TABLE I

ISOTOPIC DISTRIBUTION PATTERNS

Number of D atoms	Addition to 1-hexene		Exchange with hexane	
	42°	150°	201°	350°
0	0.6%	1.9%	95.6%	73.3
1	4.9	15.4	4.2	17.6
2	89.5	53.6	0.2	2.7
3	4.3	19.7		0.82
4	0.7	5.8		.72
5		1.7		.80
6		0.8		.89
7		.5		.84
8		.3		.69
9		.2		.57
10				.42
11				.29
12				.22
13				.10
14				.02

At 150°, however, the distribution pattern is broader (Table I) and somewhat resembles patterns observed with nickel catalysts. Intermediate temperatures yield intermediate patterns.

At 0°, ethylene gives ethane-d_2, but, at −78°, reaction is incomplete and the product is ethane-d_2 and undeuterated ethylene.

Table I presents distribution patterns for isotopic exchange between hexane and deuterium. Correction for multiple adsorption shows that only a single deuterium atom is exchanged upon adsorption of hexane. The multiple exchange of low intensity at the higher temperature probably results from dehydrogenation to hexenes followed by rehydrogenation. Metallic catalysts give quite different patterns characterized by extensive multiple exchange.[4,5,6]

Acknowledgment.—This investigation is supported by the Petroleum Research Fund of the American Chemical Society. Mr. S. Meyerson of the Standard Oil Company (Indiana) assisted us with mass spectroscopy.

(4) S. O. Thompson, J. Turkevich and A. P. Irsa, THIS JOURNAL, **73**, 5213 (1951).

(5) R. L. Burwell, Jr., and W. S. Briggs, *ibid.*, **74**, 5096 (1952); H. C. Rowlinson, R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **59**, 225 (1955).

(6) C. Kemball, *Proc. Roy. Soc. (London)*, **223A**, 361 (1954).

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FRACTIONAL DIALYSIS WITH CELLOPHANE MEMBRANES

Sir:

Preliminary data[1] concerned with fractional dialysis with cellophane indicated the possibility of unexpected selectivities for the separation of mixtures of dialyzable solutes. Further study has confirmed this indication and shown that considerable improvement in selectivity, adaptability and interpretability is possible particularly with solutes of larger molecular size which scarcely pass through the membrane.

(1) L. C. Craig and T. P. King, THIS JOURNAL, **77**, 6620 (1955).

A simple modification of the cell reported for fractionation purposes[1] adapts it for analytical work with 5–10 mg. of substance. In this the inside glass tube nearly displaces all the volume in the sac[2] and leaves only space for a thin film of solution. Stirring with nitrogen is now not required and a faster rate of dialysis is obtained by the resulting increase in the membrane area with respect to the inside solution volume. The outside solution can be replaced by fresh solvent at arbitrary intervals and analyzed for determination of the escape rate.

Under these conditions the escape rate expressed as decrease in precentage of the original remaining in the sac with time should be independent of the amount taken provided a single solute is present which behaves ideally. A plot of the logarithm of the percentage against time should give a straight line. This has been found to hold experimentally with many solutes. Thus in Fig. 1, curve 1 gives the escape rate of bacitracin A (solvent is 0.1 *N* acetic acid), curve 2 that of aspartic acid.

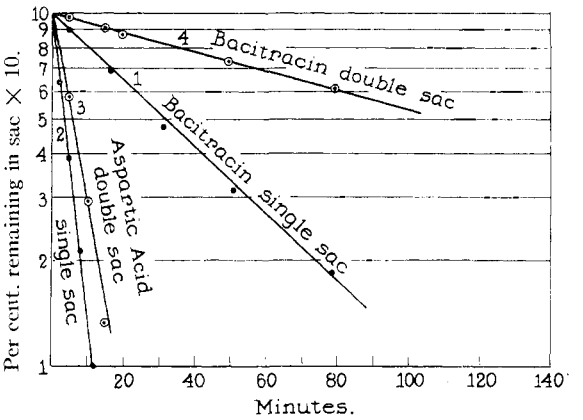

Fig. 1.

For the separation of mixtures greatly improved selectivity can be obtained by choice of solvent, the particular size of tubing, treatment of the membrane, etc. As an example curves 1 and 2 are escape rates respectively of aspartic acid and bacitracin A (mol. wt. 1421) through single membranes of Visking 18/32 seamless cellulose tubing while 3 and 4 are those found for double membranes (one sac inside the other).

That the improved selectivity holds for a mixture is shown by comparison of Figs. 1 and 2. In Fig. 2 a mixture of 10 mg. each of bacitracin and aspartic acid was studied. Curve 1 is a weight curve. Curve 2 is an optical density curve (255 mμ) referring only to bacitracin. Curve 3, that of aspartic acid, can be calculated from the values in 1 and 2.

The significance of this general approach for studying homogeneity with respect to size and/or shape (and perhaps charge) under extremely mild conditions is self evident. Comparison with similar solutes of known size gives a good estimation of size for the unknown.

Although different sizes of Visking have shown great variation in selectivity and permeability

(2) W. H. Seegars, *J. Lab. Clin. Med.*, **28**, 897 (1942).

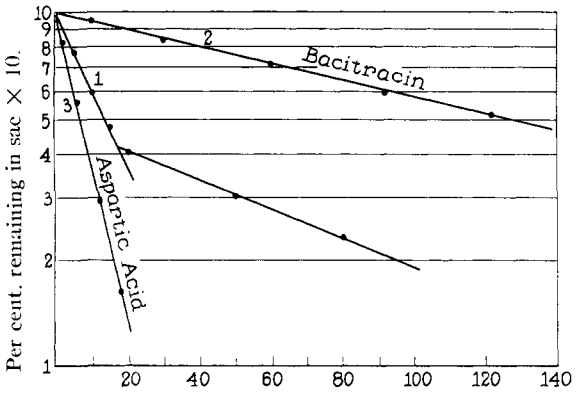

Fig. 2.

different membranes prepared from the same roll appear remarkably reproducible. The most permeable one thus far studied (No. 20/32 "Dialysis tubing")[3] has been found to pass insulin, ribonuclease, lysozyme and chymotrypsinogen in 0.1 *N* acetic acid at characteristically different rates (50% escape times in same cell are 1.6, 3.5, 3.5 and 5 hr., respectively). The membrane permeability can be increased by mechanical stretching so that ovalbumin readily passes.

A full account of this work will be reported soon.

(3) Light and Simpson, *Biochem. Biophys. Acta*, **20**, 251 (1956), found the 20/32 size to pass insulin.

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THE STRUCTURE OF OXIMES

Sir:

Pitt,[1] in a review article, has suggested that oximes should be represented as $R_2C{=}{}^{+}NH{-}O^{-}$ rather than, as ordinarily written, $R_2C{=}N{-}OH$. However, the weight of more recent evidence, set forth below, favors the classical formulation of $R_2C{=}N{-}OH$. The basis for Pitt's suggestion was a preliminary report of the crystal structure determination of *syn-p*-chlorobenzaldoxime.[2] The hydrogen bonding in this crystal was said to be: N. . .O distances of 2.82 Å., with the angles: O–N . . .O′ = 101.4° and N–O. . .N′ = 82°. Since the former is closer to that expected for a covalent bond angle (the hydrogen atom is assumed to lie on or near the N. . .O′ and O. . .N′ axes), the structure $R_2C{=}{}^{+}NH{-}O^{-}$ is indicated. The final results of this structure determination have not yet been published. Dunitz and Robertson[3] later discussed Pitt's suggestion, pointing out that the structure found for acetoxime,[4] with angles O–N. . .O′ of 124° and N–O. . .N′ of 111°, was compatible with either structure, but the results in the case of dimethylglyoxime[5] probably supported Pitt's suggestion. As pointed out by Dunitz and Robertson,[3] Merritt and Lanterman's dimethylglyoxime paper contains an obvious error, since the latter authors stated that both of the above angles equal 75.9°, an impossible situation since the two oxime groups are related by a center of symmetry; Dunitz and Robertson then assumed, apparently by inspection of the published projection of the structure on (001), that the angle N–O. . .N′ was smaller and equal to 75.9°, and that the angle O–N. . .O′ was its supplement, and therefore closer to that expected for the covalent bond. Unfortunately, there is yet another error, for the published parameters give instead for these angles 85° for N–O. . .N′ and 95° for O–N. . .O′, and these are close enough together to cause the argument to lose considerable force.

Additional information relative to this question has appeared recently, namely, the results of the crystal structure of formamidoxime.[6] For this molecule the situation is somewhat more complicated because there are more than just the two tautomeric structures possible. Nevertheless, detailed considerations show that the hydrogen bonding in this crystal is consistent with only two structures, I: $NH_2{-}CH{=}N{-}OH$, and II: $^{-}NH{-}CH{=}N{-}{}^{+}OH_2$. (Each of these has more than one resonance form.) The structure $NH_2{-}CH{=}{}^{+}NH{-}O^{-}$ is in particular eliminated because both atoms which form hydrogen bonds with the oxime nitrogen atom lie so far from the molecular plane that this atom must be the acceptor atom in these two hydrogen bonds. Structure II above, may be rejected[6] on the ground that the relative electronegativities of oxygen and nitrogen will render both of its resonance forms unstable. We are thus left with Structure I, and the observed bond lengths indicate that the formamidoxime molecule is best represented as a resonance hybrid, the predominant forms being $NH_2{-}CH{=}N{-}OH$ and $^{+}NH_2{=}CH{-}N^{-}{-}OH$, which contribute about equally, and perhaps a small contribution of the form $NH_2{-}{}^{-}CH{-}N{=}{}^{+}OH$.

At present, therefore, it appears that the usual oxime structure, $R_2C{=}N{-}OH$, is correct, but obviously a direct location of the hydrogen atoms in an oxime by use of accurate three dimensional X-ray data, or by neutron diffraction, would be highly desirable.

(1) G. J. Pitt, *Annual Reports of the Chemical Society*, **47**, 457 (1950).
(2) B. Jerslev, *Nature*, **166**, 741 (1950).
(3) J. D. Dunitz and J. H. Robertson, *Annual Reports of the Chemical Society*, **49**, 378 (1952).
(4) T. K. Bierlien and E. C. Lingafelter, *Acta Cryst.*, **4**, 450 (1951).
(5) L. L. Merritt and E. Lanterman, *ibid.*, **5**, 811 (1952).
(6) D. Hall and F. J. Llewellyn, *ibid.*, **9**, 108 (1956).

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THE STRUCTURES OF SINIGRIN AND SINALBIN; AN ENZYMATIC REARRANGEMENT

Sir:

The myronate ion, isolated as the potassium salt sinigrin in 1839, is the precursor of the isothiocyanate of black mustard and horseradish and the prototype of mustard oil glucosides. The currently accepted structure (I, R = $H_2C{=}CHCH_2$), proposed in 1897,[1] rested on the enzymatic hydrolysis of sinigrin to allyl isothiocyanate, D-glucose and bisulfate ion, the cleavage by silver nitrate to glucose and silver sinigrate, $C_4H_5O_4NS_2Ag_2$, a mer-

(1) J. Gadamer, *Arch. Pharm.*, **235**, 44 (1897).