

Table 1

Relative silver masses determined by chemical analysis	Relative radioactivities (and hence silver masses) determined by:				
	Geiger counter	Autoradiography and density measurement		Autoradiography and visual estimation	
			Observer 1	Observer 2	
16.1	13.9	15.1	17	17	
38.6	37.0	39.5	42	35	
58.8	58.7	59.4	59	52	
77.5	76.3	77.8	79	70	
91.3	92.2	93.3	91	79	
100	100	100	100	100	

each source to give a standard (but not measured) density. The quantities in the weaker sources were then expressed as percentages of the strongest source.

Table 1 shows that method (c) gave an accuracy comparable with that obtained by counting, while even without a densitometer accuracy adequate for semi-quantitative work was achieved.

Apart from its obvious usefulness in laboratories not equipped with a counter, autoradiography has certain other advantages: in its simplest form it requires no special equipment; it produces a permanent record of relative activities; in the sense that one sheet of film can be simultaneously exposed to a large number of specimens, it is equivalent to the use of a whole battery of counters, and as a result, autoradiography can simplify, or make unnecessary, corrections for decay. It also facilitates more accurate assessment of isotopes having short half-lives, and makes practicable comparisons of very weak sources which would each require a long time on a counter.

A full account of this work is being prepared for publication elsewhere.

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<sup>1</sup>(a) Zuber, K., *Helv. Phys. Acta*, **21**, 365 (1948). (b) Dudley, R. A., and Dobyns, B. M., *Science*, **109**, 327, 342 (1949).

<sup>2</sup>Ballard, A. E., Zuehlke, C. W., and Stevens, G. W. W., *Radioisotopes Techniques*, **2**, 105 (H.M.S.O., 1951).

### Bond-Lengths and Force Constants for Methane, Silane and Germane

In a recent paper by one of us (N. H. M.<sup>1</sup>), a detailed discussion of the electron distributions and potential fields for molecules of high symmetry was given on the basis of the Thomas-Fermi theory. In this work the nuclei of the outer atoms were smeared out over the surface of a sphere and the electrons then regarded as moving in the resulting spherically symmetrical field. A general discussion of the energy was also given, and the existence of a minimum in the energy curves was demonstrated. However, the theoretical bond-lengths were in poor agreement with the experimental values, and it was suggested that this might be due to the neglect of exchange.

We have now considered in detail the effect of exchange on the energy curves for methane (CH<sub>4</sub>), silane (SiH<sub>4</sub>) and germane (GeH<sub>4</sub>), for which molecules the smoothing approximation referred to above seems physically very reasonable. The Thomas-Fermi electron densities obtained previously have been used as variation functions for calculating the energy including exchange, this being analogous to

the procedure introduced by Scott<sup>2</sup> in his successful calculation of binding-energies for atoms. We are thus enabled to calculate the bond-lengths and the force constants for the totally symmetric vibrations of these three molecules, and the results are recorded in Table 1. For comparison, we also give the bond-length for methane when exchange is ignored<sup>1</sup> (the bond-lengths for silane and germane will be somewhat greater than this), together with an approximate value for the force constant for methane obtained by using the formula of Bowers<sup>3</sup> slightly outside its proper range of validity.

Table 1

	Bond-lengths (in Å.)		Thomas-Fermi with exchange
	Experimental	Thomas-Fermi	
CH <sub>4</sub>	1.09	2.1	1.38
SiH <sub>4</sub>	1.46	—	1.62
GeH <sub>4</sub>	1.48	—	1.9
	Force constants (in units of 10 <sup>8</sup> dynes/cm.)		
	Experimental	Thomas-Fermi	Thomas-Fermi with exchange
CH <sub>4</sub>	20	1	9
SiH <sub>4</sub>	11	—	5
GeH <sub>4</sub>	10	—	3

It can be seen that the bond-lengths are improved considerably by the inclusion of exchange, the errors in the calculated bond-lengths for methane and silane being 27 and 11 per cent respectively. However, for germane the error increases again to about 25 per cent, which at first sight seems surprising in view of the fact that the Thomas-Fermi method should become more reliable as the number of electrons increases. Heath, Linnett and Wheatley<sup>4</sup>, however, have concluded previously from a study of regularities in bond-lengths and force constants for a number of molecules that the bond in germane is probably "abnormally strong and short". If this is so, then it is not very reasonable to expect the Thomas-Fermi method, which distinguishes different atoms only by virtue of a change of scale depending on their atomic numbers, to be able to deal accurately with such a case. It is not so surprising, therefore, that by this method we find a larger deviation from the observed value for germane than in the case of silane.

As one would expect, the force constants are less satisfactory than the bond-lengths. Again, however, it is clear that exchange has a marked effect, the force constant for methane being improved by a factor of 9.

What has emerged from our calculations is that the exchange energy plays an essential part in determining bond-lengths and force constants from the present theory. Considering the simplified nature of the treatment, agreement with experiment is very reasonable. There is, however, some indication that the model we are using is least satisfactory for germane, in which the bonding is rather 'abnormal'. We are now investigating the application of the method to other molecules, and a detailed account of the work will be published later.

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<sup>1</sup>March, N. H., *Proc. Camb. Phil. Soc.*, **48**, 665 (1952).

<sup>2</sup>Scott, J. M. C., *Phil. Mag.*, **43**, 859 (1952).

<sup>3</sup>Bowers, W. A., *J. Chem. Phys.*, **21**, 1117 (1953).

<sup>4</sup>Heath, D. F., Linnett, J. W., and Wheatley, P. J., *Trans. Farad. Soc.*, **46**, 137 (1950).