and more reliable than the reduction with zinc dust and water, described by Gabriel and Coleman.[4]

An attempt was also made to reduce 4-methyl-2,6-dichloropurine[5] by the same method. According to E. Fischer,[6] however, the expected 7-methyl-2-chloropurine is not stable in contact with dilute alkali, but is converted into 7-methyl-2-hydroxypurine (m.p. 323°) and an unidentified substance of the composition $C_5H_7ClN_4$ (m.p. 251°). Indeed, two substances of these melting points, respectively, were isolated, when the reaction product was worked up.

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(5) E. Fischer, *ibid.*, **30**, 2400 (1897).

(6) E. Fischer, *ibid.*, **31**, 2550 (1898).

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Integral Diffusion Coefficients of Potassium Chloride Solutions for Calibration of Diaphragm Cells

BY R. H. STOKES

Gosting[1] has recently obtained absolute measurements of the differential diffusion coefficients of potassium chloride in water at 25° from 0.1 *N* to 3.9 *N* by the Goüy interference technique. Harned and Nuttall,[2] using a conductimetric method, have also obtained absolute values in the range 0.00125 *N* to 0.5 *N*, which are in extraordinarily good agreement with those of Gosting in the overlapping part of the range. Thus the combined data may be used with complete confidence for testing and calibrating other types of diffusion apparatus. For diaphragm-cell measurements, however, it is convenient to start the diffusion with solution on one side of the diaphragm and pure water on the other,[3] in which case the diffusion coefficient obtained is a rather complicated average value, $\bar{D}$, called the "diaphragm-cell integral coefficient."

Under these conditions, denoting the mean of the initial and final concentrations on the solution side by c_m', and the mean concentration on the other side by c_m'' (which is half the final concentration on the side which was initially pure water), it has been shown[3] that

$$\bar{D}^0_{(c_m')} = \bar{D} - \frac{c_m''}{c_m'}\left[\bar{D} - \bar{D}^0_{(c_m'')}\right] \qquad \text{(1a)}$$

or

$$\bar{D} = \left[\bar{D}^0_{(c_m')} - \frac{c_m''}{c_m'}\bar{D}^0_{(c_m'')}\right] \Big/ \left(1 - \frac{c_m''}{c_m'}\right) \qquad \text{(1b)}$$

Here the quantity $\bar{D}^0_{(c)}$ is the "integral diffusion coefficient for a run of vanishingly short duration" between the concentration c and pure water, given by

$$\bar{D}^0_{(c)} = \frac{1}{c}\int_0^c D\mathrm{d}c \qquad \text{(2)}$$

D being the true differential diffusion coefficient as measured for example by the optical or conductimetric methods. It is consequently very useful in diaphragm-cell work to have a table of values of the quantity $D^0_{(c)}$ for all values of c for the calibration solution, as it is then unnecessary to select a particular length of run or initial concentration of the calibration solution, and the cell may readily be checked for constancy of "cell constant" over a range of concentration. Table I provides these data, obtained by tabular and graphical integration of the results of Gosting and of Harned and Nuttall according to equation (2).

TABLE I

INTEGRAL DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE SOLUTIONS AT 25°

$\bar{D}^0 = \frac{1}{c}\int_0^c D\mathrm{d}c$. ($c$ in moles/liter, $\bar{D}^0$ in cm.^{2} sec^{-1} × 10^{-5})

c	$\bar{D}^0$	c	$\bar{D}^0$	c	$\bar{D}^0$
0.000	1.996	0.05	1.893	1.4	1.874
.001	1.974	.07	1.883	1.6	1.882
.002	1.966	.1	1.873	1.8	1.892
.003	1.960	.2	1.857	2.0	1.901
.005	1.951	.3	1.850	2.5	1.927
.007	1.945	.5	1.848	3.0	1.953
.01	1.938	.7	1.851	3.5	1.979
.02	1.920	1.0	1.859	3.9	2.000
.03	1.908	1.2	1.866		

TABLE II

FURTHER DIAPHRAGM CELL MEASUREMENTS ON POTASSIUM CHLORIDE SOLUTIONS AT 25°

c_m' in moles/liter, $\bar{D}^0_{c_m'}$ in cm.^{2} sec.$^{-1}$ × 10^{-5}

c_m'	$\bar{D}^0_{c_m'}$	c_m'	$\bar{D}^0_{c_m'}$
0.3877	1.853	0.8721	1.854
.3911	1.849	.8344	1.854
.6310	1.842	.8820	1.851
.6188	1.851	.8972	1.852
.6462	1.851		

In the figure, the data of Table I are compared graphically with the diaphragm-cell results previously reported by the writer.[3] (The open circles on this graph represent the means of each pair of approximately duplicate runs reported in Table III of reference (3).) It is clear that, though the average deviation of the points from the standard curve is less than 0.3%, most of this deviation is due to the points near the minimum. As the measurements represented by these points hap-

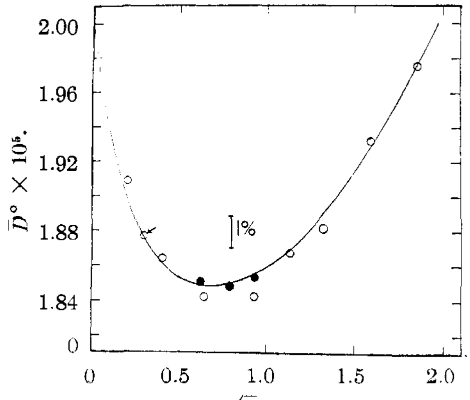

Fig. 1.—Integral diffusion coefficients of potassium chloride at 25°: full curve, calculated from differential values of Gosting, Harned and Nuttall (Table I); open circles, original diaphragm-cell measurements (reference 3); filled circles, new measurements (Table II); arrow, calibration point for diaphragm-cells.

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(1) L. J. Gosting, THIS JOURNAL, **72**, 4418 (1950).

(2) H. S. Harned and R. L. Nuttall, *ibid.*, **69**, 736 (1947); **71**, 1460 (1949).

(3) R. H. Stokes, *ibid.*, **72**, 763, 2243 (1950).

pened to be among the earliest made in the development of the magnetically-stirred diaphragm-cell, and were possibly not of the standard of precision obtained later, it seemed worthwhile to make some further measurements in this region. The technique used was closely similar to that described in reference (3), and gave the results in Table II, where the $\bar{D}$ values have been converted to D^0 values by the use of equation (1a). The means of the four new measurements using initially 1 N potassium chloride solution, the three using initially 0.7 N solution and the two using initially 0.45 N solution are shown as filled circles in the figure. It is evident that the original measurements near the minimum were in error by two or three times the estimated experimental error of 0.2%. In consequence of this, the smooth curve drawn through the open circles was appreciably different in shape near the minimum from what it should have been. Hence the differential diffusion coefficients obtained from it and reported in reference (3) differ in some cases by nearly 1% from those reported by Gosting.[1] It would appear that in using the diaphragm-cell method especially great care should be taken in regions of rapid change of slope of the integral diffusion coefficient. With this reservation it is clear that the diaphragm-cell measurements agree very well with the new absolute data obtained by Gosting.

In conclusion it would perhaps be as well to mention that in calibrating diaphragm-cells with the use of Table I, it is unwise to use any solution below 0.1 N in concentration at the start of the experiment, as at lower concentrations the anomalous surface-transport effect[3] becomes prominent.

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Allyl Butyl Ethers[1]

BY E. A. TALLEY, ANN S. HUNTER AND E. YANOVSKY

It has been suggested that in our work on allyl starch,[2] one of the butyl alcohols might serve as a reaction solvent. The obvious objection to the use of alcohols in this reaction is the formation of ethers at the expense of allyl halide used for the main reaction. When an attempt was made to separate the allyl butyl ethers by fractionation of the organic layer of the reaction, azeotropes of the ether and alcohol were obtained.[3] Since attempts to separate the two by extracting the butyl alcohols with water were unsuccessful, at least in the case of normal and isobutyl alcohols, it was deemed advisable to learn more about the properties of pure allyl butyl ethers. In the literature, only the allyl isobutyl ether has been reported.[4] It was prepared by catalytic dehydration of a mixture of the two corresponding alcohols. The boiling point (108–110°) was the only property given. We have, therefore, prepared the four allyl butyl ethers and determined some of their properties.

Experimental

Preparation and Properties of Allyl Butyl Ethers.—All ethers were prepared in the same manner. One to one and a half moles of butyl alcohol in 200 to 300 cc. of xylene was placed in a 1-liter three-necked flask furnished with a condenser, a stirrer and a separatory funnel. An equimolar quantity of sodium was gradually added to the solution. After the entire amount of sodium had been added, the reaction slowed down somewhat owing to coating of alkoxide on the metal. At this point, the bath temperature was raised to about 115° and the stirrer was started. The sodium melted, and the reaction proceeded. After all the sodium had disappeared, the flask was cooled to room temperature, and an equimolar amount of allyl bromide was gradually added through the separatory funnel. When the entire amount of allyl bromide had been added, the bath temperature was raised to 110–115° and kept at this temperature for about five hours. If any blue color remained at this time, methanol was added until the blue color disappeared. The mixture was then washed with water, dried and distilled. The theoretical amounts of allyl bromide were used for convenience of procedure at the expense of better yields. Under the conditions of the experiments, the yields were about 25% for the allyl *t*-butyl ether, 40% for the ether of isobutyl alcohol and 60% for the ethers of normal and secondary butyl alcohols.

Table I gives the properties of the four ethers.

TABLE I

PROPERTIES OF ALLYL BUTYL ETHERS

Butyl group	Allyl (by Wijs), % (theory, 36.0%)	B.p., °C.	Mm.	d^{20}_4	$n^{20}D$	Mole refraction Calcd.[a]	Mole refraction Found
Normal	36.0	117.8–118.0	763	0.7829	1.4057	35.87	35.80
Secondary	36.0	107.1–107.4	762	.7792	1.4023	35.70	35.70
Iso	36.0	106.6–107.0	749	.7735	1.4008	35.90	35.85
Tertiary	36.1	99.2–100.0	760	.7770	1.4011	35.83	35.71

[a] A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).

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[1] Contribution from one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] P. L. Nichols, Jr., R. M. Hamilton, Lee T. Smith and E. Yanovsky, *Ind. Eng. Chem.*, **37**, 201 (1945); E. A. Talley, R. M. Hamilton, J. H. Schwartz, C. A. Brown and E. Yanovsky, U. S. Dept. Agr., Bur. Agr. and Ind. Chem., AIC-140. (Eastern Regional Research Laboratory) Feb. 1947 (Processed).

[3] *Cf.* D. N. Kursanov and O. M. Shemyakina, *Doklady Akad. Nauk S. S. S. R.*, **62**, 341–343 (1948); *C. A.*, **43**, 2159*b* (1949).

[4] A. Mailhe and F. de Godon, *Bull. soc. chim.*, [4] **27**, 328 (1920).

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Unsaturated Lactones. II. The Relationship Between Chemical Constitution and Absorption Spectra in a Group of Crotonolactones[1]

BY F. W. SCHUELER AND CALVIN HANNA

In a previous report[2] we had occasion to discuss the relationship between chemical constitution and the ultraviolet absorption spectra in a group of unsaturated azlactone derivatives. In the present communication we have extended this discussion to include a series of crotonolactones which derive part of their interest from the close chemical and physical similarities that they hold with respect to the unsaturated azlactones.

Out of a group of twenty crotonolactones[3] synthesized during this investigation four were re-

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[1] This work was aided by a grant from the U. S. Public Health Service.

[2] F. W. Schueler and S. C. Wang, THIS JOURNAL, **72**, 2220 (1950).

[3] These together with the azlactones and a group of related materials have been studied for cardiac activity and reported elsewhere. F. W. Schueler and C. Hanna, *Arch. Intern. Pharmacodyn. et Therapie*, in press, 1951.