

mary product only ordinary excited molecules. Apparently these excited molecules which contain considerably more energy than the heat of dissociation undergo some change leading to dissociation upon collision with argon atoms as, indeed, Franck has already pointed out in discussing the quenching of the iodine fluorescence observed by him and Wood.

It seemed difficult, however, to understand how an argon atom, all of the excited levels of which lie over ten volts above the normal one could produce such an effect. It is possible that the effect of the argon might be to increase the probability of an already occurring predissociation. It has been pointed out elsewhere (*Zeits. f. Physik* **65**, 464, 1930) that such a predissociation is theoretically possible. (The perturbing states can be, however, the two 1_u states of the ${}^2P_{3/2} + {}^2P_{3/2}$ combination; *not* the 1_g state, as there stated, as was kindly called to my attention by R. S. Mulliken). Such an explanation may be made to seem more plausible by the following considerations. One of the selection rules for ordinary predissociation transitions is that J does not change, i.e., there must be a conservation of angular momentum. The angular momentum to be conserved can be thought of as being composed of two parts; the angular momentum of the iodine molecule itself and the angular momentum of the mutual motion of the centers of gravity of the molecule and argon atom. If only the total angular momentum is to be conserved the angular momentum of the iodine molecule or separating atoms after predissociation can have a variety of

values. In other words the angular momentum can be distributed between the iodine atoms and the argon atom in a variety of ways. One might expect such a weakening of one of the restrictions upon the transitions in the iodine molecule to increase its probability.

In order to test this hypothesis spectra of discharges in pure iodine and in iodine-argon mixtures were compared. When an exposure made with the mixture is compared with one of suitable exposure-time made with pure iodine all bands of wave-lengths longer than about 5440 Å seem to have the same intensities but the bands of shorter wave-length are considerably weakened in the spectrum of the mixture. Closer examination reveals that all bands of $v' > 29$ are weakened, the quenching setting in fairly rapidly with increasing v' . Confirmatory results have been obtained in fluorescence experiments. The fluorescence was excited by illumination with light from an intense tungsten lamp. The fluorescence bands of wave-lengths longer than 5430 Å were cut to about 1/4 of their original intensity by 16 mm of argon, those of shorter wave-length being quenched much more severely, the additional quenching setting in only moderately rapidly with decreasing wave-length.

A detailed description and discussion of these experiments will soon be submitted for publication to the *Physical Review*. A quantitative study of the quenching of iodine fluorescence by argon is being undertaken.

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The Relative Abundance of N^{14} and N^{15}

In a recent letter to the *Physical Review* Birge and Menzel¹ have considered what relative abundances of the isotopes of carbon and nitrogen it is necessary to assume in order that the chemical atomic weights shall be consistent with Aston's values and Mecke and Child's² value for the relative abundance of O^{16} and O^{18} . The value which is required for the relative abundances of the nitrogen isotopes is $N^{14}:N^{15} = 320:1$. This value agrees very closely with a preliminary value for this

¹ Birge and Menzel, *Phys. Rev.* **37**, 1669 (1931).

² Mecke and Childs, *Zeits. Physik* **68**, 362 (1931).

quantity which we have secured and this letter is for the purpose of reporting this result.

The method we are using depends on the relative intensities of the $NO\gamma$ absorption bands used by Naudé.³ The determination by Naudé of the relative abundances of $N^{14}O^{18}$ and $N^{15}O^{16}$ molecules can be criticized on the following points: (1) he states that the $N^{15}O^{16} \text{ } ^oP_{12}$ branch has the same intensity as the $N^{14}O^{18} \text{ } ^oQ_{12} + P_2$ branch, while our microphotometer curves for the (1, 0) vibrational band show that the latter is the stronger; (2) even if these heads were of the same in-

³ Naudé, *Phys. Rev.* **36**, 333 (1930).

tensity, the fact could not be used to determine the relative abundances as done by Naudé, for the $N^{14}O^{18}(P_{12}+P_2)$ branch head is superimposed on the $N^{15}O^{16}O_{P_{12}}$ branch, so that it is difficult or impossible to determine what part of the absorption is due to each molecule. In view of these difficulties we thought it advisable to redetermine this ratio.

We have compared the relative intensities of the $O_{P_{12}}$ branches of $N^{14}O^{18}$ and of $N^{15}O^{16}$ directly by putting density marks on our plates using neutral wire screens⁴ and as a source of light a hydrogen discharge tube whose intensity remains constant within about 1 percent. The $N^{15}O^{16}O_{P_{12}}$ branch is superimposed on the $N^{14}O^{18}O_{P_{12}}$ branch but they are well separated by the Hilger E 1 quartz spectrograph so that it is possible to estimate the contribution of each molecule to the absorption. Our preliminary result from 26 microphotometer curves for the ratio of $N^{15}O^{16}$ to $N^{14}O^{18}$ molecules is 0.551 ± 0.062 . The probable error given represents only the error, if no systematic error is present. Using Mecke and Child's value for the ratio of O^{18} to O^{16} of 630:1, we get for the ratio of N^{14} to N^{15} the value 347:1 in satisfactory agreement with the ratio required by Birge and Menzel of 320:1. This result is preliminary for there are two possible sources of error: (1) the lines at the head of these bands may not give a true continuous absorption so that Beer's law may not hold (a possible error in Naudé's

⁴ See G. R. Harrison, J. O. S. A. and R. S. I. 18, 492 (1929).

result also); (2) it is not certain that there are no superimposed bands of $N^{14}O^{16}$. Work is in progress to eliminate these possible sources of error. Our results have been obtained from the (1, 0) vibrational band and further checks will be secured from the (2, 0) band as well.

The study has been made on air nitrogen fixed by the Beckeland-Eyde and Haber processes and on nitrogen from Pennsylvania coal. We find no difference in relative abundances of the nitrogen isotopes in air nitrogen (17 microphotometer curves) and in coal nitrogen (9 microphotometer curves) within 3.4 percent, which is less than our probable error. Work is also being done on a sample of oxygen from Precambrian magnetite to see if the relative abundance of O^{16} and O^{18} is the same in this sample and in air oxygen.

Due to an improved hydrogen discharge tube which will be described elsewhere, exposures of the (1, 0) absorption band can be made in one minute and of the (2, 0) band in five minutes using the Hilger E 1 quartz spectrograph. The method requires only about 0.06 grams of oxygen element as NO in the absorption cell. The speed and small samples required makes this a good method for investigating the relative abundances of the oxygen isotopes in meteorites. Work on this problem is in progress in our laboratories.

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The Second Virial Coefficient

If the equation of state of a gas is written:

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \dots$$

the second virial coefficient, B , may be computed on the basis of classical statistics to be

$$B = 2\pi N \int_0^\infty (1 - e^{-E_q/kT}) r^2 dr$$

where E_q is the mutual potential energy of two molecules and r is their separation. In the deduction of this expression it is assumed that the energy is a continuous function of position in the momentum-configuration space of the system. Thus it fails to take into account quantized states which may arise in molecular collisions.

If we take as zero energy, that of two molecules at rest at infinite separation, we find upon examining the potential energy curve, let us say of helium, that the energy of the system of two molecules may be represented by a continuous spectrum when the total energy is positive and by a discrete spectrum when it is negative. Thus there will be certain regions of phase space corresponding to quantized energy states. By subtracting from the classical integral over all of the momentum-position space of the system, that part which comes from regions corresponding to quantized states, and in its place adding the sum over the discrete states in these regions, we should obtain the correct value of the virial