

Since the concentration of the radical was different in the two measurements, the linewidths observed at variable temperature were multiplied by the linewidth ratio of the two solutions at a common set of conditions (20°C , $P=1$ atm). This procedure is justified since in this range of concentration it was independently verified that the linewidth is linear with concentration.¹¹ The same linearity of linewidth with concentration was assumed in correcting the data for changes in liquid and vapor density with temperature.

The results of the variable pressure measurements in methyl cyclohexane at 20°C are presented in Fig. 2(a). It should be noted that for the deoxygenated solution, the linewidth is linear with η^{-1} , whereas a definite curvature is noticed for the two solutions containing oxygen. The dashed line in Fig. 2(a) is the theoretical plot of a $0.0024M$ deoxygenated solution, the slope of which is one-fifth that of the $0.012M$ deoxygenated solution. This relationship is also established by the linearity of W with concentration in the region of exchange rates covered by these experiments. The line was located to give the same difference in intercepts

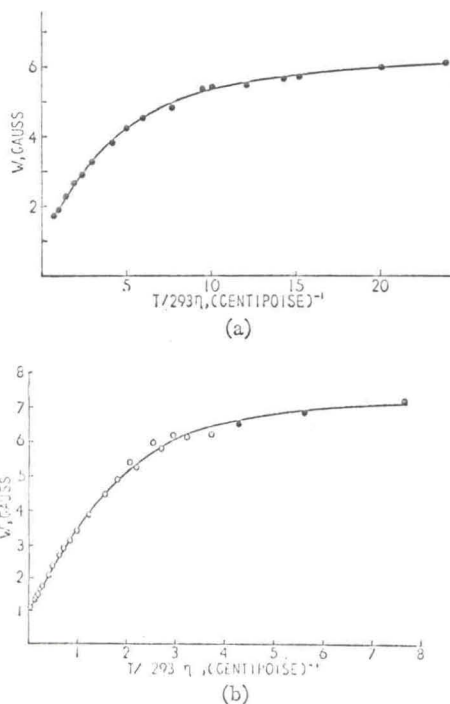


FIG. 1. (a) Linewidths of DTBN in liquid propane, $c \sim 0.01M$ at 20°C . Data obtained in sealed tube at variable temperature. (b). Linewidth of DTBN in liquid *n*-pentane. Open circles represent data at variable pressure with $T=293^{\circ}\text{K}$, while filled circles are data at variable temperature and $P=1$ atm. Liquids are deoxygenated. $c=0.012M$ for variable pressure data, and $c \sim 0.004M$ for variable temperature data. Linewidths were normalized for the concentration difference.

¹¹ A. Kwok, thesis, Harvard University, See also M. T. Jones, *J. Chem. Phys.* **38**, 2892 (1963); and J. Danner and T. R. Tuttle, Jr., *J. Am. Chem. Soc.* **85**, 4052 (1963).

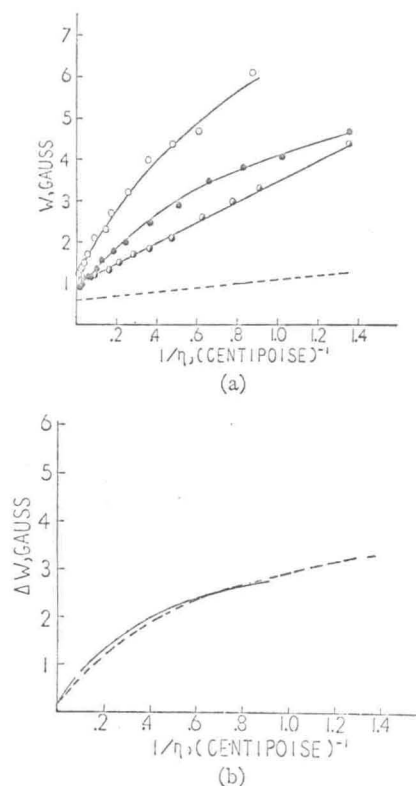


FIG. 2 (a) Linewidths of DTBN in liquid methylcyclohexane. All data are at variable pressure at $T=293^{\circ}\text{K}$. Open circles are $c=0.012M$, air saturated at $P=1$ atm, filled circles are $c=0.0024M$, air saturated at $P=1$ atm, and half-filled circles are $c=0.012M$, deoxygenated solution. The dashed line represents the expected behavior of a $c=0.0024M$ deoxygenated solution. (b) Linewidth differences ΔW between oxygen containing and deoxygenated solutions of DTBN in methylcyclohexane. Solid line is for a radical concentration of $c=0.012M$, while dashed line is for $c=0.0024M$.

between deoxygenated solutions as that observed between the oxygen containing solutions at these concentrations.

Figure 2(b) illustrates the effect of dissolved oxygen on the free radical linewidths. The solid line is the difference in linewidth (ΔW) between oxygen containing and deoxygenated solutions, at $c=0.012M$, whereas the dashed line is the difference in linewidth between the oxygen containing $0.0024M$ solution and that of the theoretical deoxygenated solution of the same concentration. It is observed that the nonlinearity of the curves in Fig. 2(a) is due to the presence of dissolved oxygen at both radical concentrations, and that the effect of oxygen is the same at both radical concentrations.

It is found that at high viscosities, the linewidth is approximately linear with T/η , which is the predicted behavior according to the theory of Pake and Tuttle² for $p=1$, whereas the slope falls off at lower viscosities. It is assumed that in the linear region $p=1$, and that the falling off of the linewidth at reduced viscosities is