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Condensation in interstellar space, by *H. A. Kramers* and *D. ter Haar* ¹⁾.

This paper deals with the various association and dissociation processes relevant for the formation and disappearance of diatomic molecules in interstellar space.

Section 1 discusses the concentration of CH and CH⁺ to be expected from what is known or may be assumed about the concentration of atoms and about the temperature and radiation conditions in interstellar space. If due attention is paid to the many uncertainties involved, the observations seem to fit in with the theoretical picture. Some objections are raised to SWINGS' treatment of the problem of the CH and CH⁺ concentrations.

Section 2 discusses some corrections to the theory of the smoke formation presented by one of us in a previous article.

The following sections deal with the theory of some elementary processes, in order to obtain the numerical estimates necessary for the first section. In section 3 the probability of the formation of some diatomic molecules by radiation capture is calculated. In section 4 the photodissociation of CH is discussed in detail, while in section 5 the electron capture by a CH⁺ molecule and the photoionization of CH are investigated.

§ 1. Concentration of diatomic molecules.

In a previous paper ²⁾ the formation of solid particles from the interstellar gas was discussed. It appeared that the rate at which diatomic carbon-hydrogen molecules are formed through radiation capture is of primary importance. Since then we have changed our opinion on some of the details regarding the first steps of the condensation process. As mentioned in *B.A.N.* 361 Prof. OORT had pointed out to us the eventual importance of the photodissociation on the concentration of the CH molecules. Although we thought at first that this process could be neglected, closer inspection has shown us that, on the contrary, photodissociation is probably the factor limiting the concentration of the CH molecules.

Another point to which Prof. OORT has equally drawn our attention concerns the large abundance of the C⁺ atoms relative to that of the C atoms. This means that the very first step in the condensation will be the formation of CH⁺ rather than of CH molecules; this too means, that the simple picture of the situation on which the calculations in *B.A.N.* 361 were based needs revision. For the sake of simplicity we will first discuss the influence of the photodissociation of CH, reasoning as if these molecules were directly formed from neutral C atoms; after this we will investigate the changes to which the inspection of the second point gives rise. It will be found that the CH concentration is hardly affected, while at the same time an estimation of the CH⁺ concentration is obtained.

The total number of CH molecules formed per sec can be calculated, if we know the probability that a

radiation capture takes place when a C atom and a H atom collide. This probability has been estimated in *B.A.N.* 361 and will be considered in more detail in section 3. We find that the total number of CH molecules formed per sec is equal to:

$$N_1 = Q_{\text{rad}} \rho_C \rho_H, \quad (1)$$

where, assuming a temperature of 10000°, $Q_{\text{rad}} = 7 \cdot 10^{-18} \text{ cm}^3 \text{ sec}^{-1}$; taking $\rho_C = 3 \cdot 10^{-3} \text{ cm}^{-3}$ and $\rho_H = 3 \text{ cm}^{-3}$, we get:

$$N_1 = 6 \cdot 10^{-20} \text{ cm}^{-3} \text{ sec}^{-1}. \quad (2)$$

The number of CH molecules photodissociating per sec, N_2 , can be estimated with fair accuracy, if we know the energy needed for this process and the density of the interstellar radiation for the corresponding frequency. From considerations given in detail in section 4 we find that the energy will be approximately 10 eV. If we adopt with EDDINGTON¹⁾ a diluted PLANCK radiation for the interstellar radiation with a dilution factor $g = 10^{-14}$ and $T = 10000^\circ$, we get for N_2 :

$$N_2 = \rho(\nu) B \rho_{\text{CH}} = g A e^{-\frac{h\nu}{kT}} \rho_{\text{CH}} = 1 \cdot 10^{-11} \rho_{\text{CH}} \text{ cm}^{-3} \text{ sec}^{-1} \quad (3)$$

(A and B are the Einstein probabilities for the transition considered and $\rho(\nu)$ is the density of the interstellar radiation at the frequency ν).

Equating N_1 and N_2 we get:

$$\rho_{\text{CH}} = 6 \cdot 10^{-9} \text{ cm}^{-3}, \quad (4)$$

which is a factor 300 less than the observed value of approximately $2 \cdot 10^{-6} \text{ cm}^{-3}$ ²⁾. At the end of this

¹⁾ Received in October 1944.

²⁾ D. TER HAAR, *B.A.N.* No. 361; 10, 1, 1943; further referred to as *B.A.N.* 361. This paper appeared also in the *Astrophysical Journal*: *Ap. J.* 100, 288, 1944.

¹⁾ A. S. EDDINGTON, *Proc. Roy. Soc. London A* 111, 424, 1926.

²⁾ TH. DUNHAM JR., *P.A.A.S.* 10, 123, 1941.

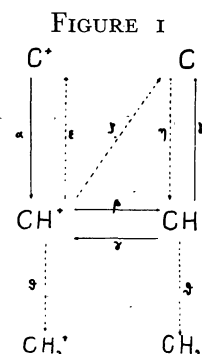
section we shall see that this discrepancy need not alarm us particularly.

Starting from a state of the interstellar gas in which as yet no molecules are present, the stationary CH concentration calculated above will have been reached after a time of the order of 10^{11} sec (cf. (3)), which is small indeed compared to the period of about 10^9 years which the condensation process has had at its disposal.

In our calculations we have neglected the disappearance of CH molecules due to the formation of triatomic molecules. In the picture of *B.A.N.* 361 this process was considered to be the only factor limiting the increase of the CH concentration and bringing about equilibrium. We think now that, compared to the photodissociation, this factor is certainly negligible, although – of course – its magnitude plays an important part for the further steps of the condensation process and for the smoke density finally reached. We will return to this later on.

We will now take into account that, due to stellar radiation, the $C^+ - C$ equilibrium in the interstellar

gas is such that practically all C atoms are ionized. Formation of CH^+ from C^+ and H will be the first stage of the molecule formation and we shall have to consider the equilibrium between C^+ , CH^+ , CH and C. Figure 1 indicates the different elementary processes to be considered. By means of rather rough



methods we have (cf. the following sections) calculated the frequencies of their occurrence, assuming $T = 10000^\circ$ and a dilution factor $g = 10^{-14}$. The results are given in the following table:

TABLE I

Process	Description	Frequency
$\alpha : C^+ + H \rightarrow CH^+ + h\nu$	(radiation capture)	$N_\alpha = 10^{-17} \cdot \rho_{C^+} \cdot \rho_H$
$\beta : CH^+ + el \rightarrow CH + h\nu$	(electron capture)	$N_\beta = 3 \cdot 10^{-13} \cdot \rho_{el} \cdot \rho_{CH^+}$
$\gamma : CH + h\nu \rightarrow CH^+ + el$	(photoionization)	$N_\gamma = 2 \cdot 10^{-11} \cdot \rho_{CH}$
$\delta : CH + h\nu \rightarrow C + H$	(photodissociation)	$N_\delta = 10^{-11} \cdot \rho_{CH}$
$\epsilon : CH^+ + h\nu \rightarrow C^+ + H$	(photodissociation)	$N_\epsilon \sim 10^{-15} \cdot \rho_{CH^+}$
$\zeta : CH^+ + el \rightarrow C + H$	(electron capture leading to dissociation)	$N_\zeta \sim 3 \cdot 10^{-14} \cdot \rho_{el} \cdot \rho_{CH^+}$
$\eta : C + H \rightarrow CH + h\nu$	(radiation capture)	$N_\eta = 7 \cdot 10^{-18} \cdot \rho_C \cdot \rho_H$
$\zeta' : CH^{(+)} + H \rightarrow CH_2^{(+)}$	("mechanical" capture)	$N_{\zeta'} \leq 7 \cdot 10^{-17} \cdot \rho_{CH^{(+)}} \cdot \rho_H$

Since 10^{-2} cm^{-3} is a lower limit which can be assigned to ρ_{el} , we see that N_ϵ and N_ζ are negligible compared to N_β . Since ρ_C/ρ_{C^+} will hardly surpass 0.01 the processes η can be neglected against the processes α . Finally ζ' can, since ρ_H is of the order of 1 cm^{-3} , be neglected versus δ . We are thus left with the processes α , β , γ and δ , indicated by full drawn arrows in Figure 1.

The stationary state (which is easily reached in the time available) is found from:

$$N_\alpha + N_\gamma = N_\beta = N_\delta$$

Thus:

$$\rho_{CH} = 10^{-6} \rho_{C^+} \cdot \rho_H, \quad (5a)$$

$$\rho_{CH}/\rho_{CH^+} = 10^{-2} \cdot \rho_{el}. \quad (5b)$$

With $\rho_H = 3 \text{ cm}^{-3}$, $\rho_{C^+} = 3 \cdot 10^{-3} \text{ cm}^{-3}$ and

$\rho_{el} = 10^{-2} \text{ cm}^{-3}$ 1) this gives:

$$\left. \begin{aligned} \rho_{CH} &= 10^{-8} \text{ cm}^{-3} \text{ (observed: } \sim 2 \cdot 10^{-6} \text{ cm}^{-3}) \\ \rho_{CH}/\rho_{CH^+} &= 10^{-4} \text{ (observed: } \sim 1) \end{aligned} \right\} (6)$$

The discrepancy between these calculated and observed values is not alarming. In the first place it must be borne in mind that our calculations are rather rough and that the numerical factors appearing in N_α , N_β , N_γ and N_δ can easily be wrong by a factor of the order 2 to 10. These uncertainties will affect mainly the factor 10^{-6} in eq. (5a), which indeed might be larger or smaller by a factor of the order 10. The factor 10^{-2} in eq. (5b) is less affected by them; its uncertainty may be a factor of the order 2. In the

1) P. SWINGS, *Ap. J.* **95**, 270, 1942.

second place the astrophysical data are not so very strict. They refer on the one hand to atomic concentrations (ρ_{C^+} , ρ_H and ρ_{el}) in the interstellar gas, on the other hand to the density of the radiation, which enters in the numerical factors of the expressions for N_γ , N_δ and N_ϵ in Table 1.

If, for instance, we had used values of ρ_H and ρ_{C^+} both 5 to 10 times as large, our calculated ρ_{CH} value would rise to a value between $2.5 \cdot 10^{-7} \text{ cm}^{-3}$ and 10^{-6} cm^{-3} . If one should consider such a rise in the value of ρ_H unacceptable, it must in any case be remembered that the ratio ρ_{C^+}/ρ_H is very uncertain and might easily be much larger than the value of 10^{-3} assumed above. As regards ρ_{el} , everything depends on the degree of ionization of the hydrogen atoms, which might also be a good deal larger than was assumed in the foregoing. This might perhaps raise the ratio ρ_{CH}/ρ_{CH^+} by a factor 100 to 1000.

For g and T we have adopted 10^{-14} and 10000° as was assumed originally by EDDINGTON¹⁾. There is a good deal of uncertainty about these values. STRUVE²⁾ assumes $g = 10^{-16}$ and $T = 15000^\circ$, while according to DUNHAM³⁾ the density of the interstellar radiation cannot for all frequencies be described by a definite g and T . If in estimating the radiation density the selective absorption (which has been neglected by EDDINGTON) is taken into account, it follows from the figures given by DUNHAM³⁾ that this density will be smaller by a factor ~ 5 in the region significant for processes γ and δ . This means that both numerical factors in eqq. (5) would be larger by a factor 5.

Further we do not know with certainty the energies of photodissociation and ionization of CH. If we should adopt for these energies values which are larger by 1 to 2 eV, the numerical factors in eqq. (5) would be larger by a factor 3 to 10.

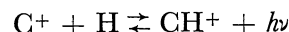
Finally it should be borne in mind that the observed values of ρ_{CH} and ρ_{CH}/ρ_{CH^+} are affected by experimental uncertainties and depend moreover on estimated values for the corresponding oscillator strengths.

Altogether—due attention being given to the margin allowed by theoretical and observational uncertainties—it seems safe to conclude that the observed presence of CH and CH⁺ may well fit in with our theoretical picture of the condensation processes in the interstellar gas.

Something should be added about the theoretical estimates of ρ_{CH^+} and of the ratio ρ_{CH}/ρ_{CH^+} given by SWINGS⁴⁾. Both were obtained by considering a quasi-thermodynamical equilibrium, but we think that

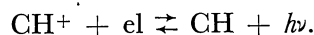
serious objections should be raised against this procedure.

The CH⁺ concentration is found by considering the equilibrium



in the diluted radiation field. Just as with us the radiation capture of a H atom (process α) is considered to take place through an electronic transition from an excited state of the CH⁺ molecule to a high vibrational level belonging to the ground state. In the equilibrium practically all molecules will occupy a few of the lowest rotational levels of the lowest vibrational state, corresponding to a temperature of only a few degrees Kelvin. The absorption processes which result in a photodissociation of CH⁺ will therefore not be the inverse of the capturing process but will have to start from the ground state and to raise the molecule in one big absorption jump (process ϵ) to an excited state in which the atoms repel each other. The $h\nu$ involved in ϵ is therefore several times larger than that involved in α and there is no foundation for the application of SWINGS' method. We think that the actual value of ρ_{CH^+} cannot be found without also taking the processes β , γ and δ into account.

Again, SWINGS finds the CH—CH⁺ ratio by considering the quasi-SAHA-equilibrium



This means that he puts $N_\beta = N_\gamma$, whereas in our picture only $N_\beta = N_\gamma + N_\delta$ would be correct. Since according to our calculations N_γ and N_δ are of the same order of magnitude, and since moreover the β and γ processes are practically the inverse of each other (in contrast to the case of α and ϵ), the ratio calculated by SWINGS should be approximately the same as that found by us. Incidentally, SWINGS discusses the possibility that the β and γ processes are not the inverse of each other; he argues that besides capturing processes leading to the lowest electronic state of CH, other captures to excited states will be possible which have no counterpart in the ionization process γ , since in the equilibrium all CH molecules are in the ground state. This will then raise the ratio ρ_{CH}/ρ_{CH^+} by a factor to which he tentatively even assigns a value as high as 100 in his attempt to bridge the gap between theory and observation. A closer consideration of the electronic structure of the CH⁺ ground state shows, however, that such a correction factor is out of the question; the ground state of CH is (if we ignore highly excited states whose contribution to the capturing will be negligible) the only attractive state of this molecule that can be attained by adding an electron to the ground state of CH⁺ (compare Table 3 in section 4).

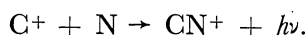
1) L.c.

2) O. STRUVE, *Proc. Nat. Acad. Sci.* **25**, 36, 1939.

3) TH. DUNHAM JR., *Proc. Am. Phil. Soc.* **81**, 277, 1939.

4) L.c.

In *B.A.N.* 361 it was asserted that the formation of CN by radiation capture was insufficient to explain the observed CN concentration. This statement needs revision. Since in the interstellar gas the nitrogen atoms are practically all neutral and the carbon atoms practically all ionized, the first step would be the process



No data on the CN⁺ molecule are at hand. The ground state of N is ⁴S and of C⁺ ²P. Combination of these two will give ³Σ, ³Π, ⁵Σ, ⁵Π. It is not unreasonable to assume that one of the triplet states (probably the ³Π state) will be the ground state of the CN⁺ whereas the other triplet state (³Σ) is an excited attractive state so that a transition between these two, involving a jump of an electron from a σ to a π state, might account for radiation capture similar to the cases discussed in section 3.

Assuming that in the expression $K \cdot \rho_{\text{C}^+} \cdot \rho_{\text{N}}$ for the number of captures per sec the same value may be taken for K as in the case of CH⁺, i.e. $K = 10^{-17}$, we get for the total number of CN⁺ molecules formed in 10⁹ years, assuming $\rho_{\text{C}^+} = 3 \cdot 10^{-3} \text{ cm}^{-3}$, $\rho_{\text{N}} = 2 \rho_{\text{C}^+} = 6 \cdot 10^{-3} \text{ cm}^{-3}$ 1):

$$\rho_{\text{CN}^+} = 5 \cdot 10^{-6} \text{ cm}^{-3}. \quad (7)$$

Since a large fraction of the CN⁺ molecules may have passed into the neutral CN state and since photodissociation of the latter may be very small, the presence of CN may well be due to radiation capture.

In *B.A.N.* 361 a value for γ_2 , i.e. the probability that a triatomic molecule is formed when a diatomic molecule collides with an atom was estimated from the observed concentration of the CH molecules. Due to the photodissociation this is no longer possible. We think moreover that the value of γ_2 estimated in *B.A.N.* 361 ($\gamma_2 \sim 1000 \gamma_1$) is by far too large. In fact, a preliminary investigation of the mechanism by which a CH molecule can capture a third atom has shown us that the actual value of γ_2 will certainly be much smaller and that according to the most favourable estimate it will hardly exceed the value of γ_1 (which is $\sim 10^{-9}$) more than by a factor of the order 10. In this way we arrived at the estimation of N_3 in Table 1, whose numerical factor is given as less than 10 times the factor in N_2 .

§ 2. Some remarks on the density of interstellar smoke.

Strong arguments were given in *B.A.N.* 361 for the view that the first step in the condensation process can only be the formation of CH and CH⁺ molecules.

1) For the ratio $\rho_{\text{C}^+}/\rho_{\text{N}}$ see e.g.: V. GOLDSCHMIDT, *Skr. Norske Vid. Selsk., Mat. Nat. Kl. No. 4*, 1937; A. UNSÖLD, *Zs. f. Ap. 21*, 76, 1942; H. C. v. D. HULST, *Ned. Tijds. v. Natk. 10*, 245, 1943.

These arguments still hold but it is clear that, with our present view of the mechanism by which the concentrations of these molecules are established, the discussion of the subsequent steps in the condensation process and of the ensuing total smoke density must be taken up anew. First of all we remark that the expression (*B.A.N.* 361, p. 7, formula (26)):

$$i_{\text{max}} = (3 \sigma \rho' v' t)^3 \quad (8)$$

for the number of atoms in the largest smoke particles built up in the time t , can only be brought in agreement with observation ($i_{\text{max}} \sim 10^9$) if the density ρ' of the heavy atoms is of the order 10^{-4} cm^{-3} . Now we have seen that it is difficult to explain the observed CH concentration even by assuming ρ_{C^+} to be as large as $3 \cdot 10^{-3} \text{ cm}^{-3}$; we should wish it to be still larger by a factor of the order 10. In this way i_{max} becomes, however, by far too large. If the hydrogen content in the particles should not be negligible (it was assumed to be so in the derivation of (8)), the discrepancy would be still worse. If therefore one adheres to the idea, that the growth of the smoke particles through condensation of atoms can go on freely, we meet with a serious difficulty. Prof. OORT¹⁾ also thinks that the upper limit of the size of the particles is kept down by processes of a kind hitherto not taken into account.

For the moment we will therefore simply take 10^9 as an approximate upper limit for i and we will investigate the smoke density reached in the period of 10⁹ years, starting from a given, equilibrium, concentration of the CH molecules ($2 \cdot 10^{-6} \text{ cm}^{-3}$). The formula on p. 8 of *B.A.N.* 361 must be changed and we now get:

$$\rho_{\text{sm}} = \frac{3}{4} m \rho_{\text{CH}} \gamma_2 2^{2/3} i_{\text{max}}^{4/3} \left(\frac{\gamma_3 3^{2/3} \tau}{1} \right) \left(\frac{\gamma_4 4^{2/3} \tau}{2} \right) \left(\frac{\gamma_5 5^{2/3} \tau}{3} \right), \quad (9)$$

where $\tau = \sigma \rho' v' t \geq 7 \cdot 10^4$ ($\sigma = 2 \cdot 10^{-15} \text{ cm}^2$, $\rho' \geq 3 \cdot 10^{-3} \text{ cm}^{-3}$, $v' = 4 \cdot 10^5 \text{ cm sec}^{-1}$, $t = 3 \cdot 10^{16} \text{ sec}$) and where only those γ_i 's, for which $\gamma_i \tau \ll 1$ give rise to a factor in (9). If we assume, for a moment, that γ_3, γ_4 , etc. are all large compared to τ^{-1} , we get, using $m = 2 \cdot 10^{-23} \text{ g}$, $\gamma_2 = 10^{-8}$, $\rho_{\text{CH}} = 2 \cdot 10^{-6} \text{ cm}^{-3}$, $i_{\text{max}} = 10^9$:

$$\rho_{\text{sm}} = 4 \cdot 10^{-25} \text{ g cm}^{-3} \text{ (observed } \sim 10^{-26} \text{ g cm}^{-3}). \quad (10)$$

This value for the smoke density is too large by a factor 40; it would become still larger by a factor of the order 100 if i_{max} were taken $\sim 10^{11}$. Now, this excess could easily be compensated by the influence of a few factors of the type $\frac{\gamma_i i^{2/3} \tau}{i-2}$.

The value given above for τ in the condition $\gamma_i \tau \ll 1$ for their appearance must be considered as a lower limit. Indeed, the concentration ρ' of the heavy atoms might well be a factor 5 to 10 larger than assumed

1) Private communication.

above (compare p. 139), and $t = 10^{17}$ sec ($= 3 \cdot 10^9$ yrs) is perhaps a more reasonable estimate for t , so that τ might easily be as large as $2 \cdot 10^6$. This higher value is rather welcome, since our preliminary consideration has shown us, that not only γ_2 is still a small quantity ($\sim 10^{-8}$ at most), but that also the probability that a molecule with only a few atoms captures the heavy atoms in the gas will still be rather small (say γ_3, γ_4 and γ_5 perhaps not larger than the order 10^{-7} or 10^{-6}) and that the number of atoms should be rather large, say 10 or more, before the limit $\gamma_i = 1$ is reached.

It is very well possible that in the very first steps of the condensation the capture of the hydrogen atoms still prevails. In the derivation of formula (9) no account was taken of this, but it can be shown that, due to the large hydrogen concentration, this formula still holds, if these H captures are disregarded and if $\gamma_3, \gamma_4, \dots$ simply mean the probabilities of the captures of heavy atoms (C, N or O) which appear for the first time, for the second time, etc. in the subsequent condensation steps.

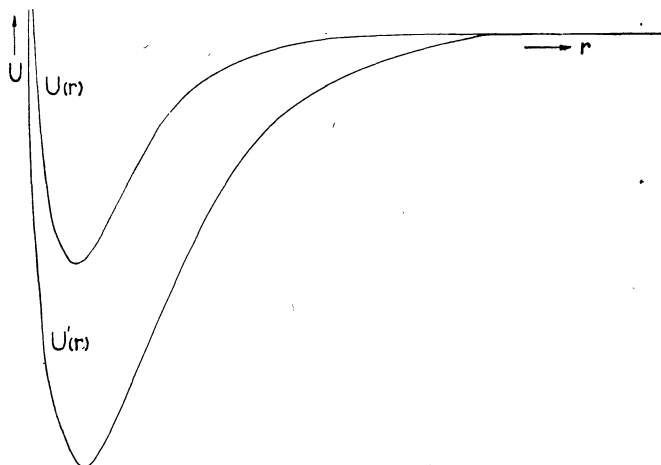
Until now we have spoken as if all condensation started from CH (process \mathcal{S}), whereas it will of course start as well from CH^+ (process \mathcal{S}'). This brings, however, no material change in the discussion and the conclusions of this section.

A more refined discussion of the initial stages of the condensation is of course highly desirable, but there is as yet no need to fear a serious discrepancy between the theoretical picture and the observational data.

§ 3. Theory of radiation capture.

In *B.A.N.* 361 an estimation was given of the probability, γ_1 , that a diatomic molecule is formed by radiation capture when two atoms collide. The case when this formation occurs without an electronic transition was considered in some detail. For the case when an electronic transition accompanies the formation we

FIGURE 2



gave formula (12) of *B.A.N.* 361, which will now be derived.

The quantity calculated is not γ_1 itself but an effective cross section, Q_{rad}/\bar{v} , for the formation of a molecule by radiation capture. The following relation between γ_1 and Q_{rad} should then exist:

$$Q_{\text{rad}} = \gamma_1 \sigma \bar{v}, \quad (11)$$

where σ is a measure adopted for the cross section for a gas-kinetic collision while \bar{v} is the mean relative velocity of the two atoms.

We shall assume that, when the two atoms approach each other, each in its ground state, not only the lowest molecular electronic state available can be realized but also other electronic states. In Figure 2 the curves for two of those states are shown. $U'(r)$ is the energy of the ground state as a function of the distance apart of the nuclei of the two atoms. $U(r)$ is the energy of a second electronic state. For the sake of simplicity we have taken for $U(r)$ also a curve with a minimum though this is not essential for the following calculations.

We will, now, assume that when the two atoms approach each other they are in the upper electronic state under consideration (viz. $U(r)$). A transition may therefore occur between the two states $U(r)$ and $U'(r)$ accompanied by the emission of a light quantum with energy $U - U'$ so that the two atoms make a transition to another type of central motion and be bound together in the ground state of the molecule. In the discussion of this transition we treat the motion of the nuclei in a purely classical way.

If $A(r)$ is the EINSTEIN probability for the transition between the two electronic states $U(r)$ and $U'(r)$ then the total probability that a radiation capture occurs when the two atoms meet will be given by:

$$q = f \int_{-\infty}^{+\infty} A(r) dt, \quad (12)$$

where the integral is taken along the classical orbit which the system would describe under the influence of $U(r)$.

Here the numerical factor f is the probability that when the two atoms meet they will find themselves in the upper electronic state ($U(r)$).

In order to get Q_{rad} we have to average qv over all possible values of the impact parameter p (i.e. the minimum distance between the two atoms when their path should be along straight lines) and over the distribution of the relative velocities:

$$Q_{\text{rad}} = \bar{q}\bar{v} = \int 2\pi p dp \int qv W(v) d\vec{v} \quad (13)$$

Here $W(v) d\vec{v}$ is the probability that the components of the relative velocity have values between v_x, v_y, v_z and $v_x + dv_x, v_y + dv_y, v_z + dv_z$.

Inserting (12) in (13) we get:

$$Q_{\text{rad}} = f \int 2\pi p dp \int v W(v) d\vec{v} \int_{-\infty}^{+\infty} A(r) dt. \quad (14)$$

From the laws of motion we have

$$dt = \frac{dr}{\sqrt{v^2 - \frac{p^2 v^2}{r^2} - \frac{2U(r)}{m}}}. \quad (15)$$

$$Q_{\text{rad}} = 4\pi f \int \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^3 dv \int A(r) dr \int \frac{2\pi p dp}{\sqrt{v^2 - \frac{2U(r)}{m} - \frac{p^2 v^2}{r^2}}}. \quad (17)$$

The values of the boundaries must be treated with some care. For a given value of v and p , r runs twice through the interval from r_{min} to ∞ , where r_{min} is the r -value for which the expression under the square root vanishes. Instead of a restriction on r and a free

For $W(v)$ we will take a Maxwellian distribution:

$$W(v) d\vec{v} = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} dv, \quad (16)$$

where m is the reduced mass and $\int W(v) d\vec{v} = 1$.

Substituting (15) and (16) in (14) we get:

distribution of p and v we can first integrate p over the interval from 0 to $p_{\text{max}} = r \sqrt{1 - \frac{2U(r)}{mv^2}}$.

This gives:

$$Q_{\text{rad}} = 8\pi^2 f \left(\frac{m}{2\pi kT}\right)^{3/2} 2 \int_0^{\infty} A(r) r^2 dr \int_{v_1}^{v_2} v e^{-\frac{mv^2}{2kT}} \sqrt{v^2 - \frac{2U(r)}{m}} dv \quad (18)$$

We have now to consider the boundaries v_1 and v_2 .

For v_1 we must take 0 when $U(r) \leq 0$ and $\sqrt{\frac{2U(r)}{m}}$ when $U(r) > 0$. Since we only have to consider those transitions for which the atoms are bound to each other in the final state $U'(r)$ we are interested only in those values of v where $U - U' > \frac{1}{2}mv^2$. This means that we must take for v_2 : $\sqrt{\frac{2}{m}(U - U')}$, provided this value is larger than v_1 ; if it should be smaller the integral should vanish. Making the substitution: $x = \sqrt{\frac{m}{2kT}} \sqrt{v^2 - \frac{2U(r)}{m}}$, we get:

$$Q_{\text{rad}} = 16\sqrt{\pi} f \int_0^{\infty} A(r) r^2 e^{-\frac{U(r)}{kT}} dr \int_{x_1}^{x_2} e^{-x^2} x^2 dx, \quad (19)$$

where $x_1 = \sqrt{-\frac{U(r)}{kT}}$ or 0 according as $U(r) < 0$ or $U(r) > 0$ and $x_2 = \sqrt{-\frac{U'(r)}{kT}}$ or $\sqrt{-\frac{U(r)}{kT}}$

or 0 according as $U'(r) < U(r) < 0$ or $U(r) \leq U'(r) < 0$ or $U'(r) > 0$. In our applications $U'(r)$ is always smaller than $U(r)$ so that the possibility $U'(r) > U(r)$ will be omitted in the following. If we put:

$$I = \int_0^{\infty} [U(r) - U'(r)]^3 [F(\sqrt{-U'(r)/kT}) - F(\sqrt{-U(r)/kT})] e^{-\frac{U(r)}{kT}} r^2 dr. \quad (25)$$

$$F(x) = \frac{4}{\sqrt{\pi}} \int_0^x e^{-x^2} x^2 dx, \quad (x \text{ real}; F(\infty) = 1)$$

$$F(x) = 0, \quad (x \text{ imaginary}) \quad (20)$$

we get:

$$Q_{\text{rad}} = 4\pi f \int_0^{\infty} A(r) r^2 e^{-\frac{U(r)}{kT}} \times [F(\sqrt{-U'(r)/kT}) - F(\sqrt{-U(r)/kT})] dr, \quad (21)$$

which is the same as formula (12) of *B.A.N.* 361.

If P is the matrix element of the polarization and ν the frequency belonging to the transition in question, we have for $A(r)^1$:

$$A(r) = \frac{32\pi^3}{3\hbar c^3} \nu^3(r) |P(r)|^2. \quad (22)$$

If we put $P(r) = e a_B \theta(r)$, where a_B is the Bohr radius and e the elementary charge, the quantity θ will be of the order of magnitude 1. Since $h\nu(r) = U(r) - U'(r)$, we get:

$$A(r) = \frac{32\pi^3}{3\hbar c^3} \frac{(U - U')^3}{h^3} e^2 \theta^2 a_B^2 = \frac{1}{4} \cdot 10^{42} \theta^2 (U - U')^3 \quad (23)$$

Substitution of (23) in (21) gives:

$$Q_{\text{rad}} = 3 \cdot 10^{42} f \bar{\theta}^2 \cdot I, \quad (24)$$

where $\bar{\theta}^2$ is an average of $\theta^2(r)$ and I is given by:

1) See for instance: H. A. KRAMERS, *Hand- u. Jahrb. d. Chem. Phys.* I, Leipzig 1938, 418.

For $F(x)$ the following formula holds:

$$F(x) = -\frac{2}{\sqrt{\pi}} x e^{-x^2} + \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy = -\frac{2}{\sqrt{\pi}} x e^{-x^2} + \Phi(x), \quad (26)$$

where $\Phi(x)$ is the error integral ¹⁾.

Using JAHNKE-EMDE for the values of the error integral and MULLIKEN ²⁾ for the approximate shape of the $U(r)$ and $U'(r)$ curves we can compute I graphically and we get Table 2. We have taken T to be 10000°; we also have inserted the notations of the electronic states to which the $U(r)$ and $U'(r)$ curves belong; for the significance of the symbols σ , π , etc. we refer to MULLIKEN (l.c.). For $\bar{\theta}^2$ we have adopted the value 0.1 (It is very difficult to infer its values from theory or experimental data, but it seems rather safe to assume that they lie between 0.05 and 0.5.).

TABLE 2

	f	$I \cdot 10^{59}$ ($g^3 cm^3 sec^{-6}$)	$U(r)$	$U'(r)$	$Q_{rad} \cdot 10^{18}$ ($cm^3 sec^{-1}$)
CH	$\frac{1}{9}$	18	$\sigma \pi^2, ^2\Sigma^-$	$\sigma^2 \pi, ^2\Pi$	6
BH	$\frac{1}{6}$	20	$\sigma \pi, ^1\Pi$	$\sigma^2, ^1\Sigma^+$	10
CN	$\frac{1}{9}$	3	$\sigma^2 \pi^3 \sigma^2, ^2\Pi$	$\sigma^2 \pi^4 \sigma, ^2\Sigma^+$	1
N_2^+	$\frac{1}{36}$	20	$\sigma \pi^4 \sigma^2, ^2\Sigma_u^+$	$\sigma^2 \pi^4 \sigma, ^2\Sigma_g^+$	2
CO^+	$\frac{2}{27}$	18	$\sigma^2 \pi^3 \sigma^2, ^2\Pi$	$\sigma^2 \pi^4 \sigma, ^2\Sigma^+$	4

For all the molecules mentioned radiation capture is also possible by electron jumps between states of higher multiplicity. Their contribution, however, turns out to be negligible.

In B.A.N. 361 we had adopted the value $Q_{rad} = 4 \cdot 10^{-19}$ in the case of CH. The difference of a factor 17 with the value calculated here is partly due to a different value for $\bar{\theta}^2$ adopted now and partly to the rather rough way in which the integral in (23) had been evaluated.

The total number of CH molecules formed per sec by means of the process of radiation capture will be given by $Q_{rad} \rho_C \rho_H$. For $(Q_{rad})_{CH^+}$ we have taken in our calculations in the first section $(Q_{rad})_{BH}$.

§ 4. Photodissociation of CH and CH⁺.

In this section we will investigate the probability of photodissociation of CH (process δ). We have therefore to inspect closely the data of MULLIKEN ¹⁾. He gives for CH the states collected in Table 3.

The CH molecules will practically all be in the lowest electronic state available, viz. the $\sigma^2 \pi, ^2\Pi$ state and they will also be in their lowest vibrational and rotational states. From the figures of MULLIKEN it follows that for photodissociation, transitions to other attractive states are excluded since predissociation is nowhere possible. We must also exclude the trans-

TABLE 3 ²⁾

State of CH molecule ³⁾	Corresponding state of the united atom (N) ⁴⁾	Corresponding state of the C atom ⁵⁾	Nature of the molecular state			
$(2p\sigma)^2(2p\pi),$	$^2\Pi$	$(2p)^3,$	2D	$(2p)^2,$	3P	attractive
$(2p\sigma)(2p\pi)^2,$	$4\Sigma^-$	$(2p)^3,$	$4S$	$(2p)^2,$	3P	attractive
$(2p\sigma)(2p\pi)^2,$	$2\Sigma^-$	$(2p)^3,$	2D	$(2p)^2,$	3P	attractive
$(2p\sigma)(2p\pi)(3s\sigma)$	4Π	$(2p)^2(3s),$	$4P$	$(2p)^2,$	3P	repulsive
$(2p\sigma)(2p\pi)^2,$	$^2\Delta$	$(2p)^3,$	2D	$(2p)^2,$	1D	attractive
$(2p\sigma)(2p\pi)^2,$	$2\Sigma^+$	$(2p)^3,$	2P	$(2p)^2,$	1D	attractive
$(2p\pi)^3,$	$^2\Pi$	$(2p)^3,$	2P	$(2p)^2,$	1D	repulsive
$(2p\sigma)^2(3s\sigma),$	$2\Sigma^+$	$(2p)^2(3s),$	2P	$(2p)^2,$	1S	repulsive

ition to the $\sigma\pi\sigma, ^4\Pi$ state because of the change of the multiplicity and the transition to the $\pi^3, ^2\Pi$ state which involves two electron jumps and will be rather improbable. The only transition practically remaining for the photodissociation is the $\sigma^2 \pi, ^2\Pi \rightarrow \sigma^2 \sigma, ^2\Sigma^+$ transition.

We will now estimate the $h\nu_1$ corresponding to this transition (cf. Figure 3). In the united atom it corresponds to the $p^3, ^2D \rightarrow p^2s, ^2P$ transition of the ni-

trogen atom, for which $h\nu = 8.3 \text{ eV}$ ⁶⁾. The ionization energy of the weakest bound σ electron in the $^2\Sigma^+$ state will, to begin with, certainly decrease with increasing distance apart of the nuclei (decrease of the

¹⁾ See for instance: JAHNKE-EMDE, *Tables of functions*, Leipzig-Berlin 1933, 97.

²⁾ R. S. MULLIKEN, *Rev. Mod. Phys.* 4, 1, 1932.

¹⁾ L.c.

²⁾ For the significance of the various symbols we again refer to MULLIKEN.

³⁾ We have left out the $(1s\sigma)^2(2s\sigma)^2$ electrons.

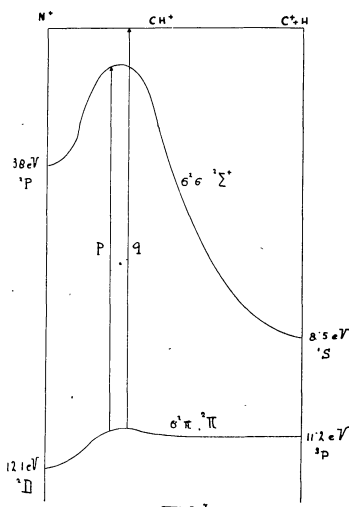
⁴⁾ Here we have left out the $(1s)^2(2s)^2$ electrons.

⁵⁾ The corresponding state of the H atom is always the $2S$ state; here also we have left out the $(1s)^2(2s)^2$ electrons.

⁶⁾ See e.g.: R. F. BACHER, S. GOUDSMIT, *Atomic Energy States*, New York-London 1932, 293.

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FIGURE 3



Probable behaviour, as a function of the atomic distance, of the ionization energy of the weakest bound electron in the CH molecule in the ground state ($\sigma^2\pi$, ${}^2\Pi$) and the $\sigma^2\sigma$, ${}^2\Sigma^+$ state.

p: jump corresponding to photodissociation.
q: jump corresponding to photoionization.

quantum defect of the 3s electron to about $\sqrt{\frac{6}{7}}$ of its original value). This decrease might amount to a few eV below its original value, even though the ionization energy must finally increase to 8.5 eV for large r . The ionization energy of the π electron in the ${}^2\Pi$ state will certainly not decrease as much as that of the σ electron in the ${}^2\Sigma^+$ state, since the quantum defect of the 2p electron is much smaller than that of the 3s electron. It might even be possible that this ionization energy should increase and reach a maximum in the neighbourhood of 1.2 Å.U. If we may adopt the value found by HERZBERG and DOUGLAS¹⁾, the ionization energy of CH should be approximately 11 eV, so that the ionization energy of the 2p π electron has decreased approximately 1 eV. We have drawn Figure 3 in accordance with their figure. The energy corresponding to the ${}^2\Pi \rightarrow {}^2\Sigma^+$ transition is thus approximately 10 eV.

We can now compute the total number of CH molecules disappearing per sec by means of photodissociation. This number is given by (remembering that $h\nu \gg kT$):

$$N = \rho(\nu) B \rho_{\text{CH}} = g A e^{-\frac{h\nu}{kT}} \rho_{\text{CH}}. \quad (27) \quad (\text{Cf. formula (3)})$$

¹⁾ Private communication to SWINGS. In view of the importance of the precise value of this ionization energy for the theoretical concentrations of CH and CH^+ , we regret that we can not judge the degree of certainty with which this value follows from experimental data.

If we use for A formula (23) with $\theta^2 = 0.1$ ¹⁾, we get for the total number of CH molecules vanishing per sec through photodissociation ($h\nu_{\delta} = 10$ eV, $g = 10^{-14}$, $T = 10000^\circ$):

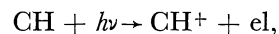
$$N_{\delta} = 10^{-11} \rho_{\text{CH}}. \quad (28)$$

If our estimate of $h\nu_{\delta}$ should be too small, say by 1 eV, the factor $e^{-\frac{h\nu}{kT}}$ is to be multiplied by a factor $\frac{1}{3}$ (Cf. p. 139).

As regards the photodissociation of CH^+ (process ϵ), we must remember that the ground state of $\text{C}^+ + \text{H}$ (${}^2P + {}^1S$) splits into two singlet and two triplet states when C^+ and H approach each other. The ground state of CH^+ is the ${}^1\Sigma$ state, while the ${}^1\Pi$ state is also attractive (Cf. BH, Table 2). An electron jump to a repulsive singlet state will therefore result in a dissociation only, if it leaves the $(\text{C} + \text{H})^+$ in an excited state. The smallest excitation energy possible is 3.5 eV (corresponding to $\text{C} + \text{H}^+$), but since it is practically certain that the repulsive state will correspond to an excited singlet state in the united N^+ atom (minimum excitation energy 16.5 eV) we feel that at the nuclear distance realized in the CH^+ molecule the energy corresponding to a photodissociation will at least amount to 14 to 15 eV. In Table 1 we have taken 14 eV and applied formula (27) with a dilution factor $g = 10^{-16}$, since we are beyond the LYMAN limit.

§ 5. Photoionization of CH and electron capture of CH^+ .

In order to estimate the frequency of the γ process:

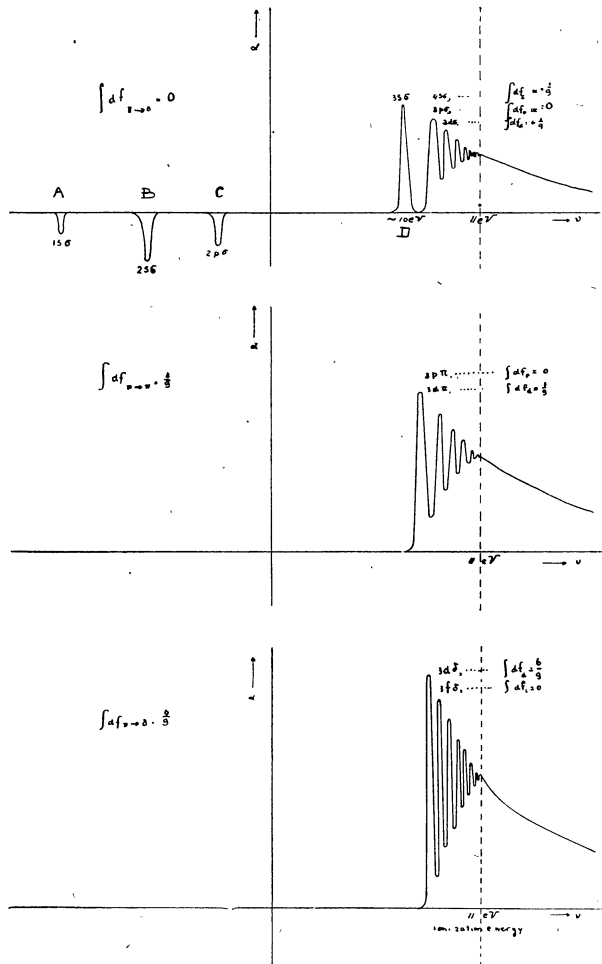


we need only consider the absorption spectrum of the weakest bound electron (2p π) in the CH ground state. In fact, the ionization potential of the other electrons, even that of 2p σ , will lie above 13.5 eV and the radiation density in interstellar space of the corresponding frequencies is too weak to contribute materially to photoionization. A qualitative sketch of the three types of absorption $\pi \rightarrow \sigma$, $\pi \rightarrow \pi$ and $\pi \rightarrow d$ is given in Figure 4, where each time the absorption cross section α is given as a function of the frequency ν . In the case of $\pi \rightarrow \sigma$ the lines of negative absorption, corresponding to the forbidden transitions to 1s σ , 2s σ , 2p σ are included. The contribution df to the oscillator strength corresponding to a frequency interval $d\nu$ is given by²⁾

$$\alpha d\nu = \frac{\pi e^2}{mc} df. \quad (29)$$

¹⁾ This corresponds here to an oscillator strength $f = \frac{1}{30}$.
²⁾ See e.g.: H. A. KRAMERS, *Atti d. Congr. Int. d. Fis. Como* 1927 (Formula (15)).

FIGURE 4



The sum rules ascertain that the total oscillator strength of 1 is distributed in the following way over the three types:

$$\int_{\nu=-\infty}^{+\infty} df_{\pi \rightarrow \sigma} = 0, \quad \int_{\nu=-\infty}^{+\infty} df_{\pi \rightarrow \pi} = \frac{1}{3}, \quad \int_{\nu=-\infty}^{+\infty} df_{\pi \rightarrow \delta} = \frac{2}{3} \quad (30)$$

In the way indicated in the figure the final σ state may be $n_s\sigma$, $n_p\sigma$, $n_d\sigma$, etc., similarly may the final π state be $n_p\pi$, $n_d\pi$, etc., where the symbols n_s , n_p , etc. refer to the limiting case of nuclear distance 0 (united atom). The sum rules tell us moreover that in this limit $\int df_{\pi \rightarrow \sigma}$ will consist of the three contributions:

$$\int df_{\pi \rightarrow s\sigma} = -\frac{1}{9}, \quad \int df_{\pi \rightarrow p\sigma} = 0 \text{ and } \int df_{\pi \rightarrow d\sigma} = +\frac{1}{9}; \quad (31a)$$

Similarly:

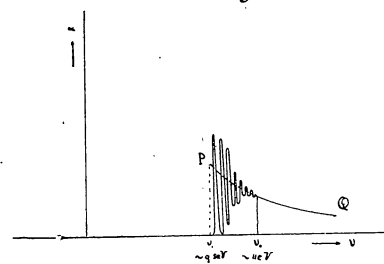
$$\int df_{\pi \rightarrow p\pi} = 0, \quad \int df_{\pi \rightarrow d\pi} = \frac{1}{3} \text{ and } \int df_{\pi \rightarrow d\delta} = \frac{2}{3}. \quad (31b)$$

From all this it seems safe to infer that the photoionization will practically all be due to the $\pi \rightarrow \pi$ and

the $\pi \rightarrow \delta$ transitions. As regards the $\pi \rightarrow \sigma$ transitions it is of interest to remark that the negative f belonging to the line A will be very small, so that the f 's of B and C together will presumably amount to a value between -0.12 and -0.20 . A value for f_C so small as -0.01 , which corresponds to our estimate of the $2p\sigma \rightarrow 2p\pi$ transition on p. 143 is perhaps too small. On the other hand our earlier estimation of $f_D \sim \frac{1}{30}$ on p. 144 is certainly not too large; it might easily be smaller by a factor 3 or so.

The absorption processes significant for photoionization are summarized in Figure 5. The absorption is for $h\nu < 11$ eV, the approximate ionization potential, represented by a series of absorption lines which stretch over an interval of the order of only 1 eV. Their oscillator strengths may be levelled out, so as to give an extrapolation of the continuous α curve

FIGURE 5



holding for $h\nu > 11$ eV; they will then correspond to the fictitious dotted absorption curve of the figure, which breaks off at about $h\nu_1 \cong 9.5$ eV. The total oscillator strength corresponding to the PQ curve may be taken equal to 1. Assuming now that this curve can be approximately described by the wellknown absorption law

$$\alpha = K\nu^{-3} \quad (32)$$

the value of K follows from

$$1 = \frac{mc}{\pi e^2} \int_{\nu_1}^{\infty} \alpha \, d\nu = \frac{mc}{\pi e^2} \frac{K}{2\nu_1^2}. \quad (33)$$

This gives, with $\frac{\nu_1}{\nu_0} \cong \frac{9.5}{11}$:

$$\alpha = 1.5 \cdot \frac{\pi e^2}{mc} \frac{1}{\nu_0} \left(\frac{\nu_0}{\nu}\right)^3. \quad (34)$$

The number N_γ of CH molecules disappearing per sec through photodissociation is then given by

$$N_\gamma = \rho_{CH} \cdot \int_0^{\infty} \frac{\alpha(\nu) \cdot \rho(\nu) \cdot c}{h\nu} \, d\nu. \quad (35)$$

Assuming for the radiation density $\rho(\nu)$:

$$\rho(\nu) = g \cdot \frac{8\pi h\nu^3}{c^3} e^{-\frac{h\nu}{kT}}, \quad (36)$$

we get, with the usual values of T and g , with sufficient approximation:

$$N_\gamma = 12\pi^2 \frac{e^2}{m} g \frac{\nu_0^2}{c^3} \frac{kT}{h\nu_0} e^{-\frac{h\nu_0}{kT}} \rho_{\text{CH}} = 2.10^{-11} \rho_{\text{CH}}. \quad (37)$$

The frequency N_β of radiation capture of an electron will, since the β and γ processes are the inverse of each other (see p. 139), be given by the wellknown formula:

$$\frac{N_\beta}{N_\gamma} = \left(\frac{h^2}{2\pi mkT} \right)^{3/2} e^{\frac{h\nu_0}{kT}} \frac{\rho_{\text{el}} \rho_{\text{CH}^+}}{\rho_{\text{CH}}}, \quad (38)$$

which for $\frac{N_\beta}{N_\gamma} = g^{-1}$ reduces to the expression for SAHA equilibrium. Inserting the numerical values it gives the value given in Table 1:

$$N_\beta = 3.10^{-13} \cdot \rho_{\text{el}} \rho_{\text{CH}^+}. \quad (39)$$

The processes ζ differ from the processes β only in

that the electron is captured in some excited doublet state of the neutral CH molecule, in which the nuclei repel each other. The $(2p\sigma)^2(3s\sigma)$ state (see Table 3) will presumably be the only state which comes into consideration. Now in the case of electron capture by an ionized atom in different states, the capture cross section will be roughly proportional to the inverse cube of the effective quantum number ¹⁾. From comparison with the states in the united N atom, which correspond to the ground state and the excited state under consideration in CH, we arrive at the following rough estimate:

$$N_\zeta/N_\beta \sim 0.1, \quad (40)$$

which value had been adopted in Table 1.

We express our thanks to Prof. Dr J. H. OORT for many clarifying discussions on the subject of this paper.

¹⁾ See e.g.: H. A. KRAMERS, *Phil. Mag.* **46**, 836, 1923.

Note on the table in B.A.N. No. 274, page 308:

Bu 2869, first line, and Bu 3238, first line, should be rejected on account of the exceedingly poor quality of the images; these stars have been photographed on one plate.

ERRATA

B.A.N. No. 201. Page 8, top of second column, for: C.P.D. 60° - 2595, read: C.P.D. - 60° 2595.

B.A.N. No. 251. Page 122, formula (2) should read:

$$p'' = p' \left(1 + \frac{V}{c} \right) + p' \frac{v - V}{c}.$$

Page 123, Table 3, first column, line 7 from top, for: 389, read: 339.

Page 123, second column, line 25 from top, for: maximum angular distance, read: projection of maximum distance.

B.A.N. No. 307. Page 222, in formula (46) and in the footnote the value of k should be: $k = 0.1720209895$.

B.A.N. No. 319. Page 340, first column, 2257, for: Σ Ari, read: ε Ari.

Page 350, second column, 4th star from bottom, for: ϑ Sgt, read: ϑ Sge.

B.A.N. No. 324. Page 38, second column, line 4 from top, for: $D_i c z_i^2$, read: $\sum_{i=1,2,3} D_i c z_i^2$.

B.A.N. No. 329. Page 101, second column, line 11 from top, for: 113/023, read: 113 \pm 023.

Page 104, first column, line 14 from top, for: c^2/T' , read: c_2/T' .

B.A.N. No. 345. Page 245, Table 1, star i, 5th column, for: 1294563, read: 1294563.

B.A.N. No. 361. Page 8, second column, line 7 from top, for: 3.10^{-4} , read: 3.10^4 .

B.A.N. No. 364. Page 44, first column, footnote, for: star σ , read: star o.