LETTERS TO THE EDITORS

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Number of Primes and Probability Considerations

THE probability that a number chosen at random is divisible by p is $\frac{1}{p}$ and consequently that it is not so divisible is $1 - \frac{1}{p}$. On simple probability considerations, that is, provided that these probabilities are independent of one another, the chance that a number is simultaneously not divisible by a group of primes is therefore $\Pi \left(1 - \frac{1}{p}\right)$. Hence the probability that a number in the neighbourhood of N^2 is prime should be $P(N^2) = \overset{p_N}{\underset{}{\Pi}} \left(1 - \frac{1}{p}\right)$ where p runs through the gamut of the primes from 2 to p_N the largest prime less than N. This product has the value $\frac{e^{-\gamma}}{\log p_N}$ where γ is Euler's constant.

If P is the probability of a number in a given region being prime, the number of primes in an interval $\triangle$ in this region must be on the average $\triangle.P$. Hence the number of primes in an interval $\triangle$ in the neighbourhood of N^2 should approach $\frac{\triangle}{e^{\gamma}} \frac{1}{\log p_N}$.

For large values of N, we may substitute $\log N$ for $\log p_N$, since the interval between successive primes is of the order $\log N$. Hence the number of primes in an interval $\triangle$ in the neighbourhood of N^2 should tend to $\frac{\triangle}{e^{\gamma}} \frac{1}{\log N}$. The correct answer, of course, is $\frac{\triangle}{2} \frac{1}{\log N}$, that is, about 11 per cent smaller.

It is curious that simple elementary probability considerations should give an answer so nearly right, but just failing by such a small fraction. It seems to imply that the probabilities are not strictly independent, that there is a slight tendency of factors to avoid one another; in other words, that after all the numbers in an interval divisible by $p_1, p_2, p_3 \ldots p_l$ have been eliminated, the chance that one of the remaining numbers should be divisible by another prime p_m is rather greater than $\frac{1}{p_m}$.

Perhaps a reader of NATURE can throw light on this question.

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Effect of Negative Groups on Reactivity

RECENT experimental and theoretical studies of bond strength[1] have shown that our forecast[2], according to which in the series of gas reactions $Na + XR = NaX + R$ (X = halogen, $R = R_1, R_2 \ldots$) the reactivity is inversely related to the bond strength C–X, holds true for hydrocarbon radicals R_1, $R_2 \ldots$ containing no negative groups. But the great acceleration caused by the presence of such negative groups ($X_1, X_2 \ldots$) in reactions of the type $Na + XRX_1 = NaX + RX_1$ is as yet unexplained. The presence of these groups is not usually considered to weaken the bond strength C–X. In fact, it has been suggested by Pauling that, when $X_1, X_2 \ldots$ are halogen atoms attached to the same carbon as X, the strength of all the halogen bonds is rather increased than decreased by resonance[3]. Moreover, observations on the bond energy of acetyl iodide[1] failed to reveal any such weakening of the carbon halogen bond by the negative substituent ($=O$), which could explain that acetyl chloride reacts much faster with sodium vapour than does C_2H_5Cl [4].

A specific effect of negative substituents on reactivity can be deduced from the fact that in the presence of a negative substituent the transition state will resonate between three structures instead of the usual two. We shall have:

1.   (*a*)   Na ... XRX$_1$
        (*b*)   Na$^+$X$^-$ ... RX$_1$
        (*c*)   Na$^+$ ... XR ... X$^-_1$

the component state *c* being due to the presence of the negative substituent X_1.

Take the case of a number of halogen atoms $X, X_1, X_2 \ldots$ in the molecule. A sodium atom approaching a polyhalogenated alkyl will interact simultaneously with each of the halogen atoms $X, X_1, X_2 \ldots$ in the sense of the transfer of an electron: Na + C̶ — X = Na$^+$ ... C̶ ... X$^-$ and likewise for C̶ — X$_1$, C̶ — X$_2$ ... Each of these transfers may be considered as leading to an alternative final state, producing a different alkali halide molecule with the pairs of ions (Na$^+$ ... X$^-$, Na$^+$ ... X$^-_1$ ...) separated by various distances. All these alternative final states will resonate jointly in any transition state arising in a reaction of a sodium atom with a polyhalogenated alkyl, and will depress the activation energy.

This resonance will increase steadily with the number of halogens $X_1, X_2 \ldots$ present in the molecule and also with their specific tendency to react with the sodium atom. The first part of this statement is patently confirmed by the observed cumulative accelerating effect which halogen atoms have on the reaction rate[4]; the second part may be analysed and tested as follows. Let us first think of all X's as being the same halogen, say, chlorine. The energy of the alternative transfer of the electron to the different Cl atoms increases with the electrostatic energy of the pair Na$^+$ ... Cl$^-$, which is inversely proportional to the distance at which the halogen is situated from the Na atom at the moment of reaction, that is, in the transition state. Hence the reactivity of di-chloro compounds should increase