electrolytes on dilution. These difficulties, if they are real, might be removed by reverting to the idea of electrons acting as binding material in compounds capable of ionisation instead of supposing that they have passed completely and irreversibly over from the positive to the negative atom and have been incorporated into the sheath of the latter. This is not to confuse electrovalency with covalency, for the essential difference between the two kinds of valency is still that electrons are transferable in the one case and not in the other.

It is apparent, however, that Dr. Langmuir regards ionisation in a wider sense than is usual from his statement that "compounds without covalency must consist of positively and negatively charged ions"; and that among such compounds he places SF_6, because the sulphur atom is sufficiently positive to yield to the powerful attraction of the fluorine atoms for electrons.

In this connection I would like to direct attention to the unique characteristics of the elements of the first short period as compared with those of the second short period and following periods, and to inquire whether Dr. Langmuir's theory can afford an explanation of them.

The hydrides of the first short period are inert compared with corresponding hydrides in subsequent periods. Compare, for example, CH_4 with SiH_4. Why is CH_4 stable and inert, while SiH_4 is rather unstable and undergoes metathesis with some salts? Presumably H is joined to C in methane by covalency, while the hydrogen of silane is "ionised." Why is this so? Comparison of HF with HCl shows an analogous difference. Why is HF so weak an acid? Certainly not for lack of electronegativeness on the part of fluorine. If we are to regard HCl as always "ionised," does covalency in the case of HF gradually give place to electrovalency as its aqueous solution is diluted and specific conductivity increases, and, if so, why? Comparison of CCl_4 with $SiCl_4$ is equally interesting, because CCl_4 is analogous to CH_4 in inertness and $SiCl_4$ to SiH_4 in reactivity. Why, then, does covalency obtain with one chloride and electrovalency with the other?

These few questions point to the fundamental problem of the gradation of properties of the elements in the periodic classification; and further developments of his theory, which Dr. Langmuir promises, will be looked for with great interest.

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September 26.

The Dushman Equation for the Velocity of a Monomolecular Reaction.

IN view of the discussion at the Faraday Society on September 28, it is perhaps of interest to direct attention to the Dushman equation for the monomolecular velocity constant (Journal A.C.S., 1921, vol. 43, p. 397). This equation, $\kappa = v e^{-\frac{Nh\nu}{RT}}$, where h, R, T, and ν have the usual significance and $e^{-\frac{Nh\nu}{RT}}$ represents the number of active molecules, is found to hold fairly accurately for certain monomolecular reactions that have been investigated. Of these the chief are the decomposition of phosphine and nitrogen pentoxide. Much dispute has arisen as to the meaning of ν. Is this related to the frequencies of the *activating* radiation, or is it a frequency characteristic of some degree of freedom in the decomposing mole-

cule? Judging from the constancy of $h\nu$ over a range of temperatures, the latter would appear to be the more reasonable assumption. The relationship between ν and the absorbed and emitted frequencies would thus be left open.

On this hypothesis it is possible to ascribe a simple meaning to the Dushman equation, for the "period of existence" of the molecule in the active condition will be $1/\nu$, i.e. the period of time corresponding to one molecular vibration. This equation could not hold if the rate of chemical decomposition of the active molecule was in any way different from its rate of decay, due to the emission of quanta to its environment. For if there is any difference between the two rates, the position of equilibrium will be disturbed, and the number of active molecules will not be given by the Maxwell relation. In general, the time of association of an activating quantum (of a lower frequency than ν) with a gaseous molecule will be greater than $1/\nu$, so that the effect of chemical decomposition will lower the concentration of the active molecules at the steady state and decrease the velocity constant. κ would in these circumstances be less than the value obtained from the Dushman equation. Tolman (Journ. A.C.S., 1921, vol. 43, p. 269) finds for nitrogen pentoxide that κ (calc.) $= 19 \times 10^{-3}$, while κ (obs.) $= 4.87 \times 10^{-3}$. The change in κ is thus in the required direction. The *exact* agreement obtained by Dushman in the case of phosphine would thus appear to be accidental.　　　　W. E. GARNER.

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The Duration of Sunrise and Sunset.

MY attention having been accidentally directed to this matter, I have made observations for the purpose of comparing the observed duration of sunrise and sunset with the duration computed from geographical position and *Nautical Almanac* data, and have now seventy-nine complete observations, made mostly with marine horizons on Manila Bay, the China Sea, the open Pacific, Vineyard Sound, and Buzzard's Bay, with a few made with land horizons. The viewpoints have been from sea-beach to 1512 metres elevation.

There seem to be two types of marine sunrise and sunset; one, type A, about twice as frequent as the
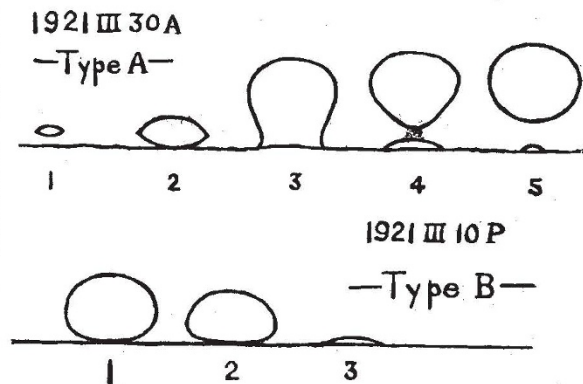

FIG. 1.—Types of marine sunrise and sunset.

other and accompanied by horizon mirage. The diagrams (Fig. 1) accompanying this letter, sketched from photographs obtained at Woods Hole, show the characteristics of the two types, which are described with historical details in *Popular Astronomy* (vol. 29,