

The synthesis of the new perfluoro acid pentafluoropropionic acid, achieved in collaboration with Mr. K. Leedham, also illustrates this reaction. Pentafluoroiodoethane (prepared from tetrafluoroethylene<sup>4</sup>) and acetylene yield 1:1:1:2:2 pentafluoro 4-iodobutene (b.p. 84.4°), which with alkaline permanganate affords pentafluoropropionic acid (b.p. c. 95°), characterized as its amide (m.p. 95–95.5°). Like trifluoroacetic acid, pentafluoropropionic acid is a strong acid which fumes in air and which has a high density and low refractive index. Similarly, heptafluorobutyric acid, described recently<sup>5</sup>, has been synthesized from heptafluorodopropane.

Thus, two general synthetic methods are now available; the first, to prepare fluoroiodides from the corresponding fluoroacids; the second, to convert fluoroiodides, prepared by various routes, into the corresponding fluoroacids. The properties of some of the compounds mentioned above are being studied and will be described in more detail elsewhere.

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<sup>1</sup> Haszeldine, *J. Chem. Soc.*, 2856 (1949).

<sup>2</sup> Haszeldine, *Nature*, **165**, 152 (1950).

<sup>3</sup> Banks, Emeléus, Haszeldine and Kerrigan, *J. Chem. Soc.*, 2188 (1948).

<sup>4</sup> Emeléus and Haszeldine, *J. Chem. Soc.*, 2948 (1949).

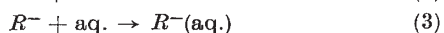
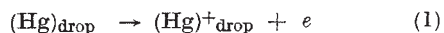
<sup>5</sup> Husted and Ahlbrecht, Abstracts, American Chemical Society, 116th Meeting, September 1949, 10K.

### Electron Affinities of Some Aromatic Molecules

EVIDENCE<sup>1</sup> is available to indicate that in the reduction of some aromatic molecules at the dropping mercury electrode one electron is added on to the neutral molecule.

From a knowledge of the absolute potential,  $E$ , at which this reduction occurs, of the photo-electric work function,  $\chi$ , of mercury and of the solvation energy,  $S$ , of the ion formed, it is possible to calculate simply the electron affinity,  $A$ , of the neutral molecule.

To do this, consider the process of reduction as taking place in three stages:



where  $R$  is the neutral molecule.

The energy used is  $\chi$  for 1,  $-A$  for 2 and  $-S$  for 3, a total of  $\chi - A - S$ . This is put equal to  $E$ , which can be determined experimentally.  $S$  may be calculated from the modified Born equation<sup>2</sup> for a singly charged anion in water, and  $\chi = 4.52$  eV. The radius of the ion needed in the Born equation can be calculated from the molar volume. For triphenyl methyl,  $S = 1.46$  eV.; hence,  $A = +2.62 (\pm 0.05)$  eV.

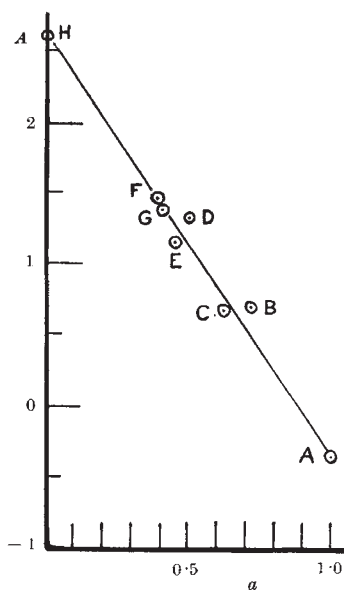
Triphenyl methyl is the only one of the compounds considered for which previously determined values of  $A$  have been found. In these cases, by methods completely different from the present,  $A$  was  $2.56 \pm 0.2$  eV.<sup>3</sup>, and  $2.09 \pm 0.2$  eV.<sup>4</sup>

Results for other molecules are quoted in the accompanying table. The order of electron affinity

Molecule	$E^a$ (eV.)	$S$ (eV.)	$A$ (eV.)	Addition of sodium <sup>b</sup>
Benzene	2.87	2.01	-0.36	nil
Diphenyl	2.15	1.67	+0.70	nil
Naphthalene	1.99	1.86	+0.67	slowly
Stilbene	1.61	1.58	+1.33	
Pyrene	1.57	1.79	+1.16	
1:4 Diphenyl butadiene	1.46	1.59	+1.47	rather easily
Anthracene	1.42	1.72	+1.38	easily
Triphenyl methyl	0.44	1.46	+2.62	very easily

increase is similar to the order of readiness of addition of alkali metals<sup>5</sup>. Thus the values of  $A$  have considerable qualitative and some quantitative support.

A seeming objection to the inclusion of  $S$  as a potential-determining factor is that the reduction (half-wave) potential was found<sup>1</sup> to give a linear plot against the coefficient,  $a$ , of the molecular orbital resonance integral, which is, of course, independent of solvation effects. But a plot of  $E + S$  against  $a$  is also linear (with deviations attributed to theoretical approximations in the admittedly first-order calculation of  $a$ ). Thus  $A$  depends linearly on  $a$  (see graph), and Maccoll's general conclusion<sup>1</sup> is unimpaired, although he made no allowance for solvation effects.



A, benzene; B, diphenyl; C, naphthalene; D, stilbene; E, pyrene; F, 1:4 diphenyl butadiene; G, anthracene; H, triphenyl methyl

Benzene is interesting because, of the molecules listed, it alone has a negative electron affinity. Benzene has not been reduced polarographically. Conditions to enable this to be done are now being sought in my laboratory. The point shown on the graph is estimated from the known  $a$  by Maccoll's original curve, corrected by the appropriate  $S$ .

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<sup>1</sup> Maccoll, *Nature*, **163**, 178 (1949).

<sup>2</sup> Hush, *Aust. J. Sci. Res.*, **A**, **1**, 480 (1948).

<sup>3</sup> Bent, *J. Amer. Chem. Soc.*, **52**, 1499 (1930).

<sup>4</sup> Swift, *J. Amer. Chem. Soc.*, **60**, 1403 (1938).

<sup>5</sup> Hückel, *Proc. Int. Conf. Physics* 1934, **2**, 1.

<sup>6</sup> Wawzownek *et al.*, *J. Amer. Chem. Soc.*, **64**, 1765, 2365 (1942); **68**, 2541 (1946).