination continua, in both the cases, start from longer wavelengths than those in the case of absorption. This fact is under-

standable from the considerations of the potential energy curves of the alkali-halides and the Franck-Condon Principle.

Schmidt Ott (1931), Sommermeyer (1929) and Hamada (1934), who have thoroughly studied the absorption and the emission spectra of the alkali-halide vapours, give the potential energy curves of these molecules of the type given in text-fig. 6. The potential energy curve for the M-X state as given by Schmidt Ott and Hamada has a depth of less than ·1 volt, whereas text-fig. 6, given here, does not show that. It can be seen from



TEXT-FIG. 6.

the discussion of the emission of the recombination spectra in the case of the non-polar molecules, given above, that this does not alter our arguments here, because we are concerned only with the part of the potential energy curve lying above the point of intersection of the curve with its asymptote *KE*. These authors have shown that in the case of the repulsive atom-atom potential energy curve, the repulsive force starts operating at a distance somewhat larger than r_e represented by *O*, the equilibrium distance of the ground state, i.e. the curve *KEFL* starts rising at some point *E*, where the interatomic distance is somewhat larger than in the ground state. The long wavelength limit of the absorption spectra corresponds to *CF*, i.e. the transition from $v'' = 0$ state of the ground state to the point in the upper repulsive state vertically above it. But in the recombination spectra the long wavelength limit should correspond to *ED*, i.e. the transition from the point *E* in the atom-atom potential energy curve, where the repulsive force becomes operative, to the end-point *D* of a vibration state of the ground state, lying vertically below. Evidently *ED* should be smaller than *CF*; and therefore the recombination spectra in such cases should start from a considerably longer wavelength.

ESTIMATION OF THE TEMPERATURE OF THE REACTION ZONE.

The atoms M and X collide with all possible velocities ranging from 0 to ∞, but there is a most probable velocity depending on the temperature. The kinetic energy

of the molecules moving with the most probable velocity is represented by the height NK. Such atoms proceed towards each other in such a manner that the total energy is represented by the height of the straight line NL above the curve $KEFL$, L being the point where the straight line cuts the potential energy curve. At L all energy becomes potential, this point being the classical turning point. From here the transition will take place to Q, the end-point, vertically below, of the vibration state of the ground state. As the largest number of molecules will undergo transition here, QL will represent the wave-number of the most probable part of the spectrum. RL the wave-number difference between the long wavelength limit of the continuum and of the most intense part of it, is a measure of the most probable kinetic energy. The most probable velocity $v = \sqrt{\frac{2kT}{m}}$ and $\frac{1}{2}mv^2 = hc\nu$, where ν is the wave-number difference RL, T the temperature, and h, c, k are the Planck's constant, the velocity of light, and Boltzmann constant respectively; m is the mass of the particles. Therefore $T = \frac{hc\nu}{k}$. The long wavelength beginning and the wavelength of the most intense part of the spectra in the case of Na and Cl, and K and Cl have been given above. The wave-number differences are 3243 cm.$^{-1}$ and 2700 cm.$^{-1}$ respectively. The value of the temperatures calculated comes out to be 4666°A. and 3881°A. respectively. Ramdas, who observed the enhanced lines of potassium in the spectra of the light emitted by potassium burning in chlorine, has calculated, by Richardson's (1922) method, the temperature of the reaction zone. The temperature he has calculated varies from 7000°A. to 18700°A. for different reaction processes.

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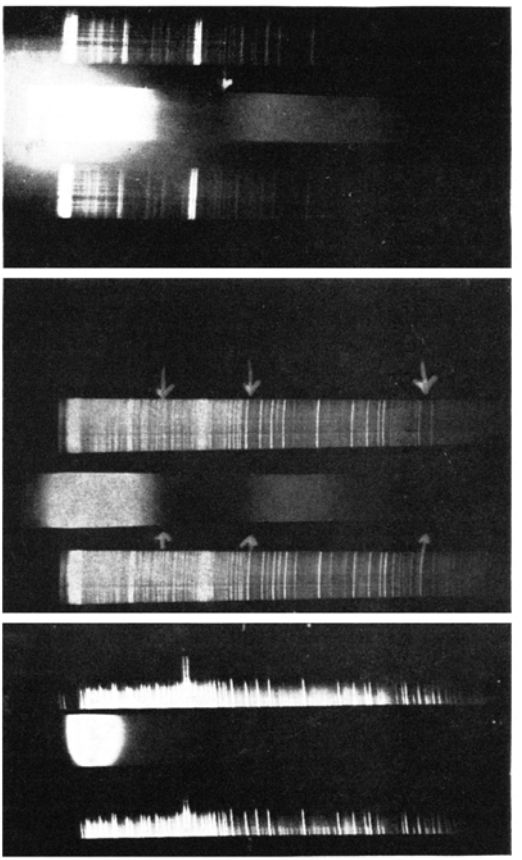

1*a* Copper arc lines.

1*b* Sodium burning in chlorine.

1*c* Copper arc lines.

2*a* Copper arc lines.

2*b* Potassium burning in chlorine.

2*c* Copper arc lines.

3*a* Copper arc lines.

3*b* Sodium burning in air.

3*c* Copper arc lines.