Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 44, No. 4, 1715–1716, 15 February 1966
Printed in U. S. A.

Use of O_2 for ESR Calibration for Quantitative Measurement of Gas Concentrations*

K. M. EVENSON† AND D. S. BURCH
Oregon State University, Corvallis, Oregon

(Received 1 October 1965)

WE wish to add further experimental support to that of Westenberg and deHaas[1] for the use of gaseous molecular oxygen ($^{16}O^{16}O$) as a calibration standard for the measurement of paramagnetic gas concentrations with ESR spectrometers. The accuracy of the intensity formulas of Tinkham and Strandberg[2] for O_2 was verified by a comparison of the results it gave with those obtained using two other standards, an aqueous solution of manganese sulfate and a sample of diphenylpicrylhydrazyl (DPPH). Westenberg and deHaas compared an O_2 calibration with O and N calibrations determined by chemical titrations with NO_2 and NO, respectively. Our calibration check was performed using nondischarged substances in order to eliminate any inaccuracies in the chemical titration due to the possible presence of metastable excited atoms or molecules in the afterglows of discharges. The data were taken with a standard X-band spectrometer with 100-kc/sec modulation and a rectangular cavity operated in the TE_{102} mode.

Rearrangement of Eqs. (11) and (20) in the paper of Westenberg and deHaas yields, in their nomenclature,

$$\frac{N_{\mathrm{at}}g_{\mathrm{at}}\sum_{JM_J}(J-M_J)(J+M_J+1)\exp(-E_{JM_J}/kT)}{Z_{\mathrm{at}}\int\chi_{\mathrm{at}}''dH}=N_{O2}g_{\mathrm{el}}^2P\Big/g_{\mathrm{eff}}Z_{O_2}\int\chi_{O_2}''dH.$$

In most cases of interest the factor $\exp(-E_{JM_J}/kT)$ can be approximated to be unity; the summation in the left-hand term then becomes $(\frac{2}{3})J(J+1)(2J+1)$, while $Z_{\mathrm{at}}=2J+1$. Defining an instrumental constant R by

$$\int\chi''dH=RI,$$

where I is the ESR signal intensity (first moment), leads to

$$R=(\tfrac{2}{3})N_{\mathrm{at}}g_{\mathrm{at}}J(J+1)/I_{\mathrm{at}}=N_{O_2}g_{\mathrm{el}}^2P/I_{O_2}g_{\mathrm{eff}}Z_{O_2}.$$

The efficacy of using oxygen for calibration may then be investigated by comparing its R value against those obtained for other calibrating materials. We employed the B line of O_2, using the value $p=0.32$ found by Westenberg and deHaas, which gives $R_{O_2}=4.50\times10^{-3}$ N_{O_2}/I_{O_2}. In $MnSO_4$ solutions the Mn^{++} ion is in a $^6S_{\frac{5}{2}}$ state, giving $J=\frac{5}{2}$, $g=2$. For DPPH, the paramagnetic constituent is an almost-free electron with $J=\frac{1}{2}$, $g=2$. Thus, we may compare experimentally determined values of the quantities appearing in

$$R=\tfrac{35}{3}(N/I)_{MnSO_4}=(N/I)_{\mathrm{DPPH}}=4.50\times10^{-3}(N/I)_{O_2}.$$

In our work, the specimens which were compared were of differing sizes and shapes, necessitating a mapping of the relative sensitivity of the ESR cavity at different positions. The mapping was performed by recording the response for various locations of a point sample of DPPH attached to a quartz fiber. The $MnSO_4$ solution was contained in a quartz capillary tube, 1 mm i.d., positioned along the axis of the cavity, while the oxygen specimen filled a 9-mm-i.d. quartz tube, and the DPPH calibration sample was located at the center. All of the mappings were made with the 9-mm-i.d. quartz tube in place, but not the 1-mm tube. It was assumed that the 1-mm tube would not alter the field patterns too seriously since it was located in the region of minimum electric field. The results for the average sensitivities were

$$(S_{MnSO_4}/S_{\mathrm{center}})=0.400\pm0.025,$$
$$(S_{O_2}/S_{\mathrm{center}})=0.44\pm0.08.$$

The over-all sensitivity was found to be lowered by a factor of 0.69 by the presence of the aqueous solution of $MnSO_4$.

The measurement of the relative values of R, after making the corrections just discussed, gave $R_{\mathrm{DPPH}}=2.20\pm0.29$, $R_{MnSO_4}=1.68\pm0.27$, and $R_{O_2}=1.80\pm0.20$. The somewhat higher value of R_{DPPH} is not unexpected since it is dubious whether very pure samples of DPPH were used; in addition, DPPH disintegrates by a few percent per year. Its R value is, however, within the experimental accuracy. The R values for $MnSO_4$ and O_2 differ by only 0.12, well within the experimental precision. We conclude that molecular oxygen is an excellent gas for use as a calibration standard for ESR measurements of gaseous radical concentrations.

* Work supported in part by a grant from U.S. Army Research Office (Durham) and Defense Atomic Support Agency.

† Present Address: National Bureau of Standards, Boulder, Colorado.

[1] A. A. Westenberg and N. deHaas, J. Chem. Phys. **40**, 3087 (1964).
[2] M. Tinkham and M. W. P. Strandberg, Phys. Rev. **97**, 951 (1955).