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Vapor Pressure of Acetylacetone below Normal Boiling Point

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Acetylacetone(2,4-pentanedione) has been used frequently in studies on keto-enol tautomerism and complex formation with metals, but no vapor pressure data are available in literature. This note describes new vapor pressure data for acetylacetone from room temperature up to the normal boiling point.

Experimental

Acetylacetone was purified by distillations under reduced nitrogen pressure. Since the affinity of acetylacetone to metals is fairly large, final distillation was carried out in a column with glass packing.

The vapor pressure was measured by means of the following apparatus:

(a) Vapor pressure apparatus (16—50°C)

(b) Isoteniscope[1] (40—70°C)

(c) A modified Swietoslawski-type ebulliometer[1] (60—138°C)

A sketch of (a) is given in Fig. 1. Purified liquid was confined in a mercury-sealed cell and degassed in a vacuum at liquid nitrogen temperature. Mercury was then introduced to form a manometer in a U-tube on the left-hand side of the cell which was immersed in a thermostat maintained on a laboratory jack. After temperature equilibrium was reached, the pressure was read both on the manometer and an open manometer with a travelling microscope and a Shimadzu Model HV-100 cathetometer.

The apparatus (b) and (c) were connected to a vacuum system and operated by conventional methods.[1] Reduced pressures required were obtained by introducing dry nitrogen into the system. A porous-disk type manostat was used to keep the whole system at a constant pressure of ±0.2 mmHg. The isoteniscope was immersed in a glycerine thermostat controlled within ±0.05°C during the course of measurement.

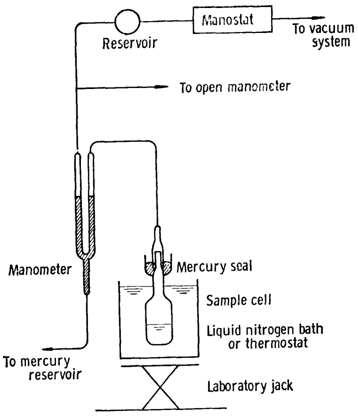

Fig. 1. Schematic diagram of vapor pressure apparatus.

The temperature was measured by a thermistor calibrated against a standard thermometer. The overall average error of the vapor pressure measurement was believed to be less than ±0.2 Torr at lower temperatures, but larger at temperatures above 100°C.

In order to confirm the validity of the data, the vapor pressure of toluene was measured between 92° and 107°C with our ebulliometer and the results were compared with the accepted values.[2] No systematic deviation from literature values was observed, and the average deviation was less than ±0.6 Torr or ±1.2%.

Results and Discussion

Vapor Pressure Data. The vapor pressure of acetylacetone from 16° to 137°C is given in Table 1. The mean value of the barometric pressure during the measurements was 733 mmHg, where acetylacetone boiled at 137.3°C. Extrapolation of the data to 1 atmosphere yields 138.3°C as the normal boiling point. This is between the two literature values, 137.7 and 140.2°C.[3] Mutual consistency among the

TABLE 1. VAPOR PRESSURE OF ACETYLACETONE

t (°C)	P (Torr)	t (°C)	P (Torr)
16.48	5.93 a	83.84	142.2 c
22.76	8.62 a	88.95	171.3 c
24.92	9.77 a	91.25	188.0 c′
29.69	11.88 a	91.49	188.3 c
33.50	14.22 a	94.20	210.1 c
38.08	18.34 a	97.09	231.3 c
40.02	19.93 a	102.38	270.4 c
41.03	20.80 b	103.68	284.8 c
48.28	30.54 a	105.25	305.2 c′
51.90	34.60 a	105.44	308.7 c
52.08	37.70 b	110.48	360.4 c
61.16	54.80 b	110.68	362.2 c′
63.65	63.30 c	115.90	424.2 c′
65.75	65.95 b	120.20	476.1 c
68.38	76.75 b	123.97	526.9 c
70.18	81.05 b	127.00	570.2 c′
74.11	94.75 c	129.08	599.9 c
76.91	108.2 c	131.19	630.0 c
79.37	121.0 c	136.45	728.2 c′
81.94	133.3 c	137.25	732.8 c

a) Vapor pressure apparatus.
b) Isoteniscope.
c) Ebulliometer.
c′) Ebulliometer (data obtained by K. Sato).

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1) E. Hala, J. Pick, V. Fried, and O. Vilim, "Vapour-Liquid Equilibrium," 2nd Ed., Pergamon, London (1967).

2) API Research Project 44, Data Sheets, Table 21k, Carnegie Inst. Tech., Pittsburgh, Pa., 1954.

3) C. H. Horsley, "Azeotropic Data," Adv. in Chem. Ser. Nos. 6 and 35, Amer. Chem. Soc., (1952 and 1962).

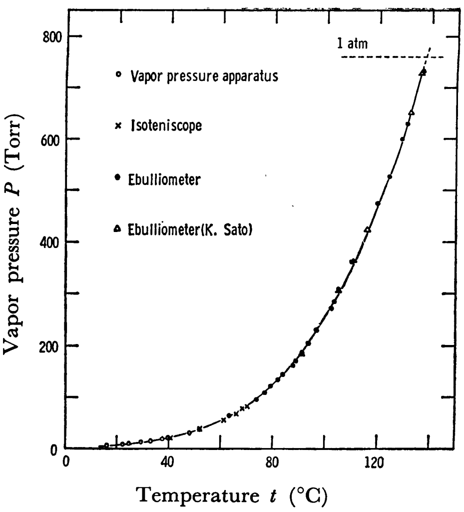

Fig. 2. Vapor pressure curve of acetylacetone.

data obtained with different apparatus may be confirmed by the P *vs.* t plot in Fig. 2, where the ranges of the applicability of each apparatus are seen to overlap.

Correlation with Empirical Equations. An attempt to correlate the data for the whole range of the measurement by means of the Antoine equation was not successful. We assigned two set of constants of the Antoine and Clapeyron-Clausius equations for different temperature ranges. They were evaluated by the method of least squares. The resulting vapor pressure equations are as follows.

$$\log P(\text{Torr}) = A - \frac{B}{C+t(^\circ\text{C})}$$

$$A = 6.86495,\quad B = 1377.34,\quad C = 208.35 \quad \text{for } t = 15\text{—}105^\circ\text{C}$$

$$A = 7.3522,\quad B = 1840,\quad C = 273.16 \quad \text{for } t = 105\text{—}138^\circ\text{C}$$

The experimental points scattered nearly at random from the values obtained by these equations, overall average deviation being ±1.2 Torr or ±2.3% in P.

In order to express the whole data by one single equation, the following Antoine-type equation is suggested.

$$\log P(\text{Torr}) = 6.86495 - \frac{1377.34}{207.35+t(^\circ\text{C})}$$

Heat and Entropy of Vaporization. The heat and entropy of vaporization at normal boiling point have been estimated from the log P *vs.* $1/T$ plot. They are 8.42 kcal/mol and 20.5 cal/deg·mol, respectively.

Discussion. The Antoine equation has been widely used and proved satisfactory for correlating the vapor pressure curve of organic liquids. In view of the relatively narrow pressure range covered by the present measurement, it was expected that any three-constant equation would correlate the data. It is tempting to ascribe this failure to the fact that the keto-enol equilibrium in acetylacetone molecule also changes with temperature.[4,5] However, acetylacetone is rather unstable at higher temperatures and, unless the atmosphere is completely inert, it undergoes partial decomposition as the temperature approaches normal boiling point. In fact, prolonged boiling has led to a pronounced brown coloration. Thus we might assume that there would be a slight boiling point elevation under such conditions. In practical distillation processes, it is possible that an even higher boiling point than that reported might be observed. We thank Mr. K. Sato and Mrs. H. Shirai-Tsujimoto for their assistance in the experiments.

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4) E. Funk and R. Mecke, in D. Hadzi ed. "Hydrogen Bond," Pergamon, New York, N. Y. (1959), p. 433.

5) G. Allen and R. A. Dwek, *J. Chem. Soc.*, *B*, **1960**, 161.