Vapor Heat Capacity and Heat of Vaporization of 2-Propanol

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The vapor heat capacity of 2-propanol was measured over a temperature range from 371.15° to 451.15° K. and a pressure range from $\frac{1}{3}$ to $\frac{4}{3}$ atmospheres. The heat of vaporization was determined at saturation temperatures and the same pressures. An equation of state to represent the data is presented based on a model of an equilibrium mixture of monomers, dimers, and tetramers.

AS PART OF A CONTINUING PROGRAM to determine the thermodynamic properties of oxygenated hydrocarbons, the vapor heat capacity and heat of vaporization of 2-propanol have been measured.

EXPERIMENTAL

The flow calorimeter and modifications have been described previously (2). The sample of 2-propanol used in the measurements was obtained from the Celanese Corp. of America. This material was over 99% pure with water as the chief impurity. The alcohol was stored over magnesium ribbon and finally distilled through a 1.2 meter column packed with glass rings. The middle cut from this distillation having a boiling range of less than 0.04° C. was vacuum distilled (bulb to bulb) into receivers for introduction into the apparatus. No changes in the color or boiling point were observed during the experimental work.

RESULTS

Calculations in this work were based on the 1956 atomic weights (16) and on the value of fundamental and derived physical constants given by Rossini and coworkers (14). All reported temperatures are on the defined International Temperature Scale.

Summaries of the experimental results are presented in Tables I and III. Temperatures at the experimental vapor pressures were calculated from the equation of Biddiscombe and coworkers (3). The saturation pressures were the result of 12 to 16 experimental runs and the estimated accuracy is ±2 mm. Hg. The latent heat can be represented by the equation:

$$\Delta H_v = 11{,}293 - 13.857t - 0.09382t^2 \qquad (1)$$

where ΔH_v is in calories per mole and t in degrees Centigrade. The accuracy uncertainty of this equation is not greater than ±0.15% in the range 57.07° to 89.52° C. Comparisons with previous results are presented in Table II.

As described in previous work (2) the model of an equilibrium mixture of monomers, dimers, and tetramers leads to the following equations:

$$V = RT/p + B + Dp^2 \qquad (2)$$

$$B = -b - RT \exp(-\Delta F_2/RT) \qquad (3)$$

$$D = -3RT \exp(-\Delta F_4/RT) \qquad (4)$$

$$C_p = C_p^\circ + Ap + Cp^3 \qquad (5)$$

$$A = \frac{\Delta H_2^2}{RT^2} \exp(-\Delta F_2/RT) \qquad (6)$$

$$C = \frac{\Delta H_4^2}{RT^2} \exp[(-\Delta F_4/RT)] \qquad (7)$$

The assignment of the constants in these equations is somewhat arbitrary. A fit to the experimental data can be obtained by choosing ΔH_2 between 3000 and 6000 cal./mole. In the authors' work on 2-butanol (2), the lower temperature heat capacity data were fit best with ΔH_2 of 5250 cal./mole. Assuming that the energy of formation of a hydrogen bond dimer is nearly the same in both secondary alcohols, the experimental heat capacity data of 2-propanol can be represented by the following constants in equation 5:

$$A = \frac{188.1}{T^2} \exp(2673/T) \text{ cal./mole atm.} \,^\circ \text{K.} \qquad (8)$$

$$C = \frac{1.633 \times 10^5}{T^2} \exp(11230/T) \text{ cal./mole atm.}^3 \,^\circ \text{K.} \qquad (9)$$

All values calculated from these equations in the range 371° to 451° K. are within the experimental uncertainty of ±0.3%. The heat and entropy of formation of the dimer, 5300 cal./mole and 22.4 entropy units respectively; and of the tetramer, 22,300 cal./mole and 74.2 entropy units, are in agreement with other data on hydrogen bonds (2, 7).

The ideal heat capacity fitted to a quadratic equation by the method of least squares is:

$$C_p^\circ = 3.9558 + 0.06275T - 1.429 \times 10^{-5}T^2 \qquad (10)$$

Table I. Experimental Latent Heat of Vaporization of 2-Propanol

Temp., ° C. From (3)	Press., Mm. Hg	ΔH_v, Cal./Mole
57.07	251.5	10,197 ± 10
72.43	506.2	9,796 ± 2
82.20	758.4	9,522 ± 2
89.52	1009.4	9,300 ± 2

Table II. Comparison of Directly Determined ΔH_v With Literature Values for 2-Propanol

Reported Temp., ° C.	Reported ΔH_v, Cal./Mole	Equation 1, Cal./Mole	%, Dev.	Ref.
b. pt.	9483	9519	0.4	(10)
b. pt.	9682	9519	1.7	(4)
81.25	9569	9550	0.2	(11)
82.22	9676 ± 90	9519	1.6	(12)
81.7	9690	9537	1.6	(1)
80.18	9625 ± 12	9582	0.4	(8)
69.96	9891 ● 4	9864	0.2	(8)
82.24	9512.3	9520	0.1	(7)
65.10	9958.9	9967	0.1	(7)

Figure 1 shows a comparison of the ideal heat capacity determined in this work with other investigators. Since some of the previous work was at only one pressure, these data were corrected to zero pressure using the above equations.

As a further check on the consistency of the results, the constant b in equation 3 can be found so that the gas imperfection $[V - (RT/p)]$ agrees with the values calculated from the Clapeyron equation. Then:

$$B = -450 - 1.085 \times 10^{-3}T \exp(2673/T) \text{ cc./mole} \qquad (11)$$

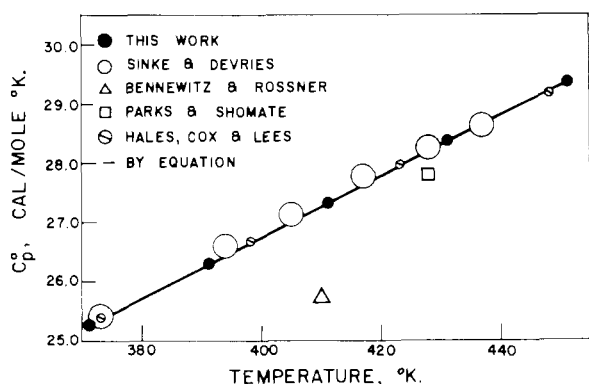$$D = -1.604 \times 10^{-14}T \exp(11230/T) \text{ cc./mole atm.}^2 \qquad (12)$$

Figure 1. Ideal vapor heat capacity of 2-propanol

At saturation pressures the calculated gas imperfections from the above equations are 1.97, 1.62, 1.47, and 1.35 liters per mole at 330.2°, 345.6°, 355.4°, and 362.7° K. compared to 2.03, 1.62, 1.47, and 1.35 liters per mole from the Clapeyron equation.

Again the representation is reasonable; but when this equation of state is compared to other data at higher temperatures, a constant b does not fit. Figure 2 shows the P-V-T data of Cox (5) and Kretschmer and Wiebe (9) and the second virial coefficient calculated from equation 11. The lower line shows a representation for B based on ΔH_2 of 3400 cal./mole and b of -100 cc./mole. The Cp data also can be expressed as a function of ΔH_2 equal to 3400 cal./mole; but then, C_p^o at 371° K. becomes 25.43 instead of 25.28 cal./mole.

Since the present work was completed, another study of the properties of 2-propanol has been reported (6, 7). The results have been shown in comparison in Table II and figure 1 and are in excellent agreement with this work. Green (6) finds by calculating the heat capacity from spectroscopic data that in order to simultaneously fit entropy data, the lower temperature heat capacity values in Hales, Cox and Lees (7) are too high. The C_p^o in this
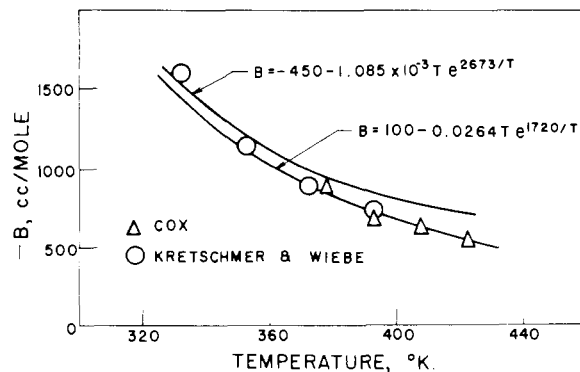

Figure 2. Second virial coefficient of 2-propanol

work using ΔH_2 equal to 5300 cal./mole agree with Green's calculation within the accuracy of the data.

It is apparent that the model of an equilibrium mixture of monomers, dimers, and tetramers does not fit all of the experimental facts unless some account of the variation of both b and ΔH_2 with temperature is included. The existence of cyclic or linear dimers or an equilibrium between the two may also be of importance.

ACKNOWLEDGMENT

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Table III. Vapor Heat Capacity of 2-Propanol in Calories Per Mole Degree

Temp., ° K.	371.15	391.15	411.15	431.15	451.15
C_p (⅓ atm. abs.)		28.55	28.52	29.10	29.86
C_p (⅔ atm. abs.)	28.74	27.74	28.16	28.88	29.72
C_p (⅔ atm. abs.)	26.98	27.15	27.83	28.69	29.55
C_p (⅓ atm. abs.)	25.95	26.75	27.54	28.55	
A[a]	1.83	1.14	0.74	0.50	0.35
C[b]	1.63	0.31	0.07	0.02	0.00
C_p^o (Experimental)	25.28	26.31	27.33	28.37	29.35
C_p^o (By equation)	25.28	26.30	27.34	28.35	29.36

[a] Parameter in Equation 5, cal./mole ° K. atm.
[b] Parameter in Equation 5, cal./mole ° K. atm.^{3}