sistent, however, with the present conclusion that the reactions of the excited species with halide ions (or $NO_2^-$ in the case of $I_2^*$) proceed with very nearly the maximum rate of the collision frequency.

In some respects the $Br_3^-$–Mn(II) photoreaction qualifies as a useful actinometer. The reaction is non-chain in character, completely reproducible, and sufficiently free from complication by thermal reactions. It has advantages over the uranyl oxalate system, since the reaction product can conveniently be estimated accurately, and arrangement for complete absorption of light can readily be made at longer wave lengths, but has the disadvantage that more accurate control of temperature is necessary.

CHICAGO, ILL. RECEIVED FEBRUARY 16, 1951

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# The Vapor Pressure and Critical Constants of Normal Pentane

BY JAMES A. BEATTIE, SAMUEL W. LEVINE AND DONALD R. DOUSLIN

The vapor pressure of normal pentane, $C_5H_{12}$, has been measured from 100° to the critical point. The results are represented quite well by the relation $\log_{10} p(\text{atm.}) = 3.752453 - (1225.960/T) + 8.06841 \times 10^{-4}\, T$ ($T = t°\text{C.} + 273.16$). The critical constants were determined by compressibility measurements in the critical region and were found to be $t_c = 196.62 \pm 0.05°$ (Int.); $p_c = 33.31 \pm 0.05$ normal atm.; $v_c = 0.295$ liter/mole (4.09 ml./g.); $d_c = 3.39$ moles/liter (0.244 g./ml.). The uncertainty in the critical volume and density is 1%.

The vapor pressure of normal pentane has been measured by Rose-Innes and Young[1,2] and by Sage and Lacey.[3] The critical point was determined by Rose-Innes and Young by the disappearance of the meniscus method, and estimated by Sage and Lacey[3] from measurements of the compressibility of the liquid and vapor using the critical temperature determined by Rose-Innes and Young.[1,2]

In continuation of a program of study of the state behavior of hydrocarbons[4] we have measured the vapor pressure of normal pentane from 100° to the critical point and have studied a number of isotherms in the critical region which permit location of the critical constants. The method of making the measurements has been described earlier[5]; the bomb with the glass liner was used.

TABLE I

VARIATION OF THE MEASURED VAPOR PRESSURE OF THE SAMPLE OF NORMAL PENTANE WITH VAPOR VOLUME AT 100°

| | | | | | | |
|---|---|---|---|---|---|---|
| Vapor vol. ml. | 95 | 74 | 51 | 29 | 6.2 | 0.26 |
| Measured atm. | 5.857 | 5.857 | 5.860 | 5.860 | 5.864 | 5.866 |

TABLE II

VAPOR PRESSURE OF NORMAL PENTANE

| Temp., °C. (Int.) | Vapor pressure in normal atmospheres: This work | Observed—Eq. 1 | | Sage and Lacey | Young |
|---|---|---|---|---|---|
| 100 | 5.857 | −0.007 | −0.12% | 5.840 | 5.80 |
| 125 | 9.902 | + .025 | + .25 | 9.884 | 9.79 |
| 150 | 15.730 | .000 | .00 | 15.736 | 15.53 |
| 175 | 23.834 | − .072 | − .30 | 23.822 | 23.57 |
| 175[a] | 23.838 | − .068 | − .29 | | |
| 196.62 | 33.31 | + .056 | + .17 | | |

[a] Vapor pressure measured after the compressibility runs in the critical region.

TABLE III

ISOTHERMS OF *n*-PENTANE, $C_5H_{12}$, IN THE CRITICAL REGION

Molecular weight, 72.0924; critical constants from Fig. 1: $t_c = 196.62 \pm 0.05°$ (Int.); $p_c = 33.31 \pm 0.05$ normal atm.; $v_c = 0.295$ liter/mole (4.09 ml./g.); $d_c = 3.39$ moles/liter (0.244 g./ml.). The uncertainty in the critical volume and density is 1%.

| Temp., °C. (Int.) | | 196.20 | 196.40 | 196.50 | 196.60 | 196.62 | 196.70 |
|---|---|---|---|---|---|---|---|
| Density moles/liter | Volume liter/mole | Pressure, normal atmospheres | | | | | |
| 4.000 | 0.2500 | 33.181 | 33.317 | 33.380 | 33.438 | | |
| 3.900 | .2564 | 33.132 | 33.249 | 33.307 | 33.371 | | |
| 3.800 | .2632 | 33.104 | 33.213 | 33.269 | 33.332 | | 33.394 |
| 3.700 | .2703 | 33.096 | 33.201 | 33.257 | 33.309 | | 33.368 |
| 3.600 | .2778 | 33.097 | 33.199 | 33.251 | 33.303 | 33.312 | 33.359 |
| 3.550 | .2817 | 33.095 | 33.197 | 33.249 | 33.301 | 33.310 | 33.354 |
| 3.500 | .2857 | 33.096 | 33.198 | 33.247 | 33.298 | 33.308 | 33.352 |
| 3.450 | .2899 | 33.096 | 33.198 | 33.248 | 33.297 | 33.306 | 33.350 |
| 3.400 | .2941 | 33.094 | 33.196 | 33.248 | 33.297 | 33.307 | 33.351 |
| 3.350 | .2985 | | 33.197 | 33.247 | 33.297 | 33.305 | 33.348 |
| 3.300 | .3030 | 33.095 | 33.195 | 33.247 | 33.295 | 33.303 | 33.349 |
| 3.250 | .3077 | | 33.196 | 33.246 | 33.293 | 33.303 | 33.347 |
| 3.200 | .3125 | 33.093 | 33.196 | 33.244 | 33.291 | 33.302 | 33.345 |
| 3.150 | .3175 | | 33.194 | 33.245 | 33.292 | 33.302 | 33.346 |
| 3.100 | .3226 | 33.095 | 33.192 | 33.243 | 33.290 | 33.301 | 33.344 |
| 3.000 | .3333 | 33.088 | 33.188 | 33.239 | 33.286 | | 33.340 |
| 2.900 | .3448 | 33.085 | 33.182 | 33.236 | 33.282 | | 33.338 |
| 2.800 | .3571 | 33.076 | 33.176 | 33.232 | 33.276 | | |
| 2.650 | .3774 | 33.060 | 33.160 | 33.214 | 33.253 | | 33.302 |

TABLE IV

CRITICAL CONSTANTS OF NORMAL PENTANE

| Source | $t_c$, °C. (Int.) | $p_c$, normal atm. | $v_c$, liter/mole |
|---|---|---|---|
| This work | 196.62 ± 0.05 | 33.31 ± 0.05 | 0.295[a] |
| Sage and Lacey | 197[b] | 33.6 | .315 |
| Rose-Innes and Young | 197 | 33.0 | .310 |

[a] $v_c = 0.295$ liter/mole (4.09 ml./g.); $d_c = 3.39$ mole/liter (0.244 g./ml.). [b] Sage and Lacey used the critical temperature given by Rose-Innes and Young to estimate $p_c$ and $v_c$ from their own measurements of the compressibility of the liquid and vapor.

The normal pentane used in this work was an API–NBS sample made available by the American Petroleum Institute and the U. S. National Bureau of Standards through the API Research Project 44. The sample was purified at the National Bureau of Standards by the API Project 6, under the supervision of Dr. F. D. Rossini, from materials supplied

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[1] J. Rose-Innes and S. Young, *Phil. Mag.*, [5] **47**, 353 (1899).

[2] S. Young, *Sci. Proc. Roy. Dublin Soc.*, **13**, 310 (1912).

[3] D. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **34**, 730 (1942).

[4] For the last report on this work see J. A. Beattie and S. Marple, Jr., THIS JOURNAL, **72**, 1449 (1950).

[5] J. A. Beattie, *Proc. Amer. Acad. Arts Sci.*, **69**, 389 (1934).

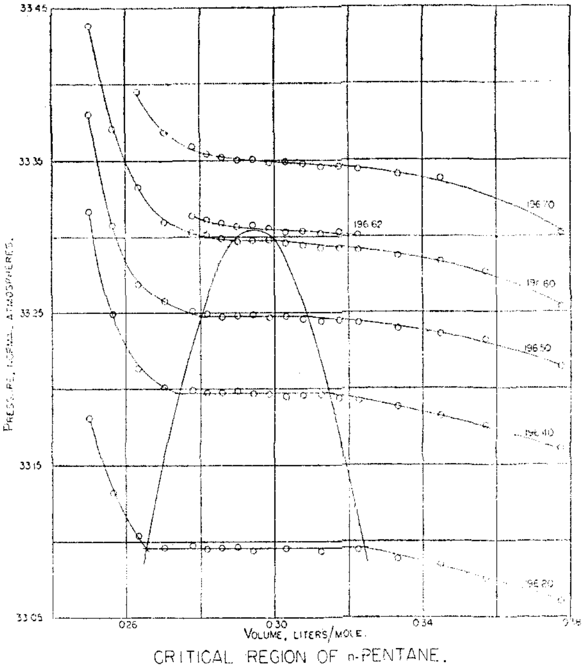

Fig. 1.—Isotherms of normal pentane in the critical region. The radius of each circle is 0.002 atm.

by the API Project 6 at the National Bureau of Standards. The impurities were stated to be 0.15 ± 0.07 mole per cent. We are very grateful to Dr. Rossini for furnishing the sample. No further purification was carried out by us except repeated freezing, distillation, and pumping in the loading system to remove air.

The purity of the pentane especially as regards contamination by permanent gases is indicated by the results given in Table I. The vapor pressure of the sample was determined at 100° while the vapor volume was varied from 95 to 0.26 ml. The increase in pressure, 0.009 atm., indicated a satisfactory purity.

The measured vapor pressures are presented in Table II together with the deviations from the equation

$$\log_{10} p(\text{atm.}) = 3.752453 - \frac{1225.960}{T} + 8.06841 \times 10^{-4}\,T \quad (T = t°\text{C.} + 273.16) \qquad (1)$$

There are also included the results of Rose-Innes and Young and of Sage and Lacey. The agreement with the measurements of Sage and Lacey is excellent.

The observations on the compressibility of pentane in the critical region are given in Table III and these results are plotted in Fig. 1. From the plot we find the critical constants listed in Table IV. The agreement with the earlier work of Rose-Innes and Young is fairly satisfactory.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 12, 1951

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[CONTRIBUTION FROM THE BASIC COTTON RESEARCH LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

# The Preparation of a Platinum Oxide Catalyst of Reproducible Activity[1]

BY VERNON L. FRAMPTON, JOSEPH D. EDWARDS, JR., AND HENRY R. HENZE

A procedure is described for the preparation of a platinum oxide catalyst of reproducible activity, which depends upon the essentially instantaneous heating of platinic chloride to 520° in the presence of sodium nitrate. A volumetric hydrogenation apparatus is also described.

Adams and Vorhees,[2] and later Adams and Shriner,[3] observed that a platinum oxide prepared by fusing a mixture of sodium nitrate and chloroplatinic acid at 540° was far more active, and more consistent in its activity, as a catalyst for the hydrogenation of carbon–carbon double bonds, carbonyl compounds, etc., than the platinum black catalysts prepared by previously known procedures. We found, however, in a study of the hydrogenation of gossypol, a considerable degree of variability in the activities of the catalyst preparations prepared by the procedure described by Adams, *et al.* For example, the hydrogenation of gossypol was substantially complete (with the production of a crystalline product melting at 258–260°)[4] in about 45 minutes with the most active preparations we obtained, but with other preparations obtained under conditions as nearly comparable as we could make them, from 48 to 72 hours were required for the hydrogenation, and with still other preparations, no hydrogenation was obtained. In each instance the catalyst was active, since test compounds were readily hydrogenated, and spontaneous combustion occurred when the hydrogen-saturated suspension of the catalyst was filtered in air.[5]

**Preparation of the Catalyst.**—The following procedure for the preparation of an extremely active platinum oxide catalyst of essentially reproducible activity evolved during the course of our efforts to hydrogenate gossypol.

Add 10 ml. of a 10% solution of chloroplatinic acid to 9 g. of sodium nitrate in a 50-ml. beaker, and evaporate to dryness over an open flame, stirring all the while with a glass

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[1] Taken in part from a thesis presented by Joseph D. Edwards, Jr., to the graduate faculty of the University of Texas in partial fulfillment of the requirements for the Ph.D. degree, June, 1950. This research was supported by funds appropriated by the Cotton Research Committee of Texas.

[2] R. Adams and V. Vorhees, THIS JOURNAL, **44**, 1683 (1922).

[3] R. Adams and R. L. Shriner, *ibid.*, **45**, 2171 (1923).

[4] Unpublished data from the studies on the hydrogenation of gossypol carried out in the Basic Cotton Research Laboratory, Oct., 1948–Jan., 1949.

[5] According to the Adams procedure, the mixture of chloroplatinic acid in sodium nitrate is first heated gently until all of the water is driven off, and then it is heated more strongly until a temperature of 540° is reached, and until almost all of the oxides of nitrogen have been expelled from the melt. We find that, although one may sense if a given preparation will be active, or only moderately so, he may not produce at will an extremely active catalyst by following the procedure. This experience relating to the variability in the activity of these platinum oxide catalysts is not unique to this Laboratory.