Vapor Pressure of Biacetyl

WILLIAM C. NEELY[1] and TERRY D. HALL
Charles Richard Saunders Chemical Laboratory, Auburn University, Auburn, AL 36830

The vapor pressure of biacetyl was measured directly using a conventional isoteniscope in the temperature range 0–75°C. The measured values were plotted as log *P* vs. 1/*TK*. An exponential least-squares computer program gave a correlation coefficient of 0.9992 using the following equation:

$$\log P = \frac{-2012.1}{TK} + 8.496$$

Extrapolation of the least-squares line was in good agreement with the known boiling point and in fair agreement with the only other published values.

The vapor phase photochemistry and excitation energy transfer characteristics of biacetyl have been studied extensively since the initial observations of Matheson and Zabor (*6*). In spite of this interest in vapor phase studies the only reported vapor pressure data are the approximate values given by Ells in 1938 (*4*). In our work on quantitative measurements of excitation energy transfer in the vapor phase, it is necessary to know the vapor pressure over the ambient temperature range. The only values reported were for temperatures below 0°C except for the boiling point (*10*).

EXPERIMENTAL

Apparatus. The vapor pressure of biacetyl was measured by the static method with an isoteniscope (*1–3*, *5*, *7–9*) in conjunction with a mercury manometer, cathetometer (calibrated to 0.1 mm), and mirror. The temperature was controlled by a Sargent Thermoniter (Model ST, S-84810) with Stirring Tower (Model NSI-12A1) working against a Sargent water bath cooler with coils at the bottom of the bath. The temperature measurements were made with a Hewlett Packard quartz thermometer (Model Dy-2801A) calibrated at the ice point of water (*7*). The thermonitor and quartz thermometer were mounted as close as possible to the isoteniscope. The water-glycerol-filled bath was insulated with glass wool and then aluminum foil, except for two shielded holes for viewing. The top was fitted with a cover.

Procedure The biacetyl (Eastman) was purified by threefold vacuum distillation taking less than 50% of the biacetyl from each distillation. All of the usual precautions were used to expel air from the sample. Readings were taken after the bath had stabilized to within 0.01°C of the nominal temperature for a period of 1 hr 20 min. After completion of measurements, samples of the biacetyl in the isoteniscope were checked for purity by nmr and were still essentially pure.

Table I. Experimental Vapor Pressure Data

Temp, ±0.01°C	Pressure, ±0.5 mm	Dev, $P_{obs} - P_{calcd}$
0.01	12.5	−1.0
3.37	14.6	−2.0
4.96	18.0	−0.2
7.92	22.8	+1.1
9.94	24.8	+0.3
12.44	30.2	+2.0
15.00	31.1	−1.5
17.07	37.1	+0.5
20.02	44.2	+1.3
22.67	48.8	−0.7
25.10	58.2	+2.0
27.24	61.9	−0.9
29.93	75.3	+3.3
32.26	80.9	0.0
34.01	91.1	+2.9
36.85	100.2	−1.0
40.00	124.3	+3.6
42.36	130.2	−1.3
45.00	150.9	+2.4
47.51	167.4	+1.0
50.00	192.5	+6.5
52.48	208.7	+1.2
55.00	238.4	+6.9
57.55	253.3	−4.7
60.00	300.3	+4.2
65.23	349.8	−4.8
70.05	420.8	−9.0
75.01	505.0	−16.0

Table II. Correlation Coefficients

	Temp range of data	Correlation coeff, *r*
I.	0–75°C	0.99926
II.	I. and 88°C[a]	0.99919
III.	II. and −30°C[b]	0.99789
IV.	III. and −70°C[b]	0.99722

[a] Boiling point data of ref. *10*. [b] Vapor pressure data of ref. *4*.

RESULTS AND CONCLUSION

The vapor pressure–temperature data of Table I were computer fitted to an exponential least-squares plot of the equation:

$$\log P = \frac{-A}{TK} + B$$

On evaluation, the constant, *A*, had a value of 2012.1 and *B* of 8.496. The computer program also generated the value of *r*, the correlation coefficient, as a measure of the goodness of fit of the data to the straight line. Differences between pressures calculated using this equation and the measured values are also given in Table I.

Table II shows the excellent correlation coefficient for the present data (0.99926) essentially unaffected after including the known boiling point of biacetyl. Although the correlation coefficient decreases somewhat when the approximate data by Ells was used, the correlation coefficient is still reasonably good.

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[1] To whom correspondence should be addressed.

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Liquid and Vapor Densities of Aluminum Chloride

II. Extension to the Critical Temperature

DAVID W. SEEGMILLER, ARMAND A. FANNIN, JR., DAVID S. OLSON, and LOWELL A. KING[1]
Frank J. Seiler Research Laboratory (Air Force Systems Command) and Department
of Chemistry, United States Air Force Academy, CO 80840

The orthobaric liquid and vapor densities of aluminum chloride were measured from 197°C to the critical point. A single empirical equation was derived which was symmetrical about the rectilinear diameter and which represented both the liquid and vapor densities. This method yielded $t_c = 355.2 \pm 0.3$°C and $\rho_c = 0.5073 \pm 0.0004$ g/cm^{-3}.

In a recent publication from our laboratory (*2*), the densities of pure aluminum chloride liquid and vapor were reported from 188–296°C. The experimental method used was rapid, and gave extremely precise results. The aluminum chloride was contained in pyrex vessels which were designed with relatively large enclosed volumes. The measurements were not continued above 300°C because of the safety hazard associated with the containment of high pressures in glass apparatus. The present paper describes a modification of the apparatus which permitted the extension of the measurements up to the critical point of aluminum chloride.

EXPERIMENTAL

Density Tubes. Eleven heavy-wall pyrex tubes, $^3/_8$ in. o.d. and about 25 cm long were used. The density tubes were calibrated and liquid $AlCl_3$ volumes measured by the method used for density tubes *A*, *B*, *C*, and *D* of ref. *2*. Calibration data are given in Table I. The manner in which $AlCl_3$ was purified and the procedure used to load the density tubes with $AlCl_3$ also were the same as used before.

Procedure. Density tubes were immersed in the molten salt bath described earlier (*2*). The bath temperature was determined by measurement of the resistance of a Leeds and Northrup Model 8163 platinum resistance thermometer with the aid of a Data Technology Corp. Model 370 digital volt meter. The platinum thermometer was an Air Force Reference Standard Thermometer, calibrated at the freezing point of zinc, freezing point of tin, boiling point of water, triple point of water, and the boiling point of oxygen by the U.S. Air Force Measurement Standards Laboratory, Aerospace Guidance and Metrology Center, Newark Air Force Station, OH.

Experimental values of $AlCl_3$ liquid volume were obtained by measuring with a cathetometer the distance from the bottom of the $AlCl_3$ meniscus to an arrow etched on the tube.

Table I. Calibration of Density Tubes

Tube	Vol. to arrow, cm^3	Vol. of capillary, cm^3/cm	Total enclosed vol., cm^3	Mass of $AlCl_3$ in tube, g
I	2.211 ± 0.003	0.2575 ± 0.0006	6.17 ± 0.05	4.794
II	2.174 ± 0.003	0.2477 ± 0.0008	5.91 ± 0.05	3.922
III	2.189 ± 0.004	0.2479 ± 0.0004	5.92 ± 0.05	2.977
IV	2.234 ± 0.008	0.2544 ± 0.0008	6.05 ± 0.05	2.046
V	2.257 ± 0.002	0.2550 ± 0.0006	5.84 ± 0.05	1.925
VI	2.389 ± 0.007	0.256 ± 0.002	5.93 ± 0.05	2.435
VII	2.238 ± 0.004	0.254 ± 0.001	6.07 ± 0.05	2.933
VIII	2.122 ± 0.006	0.249 ± 0.002	5.47 ± 0.05	3.338
IX	2.366 ± 0.004	0.249 ± 0.002	5.87 ± 0.05	3.812
X	2.234 ± 0.005	0.256 ± 0.002	5.90 ± 0.05	4.285
XI	2.176 ± 0.005	0.250 ± 0.002	5.93 ± 0.05	4.762

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[1] To whom correspondence should be addressed.