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² Heimer, Tage, *Z. Phys.*, **78**, 771 (1932).

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Relation between Activation Energy and Frequency Factor

It has been frequently observed that in some series of kindred reactions the activation energy of the process appears to be functionally related to the respective frequency factor A . For example, when one investigates a reaction taking place in various solvents, one often finds that E (the activation energy) and A change in the same direction. Such behaviour might indicate that the variation in the nature of the solvent affects the degree of solvation of the transition state, and consequently the activation energy and the entropy of activation (that is, A) in the same direction.

It appears that such relations do not hold for series of kindred unimolecular reactions taking place in the gaseous phase. For example, it has been pointed out¹ that the unimolecular dissociation processes of the type:

have a constant frequency factor (apart from the statistical factor of 2 for the xylenes). However, since the activation energies for these processes vary by about 3 kcal./mole only, and the experimental errors involved in their determinations might be as large as ± 2 kcal./mole, this evidence is not very convincing. We have, therefore, been searching for a series of kindred reactions in which activation energies vary over a wide range in order to be able to draw some definite conclusions about the behaviour of the frequency factors.

The series of unimolecular dissociation processes of the type

seems to be suitable for such studies. Activation energies were determined for the following decompositions: allyl-bromide, trichlorobromo-methane, benzyl-bromide, benzoyl-bromide, methyl-bromide and phenyl-bromide. All these reactions were studied over a sufficiently wide range of temperatures to yield a reasonably accurate determination of E , and the results, computed by the least square method, are summarized in the accompanying table. (The frequency factor for CH_3Br decomposition has been computed by a different method; see, for details, ref. 5.)

Inspection of the table reveals that the frequency factors seem to be approximately constant for a variation in the activation energies of 24 kcal./mole. The approximate constancy of the frequency factors should be contrasted with variations in the rate constants, computed for one temperature, which vary by more than 10^6 . This evidence supports strongly the claim that for a series of kindred unimolecular dissociation processes, in which one bond only is

$R-Br$	Ref.	E kcal./mole	$A \times 10^{-13}$ sec. ⁻¹	k_{900K} sec. ⁻¹
$CH_3:CH.CH_2-Br$	4	47.5	0.5	16.0
Cl_3C-Br	5	49	2	30.0
$C_6H_5.CH_2-Br$	4	50.5	1	6.0
$C_6H_5.CO-Br$	6	57.0	5	0.60
CH_3-Br	5	~67	~2	0.001
C_6H_5-Br	7	70.9	2	0.00016
$\alpha.C_6H_5-Br$		70.9	3.5	0.00028

ruptured and the molecule is split into a radical and a free atom, the frequency factor is a constant, depending on the nature of the ruptured bond and independent of the structure of the molecule. This conclusion has been drawn previously², but the experimental evidence was less satisfactory³.

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² Szwarc and Leigh, *Nature*, **167**, 486 (1951).

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⁴ Szwarc, Sehon and Ghosh, *J. Chem. Phys.*, **18**, 1142 (1950).

⁵ Sehon and Szwarc, *Proc. Roy. Soc. A*, **209**, 97 (1951).

⁶ Ladaeki, Leigh and Szwarc, *Proc. Roy. Soc.* (in the press).

⁷ Szwarc and Williams, *J. Chem. Phys.* (in the press).

The Born Approximation in Electron Diffraction

THE Born approximation for the electron wave scattered by an atom has been universally employed for the interpretation of electron diffraction experiments directed toward the determination of molecular or crystal structure. There is some justification for this. Quantitative measurements of diffraction intensities performed to test the applicability of the approximation for electrons of the energies usually used in structure work have, on the whole, been regarded as satisfactory verifications. In structure work itself—in the work on gas molecules, for example—the considerable success resulting from its use has led to the feeling that even in the presence of heavy atoms there might not be serious error. There has perhaps been the implicit faith that whatever theoretical refinements were lacking would at least not alter substantially the structures to be derived. We have found, however, that there is a phase shift on scattering, not given by the first Born approximation (this is the familiar Born approximation, the first term of a power-series expansion in the parameter $\alpha = -Ze^2/hv$), which is approximately proportional to atomic number, depends on angle of scattering, and may become large and important. The suggestion of the existence of this phase shift arose from the cases of uranium hexafluoride (UF_6) and some other gas molecules.

Interpretations of electron diffraction data from uranium fluoride have uniformly led¹ to the conclusion that the U—F bond-lengths are not all equal; but other physical data (spectra, entropy, dipole moment) have all been interpreted² as demanding the regular octahedral structure. Altogether, although various arguments have been made to support the possibility of unequal bond-lengths, it would seem that the greater weight of the evidence is against it. The electron diffraction conclusions for a number of other molecules MX_n are strikingly similar, and show no obvious relation to known structural chemistry. On the contrary, they all split the bonds into essentially two equal