

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.