changes of graphite at very high neutron doses. Some of the results obtained are given in Table 2.

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CHEMISTRY

Negative Surface Ionization of Complex Molecules

The formation of negative ions by the surface ionization of gases on hot metallic filaments has been used as a means of determining electron affinities. In the method of Sutton and Mayer[1], the total negative ion current and the total electron current were measured as functions of temperature, by means of a magnetron. This technique has been refined by Page[2] and extended to more complex molecules[3]. In the absence of mass analysis, the process giving rise to the negative ions is postulated *a priori* and justified on the basis of reasonableness and internal consistency.

Mass spectrometric investigations of negative surface ionization have been confined to simple molecular species such as the halogens, oxygen, sulphur, etc.[4]. Results for more complex molecules are recorded here.

The mass spectrometer used in this work was a 12″ radius of curvature, 60° sector field instrument. It had a base pressure of 10^{-8} torr. (A torr is defined as 1/760 of a standard atmosphere.) The gaseous species was passed over an incandescent tungsten or platinum filament located in the ion source of the mass spectrometer. Total pressure in the filament zone was about 10^{-3} torr. The temperature, as measured with an optical pyrometer, was varied from 900 to 1,600° C.

The results are summarized in Table 1. Only the largest ion peaks are included, accounting for about 90 per cent of the total ion current. The ion current varied with temperature, having a maximum value of about 10^{-11} amp, and a minimum value of about 10^{-16} amp. In general, the relative magnitudes of the ion currents did not change significantly with temperature. These are shown in column 3 of Table 1, in order of decreasing intensity. The ions predicted by the magnetron experiments of Page *et al.* are shown in column 4.

It is obvious that there is a considerable discrepancy between what is postulated and what is observed. Some of the discrepancy may arise from differences in total pressure, filament purity, etc., between the two sets of experiments. It is more probable, however, that the discrepancy arises from the impossibility of predicting the nature of the ions which may be formed from a given molecular species. If this is the case the electron affinities determined by the magnetron technique are probably unreliable.

Table 1

Molecule	Filament	Ions observed	Ions predicted
O_2	W	WO_3^-	O^-*
N_2O	W	O^-, WO_3^-	O^-*
NO_2	W	WO_3^-, O^-, NO_2^-	—
H_2S	W	HS^-, S^-, S_3^-, S_2^-	S^-†
SF_6	W	SF_5^-, SF_6^-, F^-	SF_6^-, $T < 1{,}320°$ K‡
$C_2(CN)_4$	Pt	$C_2(CN)_4^-$	$C_2(CN)_4^-$§
$[(CH_3)_3CO]_2$	Pt	$(CH_3)_3CO^-$, $CH_3COCH_2^-$	—
C_6H_6	W, Pt	C_2H^-, C_2^-, CN^-	$C_6H_5^-$¶
$(CH_3N)_2$	W	CN^-	—

* Page, F. M., *Trans. Faraday Soc.*, **57**, 359 (1961).

† Ansdell, D. A., and Page, F. M., *Trans. Faraday Soc.*, **58**, 1084 (1962). Our results are complicated by the presence of a large Cl^- peak arising from an impurity in our sample.

‡ Kay, J., and Page, F. M., *Trans. Faraday Soc.*, **60**, 1042 (1964). At our lowest temperature, 1,270° K, SF_5^- is the predominant ion.

§ Page, F. M., and Kay, J., *Nature*, **199**, 483 (1963).

¶ Gaines, A. F., and Page, F. M., *Trans. Faraday Soc.*, **59**, 1266 (1963).

The presence of CN^- as a major peak in the case of the hydrocarbons points up the very great importance of the interaction of gas and filament. The nitrogen is probably present originally either in the form of physically absorbed or trapped nitrogen, or as metallic nitrides.

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Discrepancies between Micellar Molecular Weights by Number-Average and Weight-Average Methods

In recent years, light-scattering techniques have been widely used for the determination of micellar molecular weights. On the other hand, a few workers[1–3] have chosen to make such determinations through measurement of colligative properties, in particular, by measurement of the lowering of the vapour pressure.

In general, such measurements give values for the micellar molecular weight which are much lower than those determined by light-scattering. This is not altogether surprising since, as is well known, light-scattering techniques give 'weight-average' molecular weights, while measurement of the colligative properties results in 'number-average' weights. Only in completely monodisperse systems will these two averages coincide; in all other cases, the weight-average value will be greater than the number-average, and, indeed, the ratio of the two is a measure of the polydispersity.

However, the ratio between the values for micellar systems seems to be much larger than can be accounted for on the basis of what is known about the distribution of micelle size, that is, on the basis of modern theories of micelle formation, the distribution of micelle sizes should be fairly sharp.

In fact, Debye and Coll[1] have rejected polydispersity as the explanation, but rather ascribe the higher results obtained from light-scattering measurements to the presence of dust and other impurities.

Totally disregarded in all discussions of these discrepancies has been the fact that the distribution of molecular weights in a micellar system is not a simple unimodal one (to which the statements about the significance of the weight average-number average ratio apply), but rather a bimodal distribution, possessing one peak at a molecular weight M_0, corresponding to the monomer of surface-active agent and a second, distant peak at M_m ($= nM_0$), corresponding to the micelles, and where n = aggregation number. Furthermore, and most significant, the ratio between the heights of the modes is a function of concentration. (It should be pointed out that Debye and Prins[4] noted that the definition of number-average molecular weight in micellar systems could explain the concentration-dependence observed in such measurements, but they failed to make the next step.)

What we have, in fact, is a system in which the peak corresponding to detergent monomer increases in size linearly with concentration until the critical micelle concentration (c_0) is reached, during which time the peak