$$E_r = (1.5 + n_r - n_p)\alpha, \quad (1)$$

where α is the valence-bond exchange integral and n_r and n_p are the coefficients of α in the expression for the resonance energies of the reactant and product molecules respectively.

It would appear likely that the concept of the reactive structure might prove useful in a discussion of homolytic bicentric reactions between a series of molecules and a common reaction partner. Catalytic hydrogenation would appear to be a reasonable reaction to choose "since all the observed facts are in harmony with the conception that the catalyst in hydrogenation combines with both the hydrogen acceptor and the hydrogen"².

The main feature of catalytic hydrogenation may be explained on the basis of the reactive structure. The ease of hydrogenation of an isolated double bond follows at once from the low E_r for such a reaction ($n_r = n_p = 0$). On the other hand, the resistance of benzene to catalytic hydrogenation can be explained in terms of the large value of E_r , due to n_r being much greater than n_p . However, in the event of two atoms of hydrogen being added, E_r for the further addition becomes considerably decreased, and this is evidenced by the tendency for complete reduction of a benzene ring in a polycyclic compound. In general, the difficulty of reduction of conjugated systems relative to an isolated double bond is explicable in terms of n_r being greater than n_p , leading to large values of E_r . Another example of the use of the concept is afforded by the relative indifference to the position of addition in the case of butadiene, for in this case E_r is the same for both $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_2$ and $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2$.

The concept of the reactive structure lends theoretical support to the assumption used by Pauling and Sherman³ in their discussion of conjugated systems. These authors assumed that the product will be formed the more readily the greater its thermodynamic stability. This hypothesis was used in a discussion of the position of hydrogenation within a given molecule, and follows directly from (1). The purpose of the present note is to provide a basis for a discussion of relative ease of hydrogenation.

A fuller discussion of this subject will be presented elsewhere in due course.

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² Adkins, "Reactions of Hydrogen" (University of Wisconsin Press, 1937).

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Estimation of Polymer Distribution on the Basis of Differences between the Average Molecular Weights of Different Order

It is well known that the magnitude of the difference between the number and weight average molecular weight (M_n and M_w) in a polymer affords an indication of the degree of polydispersity. In order to obtain a numerical measure of the spread of molecular weights, and to reconstruct the distribution, the assumption is often made—though admissible only under certain conditions—that the distribution function is that of the log normal law¹⁻³, where the ratio between averages (the r th roots of

the r th moments about zero) of successive order is an exponential function of the logarithm of the geometric standard deviation, which is equal to the standard deviation of the logarithmic distribution.

It has, however, so far escaped observation that from a knowledge of M_n and M_w the standard deviation of the molecular weights can be calculated directly and exactly without any assumption whatsoever about the distribution law.

Defining M_n as

$$M_n = \frac{\sum M_i n_i}{\sum n_i},$$

as obtained, for example, by the osmotic pressure method; and M_w as

$$M_w = \frac{\sum M_i g_i}{\sum g_i} = \frac{\sum M_i^2 n_i}{\sum M_i n_i},$$

as obtained, for example, by the light scattering method, where n_i , g_i are the frequencies and weights, respectively, of the molecular species M_i , we form the product

$$M_n M_w = \frac{\sum M_i n_i}{\sum n_i} \times \frac{\sum M_i^2 n_i}{\sum M_i n_i} = \frac{\sum M_i^2 n_i}{\sum n_i}.$$

Since

$$\sigma_n = \sqrt{\frac{\sum M_i^2 n_i}{\sum n_i} - \left(\frac{\sum M_i n_i}{\sum n_i}\right)^2},$$

we have at once for the standard deviation of the number distribution:

$$\sigma_n = \sqrt{M_n M_w - M_n^2}.$$

Similarly, if in addition to M_w , M_z is defined by

$$M_z = \frac{\sum M_i^2 g_i}{\sum M_i g_i} = \frac{\sum M_i^3 n_i}{\sum M_i^2 n_i},$$

as obtained, for example, by the sedimentation equilibrium method (if the concentration gradient is observed by the refractive index method), we form again the product

$$M_w M_z = \frac{\sum M_i g_i}{\sum g_i} \times \frac{\sum M_i^2 g_i}{\sum M_i g_i} = \frac{\sum M_i^3 g_i}{\sum g_i},$$

and have for the standard deviation of the weight distribution

$$\sigma_g = \sqrt{M_w M_z - M_w^2}.$$

Knowing the mean and the standard deviation in either number or weight distribution of molecular weights, we are in a position to obtain a conservative estimate of the whole distribution by using the so-called Tchebycheff inequality⁴. According to that relation, the proportion of molecules with molecular weights differing from the mean weight by an amount not exceeding $\pm t$ times the standard deviation is, at least, $1 - 1/t^2$. By substituting arbitrary values for t ($5 > t > 1$), and subtracting the proportion for the smaller t from that for the next higher one, we obtain the relative frequencies (number distribution) or the weight fractions (weight distribution) of the molecular weight species at the specified distances from the mean.

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⁴ Weatherburn, C. E., "A First Course in Mathematical Statistics", 32 (Cambridge Univ. Press, 1947).