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Saturation Properties and Liquid Compressibilities for Benzene and *n*-Octane

J. F. CONNOLLY and G. A. KANDALIC

Research and Development Department, American Oil Co., Whiting, Ind.

CALCULATION of accurate thermodynamic properties of solutions at high temperature and pressure requires, among other things, precise knowledge of the properties of the pure components. In the course of correlating high pressure measurements on solutions that contained benzene or *n*-octane, gaps in the available liquid-phase properties and discrepancies in the vapor pressures were encountered.

The compressibilities of liquid benzene have been measured by Glanville (5) up to 237.78° C.; the rapid change with temperature does not permit extrapolation of his data to higher temperatures. Compressibilities of liquid *n*-octane have been measured by Felsing (3) up to 275° C., but the 25° C. spacing between isotherms makes interpolation in the high-temperature region uncertain.

Numerous measurements have been made of the vapor pressure of benzene at high temperatures. Nevertheless, two recent sets of measurements (1, 6) disagree by more than 1%. An independent check appears necessary. The only available high-temperature vapor pressure measurements on *n*-octane date from 1900 (11)

With these deficiencies in mind, four kinds of measurements have been made on benzene and *n*-octane. These measurements, made at 10° C. intervals, were:

Property	Temperature Range, ° C.	
	Benzene	<i>n</i> -Octane
Vapor pressure	130- <i>t_c</i>	150- <i>t_c</i>
Saturated vapor volume	160-280	190-280
Saturated liquid volume	130-280	190-280
Liquid compressibility	130-270	130-280

The saturation properties were used to derive heats of vaporization for benzene from 160° C. to the critical temperature and for *n*-octane from 190° C. to the critical temperature.

EXPERIMENTAL

The benzene and *n*-octane used were American Petroleum Institute standard samples with stated purities of 99.98 and 99.94 mole %. The samples arrived with magnetic break-off tips and were not exposed to air during handling. No further purification was attempted, except to remove any traces of air by distillation in vacuo. The pressure rise on going from the dew point (no liquid present) to the bubble point (no vapor present was 0.01 atm. at 200° C.

In the experimental method (2), a sample was confined

above mercury in a calibrated glass capillary and stirred with a magnetically driven steel ball to achieve an equilibrium distribution of mercury. Volumes were determined by measuring lengths to 0.05 mm. with a cathetometer. The sample length was greater than 150 mm., so that volume measurements should be within 0.1%. Corrections were made for the effect of temperature and pressure on the capillary area. Pressures were measured with a dead-weight gage; temperatures, with a platinum resistance thermometer. Critical points were determined visually.

Two sets of measurements made with different capillaries agreed within 0.1% on the average.

VAPOR PRESSURES AND CRITICAL CONSTANTS

The measured vapor pressures can be represented by adding small corrections to the vapor pressure equations of A.P.I. Project 44 (9) that apply up to 1500 mm.:

$$\text{Benzene: } \log p = 4.02484 - \frac{1211.033}{t + 220.790} + \Delta$$

$$\Delta = 0, t \leq 100^\circ \text{ C.}$$

$$\Delta = 0.511 \times 10^{-8} (t - 100)^3, 100^\circ \leq t \leq 288.84^\circ \text{ C.}$$

$$n\text{-Octane: } \log p = 4.04296 - \frac{1355.126}{t + 209.517} + \Delta$$

$$\Delta = 0, t \leq 150^\circ \text{ C.}$$

$$\Delta = 0.794 \times 10^{-4} (t - 150) - 0.1146 \times 10^{-5} (t - 150)^2 + 0.1364 \times 10^{-7} (t - 150)^3, 150^\circ \leq t \leq 295.62^\circ \text{ C.}$$

where p is in atm. The standard deviation in pressure for these equations, in the range of present measurements, is 0.08%; the maximum deviation is 0.20%.

For benzene, present measured vapor pressures agree with those of Bender (1) within 0.08% on the average and 0.15% at the maximum. For n -octane, the authors measured values agree with those of Young (11) within 0.7% on the average and 1.1% at the maximum. Our measured critical constants are 288.84° C. and 48.28 atm. for benzene, and 295.62° C. and 24.55 atm. for n -octane.

SATURATED VAPOR AND SATURATED LIQUID VOLUMES

The volumes of the vapor at its saturation points were obtained by detecting the discontinuity in the pressure-volume isotherms of the gas phase. They are listed in Table I.

Saturated liquid volumes were obtained by visually noting the volume at which the last trace of vapor disappeared upon an increase in pressure of 0.01 atm. The results

Table I. Saturated Vapor Volumes

Temp., ° C.	Benzene, L./Mole	n -Octane, L./Mole
160	4.388	...
170	3.635	...
180	3.035	...
190	2.539	7.115
200	2.136	5.834
210	1.798	4.806
220	1.517	3.970
230	1.282	3.284
240	1.078	2.716
250	0.903	2.242
260	0.747	1.834
270	0.606	1.482
280	0.473	1.168

were represented, with a standard deviation of 0.06% and a maximum deviation of 0.15%, by the equations:

$$\text{Benzene, } 130^\circ \leq t \leq 280^\circ \text{ C.}$$

$$\log v_0 = 0.10117 + 0.84465x - 3.3522x^2 +$$

$$10.0208x^3 - 14.7420x^4 + 8.7872x^5$$

$$n\text{-Octane, } 190^\circ \leq t \leq 280^\circ \text{ C.}$$

$$\log v_0 = 0.21338 + 0.46260x - 0.57736x^2 + 0.59972x^3$$

where

$$x = 10^{-10}t^4, \text{ and } v_0 \text{ is in cubic centimeters per gram}$$

LIQUID COMPRESSIBILITIES

For each pressure-volume isotherm, the observed liquid specific volumes were fitted to equations of the form:

$$v = a + bp^{-1} + cp + dp^2 + ep^3 \quad (1)$$

where v is in cubic centimeters per gram and p is not greater than 180 atm. The constants for this equation and the standard deviations are given in Table II.

The benzene isotherms at 237.78° C. and the n -octane isotherm at 275° C. were measured to obtain direct comparisons with the highest temperature measurements of Glanville (5) and Felsing (3). At 237.78° C., the authors specific volumes for benzene lie 0.9% above Glanville's. At 275° C. present 20-atm. specific volumes for n -octane are 0.1% smaller than those of Felsing and the authors 150-atm. specific volumes are 0.4% larger.

HEATS OF VAPORIZATION

The heats of vaporization of liquid benzene and n -octane were derived by the Clapeyron equation from the saturated vapor and saturated liquid volumes and the slopes of the vapor pressure curves. These derived heats were combined with calorimetric values, measured at lower temperatures (4, 7-10) and fitted by least squares to obtain the following equations (Griffith's values were taken from the equation of Sutcliffe (4). A.P.I. Project 44 values and the value of zero at the critical point were each given a weight of 5 in the least-squares procedure.)

Benzene,

$$\Delta H_v = 46.25 + 178.38y - 201.8y^3 + 224y^4 \quad (2)$$

n -Octane,

$$\Delta H_v = 38.61 + 146.03y - 142.5y^3 + 169y^4 \quad (3)$$

ΔH_v is in calories per gram (1 cal. = 4.1840 absolute joules) and

$$y = \left[\left(\log \frac{T_c}{T} \right)^{1/3} - 0.3 \right],$$

where T_c is the critical temperature from this work in ° K. ($T_c = 273.16^\circ \text{ K}$). These equations are valid from 25° C. to the critical temperature. The standard deviation from the experimental values is 0.09 cal. per gram for benzene and 0.18 cal. per gram for n -octane. The deviations are plotted in Figure 1, where the zero line represents zero deviation from Equations 2 and 3.

Table II. Liquid Compressibilities, Constants For Equation 1

$t, ^\circ\text{C.}$	a	b	$c \times 10^2$	$d \times 10^4$	$e \times 10^6$	Std. Dev., %
Benzene						
130	1.3259	-0.0008	-0.03389	0.00321	0	0.03
140	1.3488	0.0010	-0.03923	0.00439	0	0.03
150	1.3733	0.0039	-0.04374	0.00512	0	0.03
160	1.3992	0.0065	-0.04956	0.00583	0	0.04
170	1.4276	0.0161	-0.05737	0.00724	0	0.03
180	1.4578	0.0318	-0.06522	0.00831	0	0.04
190	1.4907	0.0517	-0.07563	0.01028	0	0.04
200	1.5275	0.1062	-0.09061	0.01409	0	0.04
210	1.5659	0.2134	-0.10350	0.01637	0	0.05
220	1.6106	0.3840	-0.12189	0.01971	0	0.05
230	1.6589	0.7126	-0.14717	0.02645	0	0.05
237.78	1.6926	1.2474	-0.16040	0.02838	0	0.05
240	1.7019	1.4461	-0.16528	0.02942	0	0.05
250	1.7387	3.0596	-0.18012	0.03309	0	0.05
260	1.7185	7.1868	-0.14370	0.02105	0	0.02
270	1.5578	17.2990	+0.00666	-0.02080	0	0.16
<i>n</i> -Octane						
130	1.6471	0	-0.05551	0.00684	0	0.00
150	1.7040	0	-0.07070	0.00944	0	0.03
170	1.7674	0	-0.09147	0.01377	0	0.03
190	1.8472	0.0027	-0.14396	0.04913	-0.00983	0.02
200	1.8910	0.0123	-0.16541	0.05538	-0.01015	0.02
210	1.9435	0.0288	-0.20228	0.07360	-0.01351	0.02
220	1.9931	0.0761	-0.23736	0.09200	-0.01787	0.03
230	2.0551	0.1539	-0.29022	0.12135	-0.02402	0.03
240	2.1194	0.3415	-0.34655	0.15275	-0.03099	0.04
250	2.1899	0.7176	-0.41331	0.19155	-0.03985	0.04
260	2.2426	1.7529	-0.44795	0.20452	-0.04153	0.04
270	2.2334	4.4497	-0.38120	0.14705	-0.02605	0.03
275	2.1725	7.1605	-0.25548	0.05582	-0.00359	0.04
280	2.0119	11.9890	+0.03379	-0.14164	+0.04268	0.12

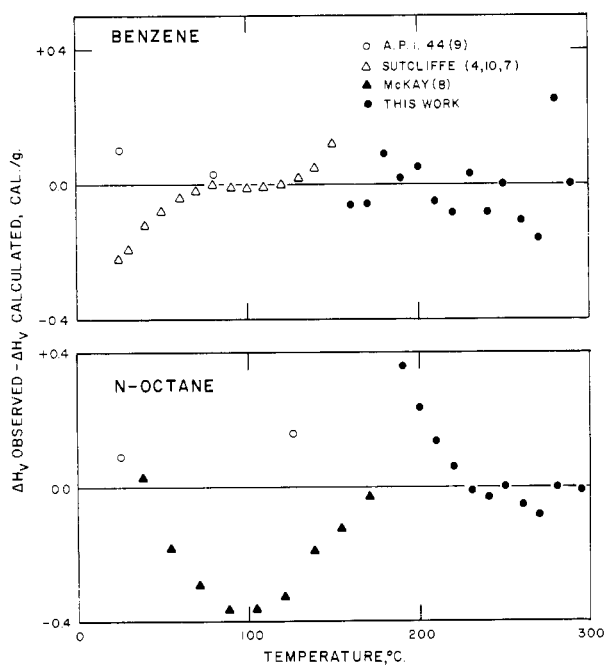


Figure 1. Comparison of Equations 2 and 3 with experiment

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