The Perfect Buffer

CONSIDER a solution containing (*a*) equivalents of a weak acid, HA, and (*b*) equivalents of a strong base. For this to be a perfect buffer it may presumably be stated that the rate of change of *p*H with added acid or base must be a minimum; that is, $dp\mathrm{H}/db$ is to be a minimum, or $d^2p\mathrm{H}/db^2 = 0$. For a weak acid: $C_{\mathrm{H}} \cdot C_{\mathrm{A}}/C_{\mathrm{HA}} = k$. Since the salt will be practically 100 per cent ionized and the acid negligibly so, it follows that $C_{\mathrm{A}} = b$, and $C_{\mathrm{HA}} = (a - b)$, $\therefore\ C_{\mathrm{H}} \cdot b\,(a - b) = k$ (1). By taking natural logarithms and differentiating twice with respect to *b* it is easily shown that $b = \frac{1}{2}\,a$ (2), and by substitution from (1) that $C_{\mathrm{H}} = k$. The perfect buffer solution should thus consist of two equivalents of a strong base together with one equivalent of a weak acid having a dissociation constant equal to the hydrogen-ion concentration required. This has long been known as an empirical relation, but we believe the above derivation to be original.

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Reactions of Organic Halides in Solution

IN a recent note[1], I discussed those reactions of organic halides in solution which involve substitution by a nucleophilic reagent at a saturated carbon atom. In reply to the letter by Profs. Hughes and Ingold[2] on this subject, I wish to make the following points.

In my note[1] I stated that the decrease in the bimolecular S_N2 reaction-rate of the halide $R-X$ as R varies along the series methyl, ethyl, *sec.*-propyl, *tert.*-butyl, is attributed by Hughes and Ingold to the increase in electron accession to the reaction centre. In disagreeing with this statement, Profs. Hughes and Ingold say that they regard the polar and steric effects as both contributing to the structural influence on rate[2]. At the time of publication of my note, however, Hughes had estimated the steric compressions involved in the S_N2 reactions of $R-X$ for the methyl, ethyl, *n*-propyl, *iso*-butyl, *neo*pentyl series only. For the reaction of these halides with sodium ethoxide, Hughes had concluded (as mentioned in my communication[1]) that "The rate relationships for the first four members are fairly normal for the bimolecular mechanism, the rate of which is decreased by electron-accession to the reaction centre, but the introduction of the last β-methyl substituent has obviously introduced an effect which is far larger than that to be expected on the basis of its capacity for the release of electrons. . . . This effect is believed to be of steric origin."[3] This indicates that steric hindrance was considered to be unimportant in the bimolecular S_N2 reactions of $R-X$ when R is methyl and ethyl. The part played by steric hindrance in these reactions when R is *sec.*-propyl and *tert.*-butyl had not been specifically considered by Hughes and Ingold at this time. (Calculations of the steric compressions involved in the methyl to *tert.*-butyl series had been made, however, by A. G. Evans and M. Polanyi[4].)

With regard to the fact that an electron-attracting group often accelerates bimolecular nucleophilic substitutions in spite of steric hindrance, I did not state that the polar effect is "absent in general from bimolecular nucleophilic substitutions"; I stated that there is strong evidence that the decrease in rate of the bimolecular substitution reactions of $R-X$ with nucleophilic reagents for the series methyl, ethyl, *sec.*-propyl, *tert.*-butyl, and ethyl, *n*-propyl, *iso*-butyl, *neo*-pentyl, can be interpreted in terms of steric hindrance, but not in terms of electron accession to the reaction centre.

As regards the ambiguity of the polar effect in bimolecular reactions, I compared the behaviour of allyl chloride and its α- and γ-methyl derivatives, because I believe that this is an example in which ambiguity concerning the polar effect of the methyl group can be eliminated, and that the importance of the steric effect in bimolecular substitution reactions can thus be demonstrated for α-methyl groups and hence for the series methyl, ethyl, *sec.*-propyl, *tert.*-butyl.

Finally, the activation energy for the ionization of $R-X$ is determined not only by (*a*) the ionization potential of R, but also by (*b*) the bond strength of $R-X$, and (*c*) the heat of solution of R^+. For the methyl, ethyl, *sec.*-propyl, *tert.*-butyl series, changes in factors (*b*) and (*c*) are approximately equal in magnitude and have opposite effects upon the activation energy of the ionization reaction. Thus, along this series it is the great decrease in factor (*a*), the ionization potential of R, which is responsible for the marked increase in the rate of ionization (this point is discussed in detail in a forthcoming publication). For some other series, on the other hand, it may well be that the sequence of ionization rates is mainly determined by changes in factor (*b*), the bond strength of $R-X$, or in factor (*c*), the heat of solution of R^+.

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[1] Evans, A. G., *Nature*, **157**, 438 (1946).
[2] Hughes and Ingold, *Nature*, **158**, 94 (1946).
[3] Hughes, *Trans. Farad. Soc.*, **37**, 621 (1941).
[4] Evans, A. G., and Polanyi, *Nature*, **149**, 608 (1942).

Survival of Oyster and Other Littoral Populations

THE problem of the maintenance of marine littoral populations and especially that of the European oyster (*O. edulis*) in Great Britain as discussed by Gross and Smyth in *Nature*[1] is one of great interest. In all species it is reasonable to assume that the properties of each particular organism give a measure of its attunement to the environment in its recent past, if not to the present. The supreme criterion and one hard fact of the sum of its relationships to life conditions is the number of young (larvæ) produced during the life of the individual. This provision of young has ensured survival of the species in the past against predators, parasites, competitors and normal and abnormal deviations in the total of chemico-physical conditions over the range of the environment. In a given locality, however, it is reasonable to infer that extinction may occur or tend to occur if the full span of life is not attained by the normal adult population. If, therefore, the normal span of life is reduced in any locality, fewer young will be produced over that period of time which has ensured survival in the species as a whole, and a combination of local unfavourable conditions—or indeed any single one of a significant nature—will reduce the chance of survival and may result in local extinction.

As there is a tendency on oyster beds for all the larger oysters to be removed, it is fairly certain that the span of life in many localities has been reduced in the last few centuries; this factor must therefore be added to those given by Gross and Smyth as inimical to survival. The provision of a central spawning stock of large oysters has been advocated[2] and would be generally valuable in all producing areas.

Another important factor of biological significance is the great reduction in the number of holders of scattered small plots. An oyster bed is only assured of survival when the larvæ set free are returned in oscillations of the estuarine water[3] to that bed. Where there is only one part of a locality used as an oyster bed, the chance of larvæ returning to that particular spot has a low degree of probability; if there are twenty places in the same locality, the chance of larvæ returning to one or other of the twenty suitable places has a relatively high degree of probability, and survival in that locality is enhanced.

With regard to the suggestion of mass hybridization, this has virtually had a chance of operating in the Thames Estuary, where oysters have been imported by the oyster merchants themselves at one time or another from Brittany and other parts of France, Scheldte, Norway, Falmouth, Poole, Swansea and other parts of England and the west coast of Ireland. But the assumption that cross-fertilization occurs is not entirely warranted. "Fertilisation almost always occurs in the oviduct as Hoek deduced long ago (1883); but it is still a matter of conjecture to what extent cross-fertilisation occurs. Since females on English beds nearly always carry some sperm-morulæ amongst the eggs, self-fertilisation will nearly always be possible. On the other hand [functionally] pure males undoubtedly exist and spawn, and Hoek has described accumulations of sperm in diverticula of the renal duct of egg-bearing individuals. Thus sperm may be either collected from the individual itself [as a relict from the male phase] or from some other individual, so far as we know at present. Researches on this important aspect of oyster-culture are difficult and are [still] urgently needed. It is quite clear therefore that self-fertilisation may occur; whether cross-fertilisation occurs is not known, but is biologically probable."[4]

It should not be forgotten that *O. edulis*, like its near allies, is essentially an inhabitant of temperate regions, and it is significant that no temperate allied form occurs on the north-west shores of the United States of America—which come under the influence of the cold Labrador current—at latitudes similar to those of the prolific oyster-producing beds of France.

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[1] Gross, F., and Smyth, J. C., *Nature*, **157**, 540 (1946).
[2] Orton, J. H., *J. Mar. Biol. Assoc.*, **14**, 626 (1927).
[3] Orton, J. H., *Nature*, **123**, 453 (1929).
[4] Orton, J. H., *Mem. Roy. Hist. Mus. Nat. Belg.*, Ser. 2, **3**, 1003 (1936).

A Revival of Natural Oyster Beds ?

AT one time immensely rich natural oyster beds fringed many of the coasts of western Europe. Those of the French and Scottish coasts yielded tens of millions of oysters annually, but the banks along the English, Dutch, German and Danish coasts were by no means negligible. These oyster beds disappeared, no doubt through overfishing, and a few poor remnants, scattered along our coasts, economically of little or no importance, remind us of the once important fishery on the natural oyster beds. Only in France and Holland were new methods adopted in time, and an intensive oyster culture, spreading prosperity in the regions concerned, took the place of the old free fishery on the natural beds.

Recently, both British and German men of science[1,2] have tried to contrive a plan to restore the wealth of the natural oyster beds. Both recognize fully that overfishing was the cause of the decline, but they cannot understand why the natural oyster beds failed to recover after the termination of the fishery and even after re-laying reasonable quantities of French and Dutch oysters. Both ascribe recent failures of efforts to raise the population of remnants of natural oyster beds to inadequate properties of the mother-oysters used, and suggest the selection of certain strains of oysters, or even mass-hybridization; and both hope that a general revival of the once prolific oyster beds will start from the moment that a limited stock of mother-oysters of the desired qualities occupies the banks.

I feel fairly sure, however, that both plans are doomed to failure, as in both the same mistake is made: the reproductive power of the oyster, *Ostrea edulis* L., has been over-rated. Repopulation of natural oyster banks is possible as soon as natural reproduction surpasses natural mortality. Mortality in oyster populations is far from negligible, and the possibilities for natural reproduction are generally highly over-rated. 500,000–1,000,000 larvæ in one incubating mother oyster is indeed an enormous and promising number. But my data[3] collected in the Oosterschelde show that about 10 per cent of the planktonic larvæ are destroyed by plankton-eating animals during each tidal cycle, and 4 per cent are swept away by currents to areas unfavourable for fixation in the course of one tidal cycle; the latter figure will certainly be much higher in estuaries less enclosed than the basin of the Oosterschelde. Water-temperature influences the rate of development of the larvæ, low temperatures slowing it up. In the Oosterschelde, about 5 per cent of the larvæ produced reach the 'mature' stage, ready for fixation, at 20° C.; about 2½ per cent at