

Whence

$$[C_4H_8'] = \frac{k_1 [C_2H_4]^2}{k_2 + k_3 [C_2H_4] + k_4 [C_2H_4]}$$

Finally

$$\begin{aligned} + \frac{d[C_4H_8]}{dt} &= k_3 [C_2H_4] [C_4H_8'] \\ &= \frac{k_1 k_3 [C_2H_4]^3}{k_2 + k_3 [C_2H_4] + k_4 [C_2H_4]} \end{aligned}$$

When the ethylene concentration is high, this reduces to

$$+ \frac{d[C_4H_8]}{dt} = \frac{k_1 k_3}{k_3 + k_4} [C_2H_4]^3$$

which is the second order form. With suitable values of the temperature coefficients of the various velocity constants involved, the experimentally observed coefficient could be fitted. At very low concentrations of ethylene, the equation becomes

$$+ \frac{d[C_4H_8]}{dt} = \frac{k_1 k_3}{k_2} [C_2H_4]^3$$

that is, the reaction is third order.

Summary

The rate of polymerization of ethylene has been measured at 2.5, 5 and 10 atmospheres from 350 to 500°. At least 50% of the ethylene may be polymerized to gaseous and liquid mono-olefins without the formation of more than a few per cent. of hydrogen and saturated hydrocarbons.

The reaction is of second order and has an abnormally low temperature coefficient. This is discussed in the light of the fact that the reaction is of the association type.

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NOTES

A Note on Diffusion in Gelatin Gels.—In a recent paper on the diffusion of non-electrolytes in gelatin gels, Friedman and Kraemer¹ have observed that the coefficient of diffusion is diminished by an increase in the concentration of the gel. A similar diminution was observed by Stiles and Adair,² who found that the coefficient of diffusion of sodium chloride decreased from 0.675×10^{-5} in a 4% gel to 0.483×10^{-5} in a 16% gel.

The results of Friedman and Kraemer are consistent with the formula we published, to show the relation between coefficient of diffusion and gel concentration. The formula is

$$k = a(1 - bc)$$

where k is the diffusion constant of sodium chloride in the gelatin gel, c is concentration of gelatin in percentage by weight, a is a constant = 0.74

¹ L. Friedman and E. O. Kraemer, *THIS JOURNAL*, **52**, 1295 (1930).

² W. Stiles and G. S. Adair, *Biochem. J.*, **15**, 621 (1921).

$\times 10^{-5}$ at 0° , and 1.35×10^{-5} at 20° , and b is a constant, approximately 0.018.

The range of application of this formula is restricted to systems containing from 2 to 16% of gelatin. The constant b is a measure of the effect of the gelatin in arresting diffusion. In our experiments with sodium chloride the term b appeared to be practically constant. The values calculated from the data for urea, given by Friedman and Kraemer, show very considerable irregularities; one experiment gave a result for b which was the same as ours, but another gave a higher value, nearly 10 times as great. Their experiments with glycerol and with sucrose gave values for b of about 0.034 and 0.058, respectively. It is interesting to note that the values of b obtained with non-electrolytes are of the same order of magnitude as those obtained by us with sodium chloride.

It seems desirable to draw attention to the essential agreement of the results obtained in both investigations, because the following passage occurs in Friedman and Kraemer's paper: "A decrease in the rate of diffusion of 20% as the concentration of the gel increased from 2.5 to 5% is shown, contrary to the statement by Stiles and Adair that above 2% there is very little change." Their abbreviated quotation conveys an entirely different meaning from the actual statement of Stiles and Adair, namely, "with concentrations above 2% the curve connecting the coefficient of diffusion and concentration is approximately a straight line, the rate of decrease of the diffusion coefficient with increasing concentration of the gel being less than with concentrations less than 2%."

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Glass Electrode Measurements by Means of a Galvanometer with Condenser Attachment.—Due to the high resistance of glass electrodes and to a possible polarization of their membranes on the passage of a direct electrical current, e. m. f. measurements of glass electrode potentials have hitherto not been carried out with the ordinary galvanometer-potentiometer systems. Jones and Kaplan have recently invented a condenser galvanometer system which enables potential measurements on cells of high resistance to be made with a ballistic galvanometer.¹ By means of

¹ Grinnell Jones and B. B. Kaplan, *THIS JOURNAL*, 50, 1853 (1928); see W. E. L. Brown, *J. Sci. Instruments*, 2, 12 (1924), for a brief mention of a similar arrangement. H. T. Beans and E. T. Oakes, *THIS JOURNAL*, 42, 2116 (1920), and H. T. Beans and G. H. Walden, Jr., *ibid.*, 50, 2673 (1928), have used a condenser for making potential measurements, but as their method is not a null-point method it was not used here.

this instrument it is now possible to test the applicability of galvanometers to glass electrode measurements and to test the question of membrane polarization.

Through the courtesy of Professor Jones, the same apparatus that he and Kaplan used was made available for this research; the details of operation and manipulation are fully described in their paper and need not be repeated here. Similarly, the glass electrode technique has already been given by MacInnes and Dole.² In Table I a typical example of a cell reading is given. There was no indication of any drift of potential due to polarization of the electrodes by the current charging the condenser.

TABLE I
MEASUREMENT OF A GLASS ELECTRODE CELL USING THE CONDENSER ATTACHMENT

Potentiometer setting, volt	Time allowed for condenser to charge, seconds	Galvanometer deflections on scale, millimeters
0.44	15	L, 10.0
.43	15	L, 2.0
.42	15	R, 3.0
.427	30	L, 1.0
.426	30	L, 0.1
.4258	60	0
.4258	120	R, 0.2
.4260	120	L, .2
Accepted potential 0.4259		L = left. R = right

In Table II are given the asymmetric potentials and resistances of the glass electrodes used in the final measurements. One electrode was prepared from glass furnished by the Corning Glass Company (their 0.012 glass) and the other from glass made in the manner described by MacInnes and Dole.

TABLE II
ASYMMETRIC POTENTIALS AND RESISTANCES OF GLASS ELECTRODES USED

	Asymmetric potentials, volt	Resistances, megohms
Corning glass	-0.0010	51.5
MacI.-D. glass	- .0020	21.1

The hydrogen half-cell and the glass electrode half-cell were measured in two solutions of different *PH* against a saturated calomel reference electrode at 27.3°. The solutions were made up only approximately.

The final measurements are given in Table III. The hydrogen-calomel cell was measured without using the condenser. From the last column of Table III it is evident that both Corning glass electrodes and MacInnes and Dole glass electrodes give the correct hydrogen electrode potential changes as measured with the ballistic galvanometer-condenser system.

² D. A. MacInnes and Malcolm Dole, *Ind. Eng. Chem. (Anal. Ed.)*, 1, 57 (1929); *THIS JOURNAL*, 52, 29 (1930).

TABLE III

COMPARISON OF HYDROGEN AND GLASS ELECTRODE POTENTIALS USING THE GALVANOMETER WITH CONDENSER ATTACHMENT

Electrode (against calomel)	Potentials in volts Solution		ΔE
	0.1 N HCl	0.1 N Na ₂ HPO ₄	
Hydrogen (1)	0.3084	0.7780	0.4696
Hydrogen (2)	.3084	.7778	.4694
Corning glass	— .0433	.4261	.4694
MacI.-D. glass	— .0425	.4268	.4693

There is again no evidence of polarization and the results are as accurate as can be obtained with other methods of glass electrode measurements.

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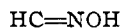
THE REACTIVE FORM OF GLUCOSE OXIME¹

BY M. L. WOLFROM AND ALVA THOMPSON

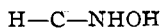
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The fact that glucose reacts with hydroxylamine to form an oxime has been used as proof for the presence of an aldehyde group in the molecule of this sugar. Glucose oxime was first prepared in crystalline form by Jacobi² and its structure was tacitly assumed to be of the true oxime type, R—CH=NOH. The establishment of the ring or cyclic hemiacetal structure for the crystalline forms of glucose raised the question whether this ring opened or remained intact in the nitrogen condensation products of the sugar. In the case of the oxime, these two possibilities are illustrated as follows



True oxime



Ring type oxime

Each of the above types could exist in two isomeric forms, *syn* and *anti* in the true oxime structure and alpha and beta in the other. In the latter case, the formation of more than one ring would indeed give rise to further isomers, but this possibility is not pertinent to the following discussion

¹ (a) Constructed from a thesis presented by Alva Thompson in candidacy for the degree of Doctor of Philosophy in Chemistry at The Ohio State University. (b) Presented before the Division of Organic Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Georgia, April 7 to 11, 1930.

² H. Jacobi. *Ber.*, 24, 697 (1891).