The Infrared Absorption Spectra of Some Polyatomic Fluorides

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Chemical Atomic Weights and the Relative Abundance of the Oxygen Isotopes

Nuclear disintegration experiments on the lighter elements have furnished precise atomic weights,[1] which have been confirmed in most cases by mass-spectrographic analysis. The results indicate that the whole atomic weight scale should be increased by several parts in ten thousand. These atomic weights are based on the physical scale which takes $O^{16} = 16.0000$ whereas chemical atomic weights are based on the naturally occurring mixture of oxygen isotopes, $O = 16.0000$. Several comparisons of chemical and physical atomic weights have been made in the past,[2] but the conversion factor is uncertain since the relative abundance of the oxygen isotopes is not known with sufficient precision. A more satisfactory conversion factor should be obtained with nonisotopic elements such as He, Be, F, Na, Al and P. However, only the chemical atomic weight of He is precise enough for this purpose. The mass of He^4 on the physical scale is 4.00395 ± 0.00007[3] and on the chemical scale, it is 4.0018 ± 0.0003.[4] An atomic weight on the physical scale may thus be converted to the chemical scale by dividing the former by 1.00054 ± 0.00008. This is considerably larger than the factor of 1.00025 previously obtained from the measured abundance of the oxygen isotopes and now used by the International Atomic Weight Committee.[5] The higher factor, however, is not unreasonable as may be seen from the following table where chemical atomic weights for several nonisotopic atoms are compared with values calculated from the physical scale by the two factors above. Definitely better agreement is noted for the higher factor except for phosphorus where the chemical atomic weight is apparently in error. The value quoted by the Atomic Weight Committee[6] is 31.02 which cannot be made to agree with the physical scale by any reasonable factor. The only other nonisotopic atoms of low atomic weight are Be and Na. For the former, there is no reliable chemical atomic weight and for the latter no precise physical atomic weight. If we take the chemical atomic weight[6] of Na as 22.9985 ± 0.0012 and convert to the physical scale, we obtain $Na^{23} = 23.0009 \pm 0.0022$.

Comparison of the atomic weight of other light elements does not seem worthwhile because of the uncertainty in the isotopic composition. We have, however, made this comparison with both factors given above and find that no decision between the two can be made although the higher one is not excluded.

The conversion factor may also be used to compute the relative abundance of the oxygen isotopes. Since there are three of them, it was assumed that O^{18} is five times more abundant than O^{17}. The relative abundances of O^{16}, O^{17} and O^{18} are then 0.9952, 0.0008 and 0.0040, respectively. This somewhat surprising result is considerably different from the values 0.9976, 0.0004 and 0.0020 reported by the Committee on Atoms of the International Union of Chemistry.[7] We have no explanation to offer for this discrepancy but we believe that some inconsistency exists. There is no indication that the physical masses are incorrect and hence either O^{17} and O^{18} are more abundant than suspected or the chemical atomic weights of He, F and Al are considerably in error.

	Chemical Atomic Weight	Factor = 1.00025	Factor = 1.00054 ± 0.00008
He	4.0018 ± 0.0003[4]	4.0029	4.0018 ± 0.0003
F	18.995 ± 0.005[8]	19.000	18.994 ± 0.002
Al	26.974 ± 0.002[9]	26.984	26.976 ± 0.002
P[11]	30.977 ± 0.003[10]	30.976	30.968 ± 0.003

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[1] For a review of the results obtained, see O. Hahn, Berichte d. deutschen chem. Gesellschaft, **70A**, 1 (1937).
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The Infrared Absorption Spectra of Some Polyatomic Fluorides

We have recently completed an examination of the infrared spectra of the fluorides of boron, carbon, nitrogen, and silicon. These may well be taken together since a knowledge of the four spectra is necessary before one can be certain as to the state of purity of any individual. We have been helped in the assignment of frequencies by the existence of Raman data obtained by Professor Yost for all except NF_3.

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BF$_3$ (Anderson, Lassettre, and Yost)[1]

We find $\omega_2(||) = 722$; $\omega_3(\perp)$: $B^{11} = 1448$, $B^{10} = 1501$ cm^{-1}. $\omega_1(||) = 886$ is inactive in the infrared, and $\omega_4(\perp)$ was also located in the Raman effect at 440 cm^{-1}. Yost took ω_3 as 1038 cm^{-1}, but the isotopic doubling in the infrared leaves no doubt that it is considerably higher. K for B$-$F is 0.669 megadynes/cm. The molecule is plane.

NF$_3$

The fundamental frequencies observed are $\omega_1 = 908$, $\omega_2 = 505$ (both $||$), and $\omega_3 = 1004(\perp)$. The other ($\perp$) frequency ω_4 was estimated to be (420) cm^{-1}. The assignments should be taken as provisional in the absence of Raman data. The molecule is a very flat pyramid, the bond angle being 110° or more. The force constant K for N$-$F is low, the value 0.410 megadynes/cm corresponding to $r_e = 1.45$A, instead of 1.34 from Pauling's data.

CF$_4$ (Yost, Lassettre, and Gross)[2]

We have succeeded in placing the active fundamental frequencies ω_3 and ω_4 at 1252 and 630 cm^{-1}, respectively. Eucken and Bertram[3] assigned ω_3 and ω_4 to two bands observed by them at 1350 and 653 cm^{-1}: the first appears to be a combination tone, and the second is too high. The Urey and Bradley force field[4] for tetrahedral molecules fits CF$_4$ and SiF$_4$ very well: K for C$-$F is 0.399 megadynes/cm.

SiF$_4$[2]

Of the active fundamentals we found $\omega_3 = 1022$ cm^{-1}. The other ω_4 was estimated by Yost to lie at (431) cm^{-1}. The inactive modes ω_1 and ω_2 were, respectively, found and calculated by Yost to be 800 and (285) cm^{-1}. K for Si$-$F is about 0.57 megadynes/cm.

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  of Inorganic and Physical Chemistry,
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    February 19, 1937.

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The Thermal Decomposition of Ethane. A Note on the Paper by H. Sachsse

The main theme of the paper by Sachsse in the March issue under the above title is that the new value of E_4 (the activation energy of reaction (4) in the Rice-Herzfeld scheme for the decomposition of ethane) determined by us does not make as large a change in the calculated value of [H] as we say it does, our calculations being in error due to a "misunderstanding." Sachsse then recalculates [H] and shows that even with our value of E_4 the calculated values of [H] are still higher than the observed values of Sachsse by a factor of about 70.

Actually the discrepancy lies in the fact that we used the complete Rice-Herzfeld mechanism *and Rice and Herzfeld's methods of calculation* to get [H]. Sachsse, on the other hand, uses Rice and Herzfeld's set of reaction steps, but calculates the results by assuming steric factors, collision numbers, etc., which they did not use. Furthermore he puts $E_6 = 8$ kcal. Rice and Herzfeld do not explicitly give E_6, but from a combination of Table A and Eq. (22) of their paper it follows that they use $E_6 = 0$. This is the value which we used in our calculations.

On the Rice-Herzfeld mechanism $[H] = \left(\dfrac{k_1 k_3}{2 k_4 k_6}\right)^{\frac{1}{2}}$.

Assuming, as they do, that all bimolecular velocity constants are given by $k = 10^9 e^{-E/RT}$, and all unimolecular constants by $k = 10^{14} e^{-E/RT}$, we obtain:

(a) *With $E_4 = 6$ kcal. as found by us, and $E_6 = 0$ as assumed by Rice and Herzfeld.*

$[H] = 1.4 \times 10^{-12}$, i.e., 4 times *less* than the value found by Sachsse experimentally.

(b) *With $E_6 = 8$ kcal. as assumed by Sachsse but not by Rice and Herzfeld.*

$[H] = 17 \times 10^{-12}$, which is only 3 times the experimental value.

(c) *Assuming $E_6 = 0$ and that the reaction occurs by a triple collision so that $a_6 = 0.001$.*

$[H] = 46 \times 10^{-12}$, which is still within one power of 10 of the experimental value.

We were therefore entirely justified in saying that the value of [H] *calculated from the Rice-Herzfeld mechanism* is in almost exact agreement with Sachsse's experimental value. It follows that Sachsse's argument is with Rice and Herzfeld over the validity of their approximations, and not with our calculations. There was no "misunderstanding" on our part.

It should be emphasized that we are in complete agreement with Sachsse on the main point at issue, namely that our determination of E_4 supports the conclusion reached by Sachsse from his experiments that the Rice-Herzfeld mechanism for the decomposition of ethane is untenable. We argued that while the mechanism with the new value of E_4 now gave the approximately correct value for the hydrogen atom concentration, it could no longer be made to give the correct order or activation energy for the over-all decomposition. Sachsse argues that the predicted value of [H] is still incorrect.

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