Vapor Pressures of Alkyl Aromatic Hydrocarbons

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VAPOR PRESSURE data for the aromatic hydrocarbons in the high pressure region are limited. Consequently, it becomes necessary to extrapolate the low pressure data to obtain information near the critical point. The usual straight-line extrapolation expressing the logarithmic vapor pressure–reciprocal absolute temperature relationship is inadequate for properly defining the vapor pressure of liquids over the entire range included between the triple point and the critical point. For normal paraffins, a nonlinear vapor pressure relationship exists which exhibits a reversal in curvature in the high pressure region (*14*). This vapor pressure function resembles an elongated S-shaped curve between the triple point and the critical point. Numerous equations have been employed to define the vapor pressure function accurately over limited ranges. For example, the Antoine equation (*2*)

$$\log P = A - \frac{B}{t + C} \tag{1}$$

gives reliable results in the low pressure region, but fails in the critical region. Gamson and Watson (*6*) propose the following empirical reduced state vapor pressure equation:

$$\log P = A + \frac{B}{T_r} - e^{-20 \cdot Tr - C^2} \tag{2}$$

Equation 2 becomes linear in the high pressure region where the exponential term becomes insignificant. Waring (*15*) reviews several vapor pressure equations and proposes a method for testing the consistency of experimental data over the entire range. Barrow (*3*) uses the heat capacities of the liquid and vapor in equilibrium to define the vapor pressure function as

$$\log P = A + \frac{B}{T} + (C_{pv} - C_{pl}) \log T + \frac{C}{T^2} \tag{3}$$

Equation 3 does not satisfactorily define vapor pressures near the critical point. Frost and Kalkwarf (*5, 8*), beginning with the Clausius-Clapeyron equation and assuming the van der Waals equation to apply, developed the relationship

$$\log P = A + \frac{B}{T} + C \log T + D \frac{P}{T^2} \tag{4}$$

Equation 4 accurately defines the vapor pressure function over the entire range included between the triple point and the critical point and also accounts for the reversal of curvature in the high pressure region. This fact is verified by Perry and Thodos (*11*), who investigated the vapor pressure behavior of the normal paraffins through n-dodecane. From their studies they reported an over-all deviation between calculated and literature reported values of 0.27% for these normal hydrocarbons.

TREATMENT OF LITERATURE DATA

The experimental results of several investigators (*4, 7, 10, 12, 16, 17*) are presented in the literature for a number of alkyl aromatic hydrocarbons. The work of Willingham and others (*16*) and that of API Project 44 (*12*) constitute the bulk of data available for these types of compounds. For over 40 aromatic hydrocarbons, vapor pressure data are limited in the range of 10 to 1500 mm. Vapor pressures above 1500 mm. have been reported only for benzene (*4, 7, 17*) and extend to the critical point. In spite of the lack of vapor pressure data in the high pressure region, critical constants have been reported for many aromatic compounds. These values are summarized by Kobe and Lynn (*9*). Utilizing this information, Thodos (*13*) has developed a method for predicting the critical constants of aromatic hydrocarbons with an estimated deviation of 1% for over 20 such compounds. This method predicts the van der Waals constants a and b from the molecular structure of the aromatic hydrocarbons. The van der Waals constants are then used to calculate the critical temperature and critical pressure of the substance. Following this approach, the critical temperatures and pressures of all the aromatic compounds investigated in this study have been calculated and were used in the subsequent treatment of the data. The calculated critical constants for the aromatic hydrocarbons included in this study are presented in Table I.

Vapor Pressure Constant *D*. A knowledge of any three of the four constants of Equation 4 suffices to define the vapor pressure function if one reliable vapor pressure measurement is available. Hence, the normal boiling point can be used as the reliable vapor pressure point. In their original development of Equation 4, Frost and Kalkwarf (*5*) show that $D = \frac{a}{2.303R^2}$, where a is the pressure van der Waals constant and R is the gas constant. The pressure van der Waals constant, a, was calculated for the alkyl aromatic hydrocarbons (*13*) and was used to evaluate the constant D which is presented in Table I. For m-xylene (*13*), $a = 30.909 \times 10^6$ (cc. per gram mole)^2 atm.; therefore,

$$D = \frac{(30.909 \times 10^6)760}{2.303(62{,}360)^2} = 2.62296$$

Vapor Pressure Constant *B*. Using a reliable pressure point in Equation 4, preferably the normal boiling point, and subtracting the resulting equation from the general form, the following expression results:

$$\log \frac{P}{P_b} = B\left(\frac{1}{T} - \frac{1}{T_b}\right) + C \log \frac{T}{T_b} + D\left(\frac{P}{T^2} - \frac{P_b}{T_b^2}\right) \tag{5}$$

where subscript b refers to any arbitrary reference point. Rearranging and dividing Equation 5 by $\log T/T_b$, yields the following equation:

$$\frac{\log \frac{P}{P_b} - D\left(\frac{P}{T^2} - \frac{P_b}{T_b^2}\right)}{\log \frac{T}{T_b}} = B\,\frac{\frac{1}{T} - \frac{1}{T_b}}{\log \frac{T}{T_b}} + C \tag{6}$$

Equation 6 serves to define constants B and C as the slope and intercept, of the function:

$$Y = \left\{ \log \frac{P}{P_b} - D\left(\frac{P}{T^2} - \frac{P}{T_b^2}\right) \right\} \Big/ \log \frac{T}{T_b} \textit{ vs.}$$

$$X = \left(\frac{1}{T} - \frac{1}{T_b}\right) \Big/ \log \frac{T}{T_b}$$

Values of X can be evaluated from any set of vapor pressure measurements and a reference point. Corresponding values of Y can then be calculated from these vapor pressures

Table I. Vapor Pressure Constants of Equation 4 and Critical Values for Some Alkyl Aromatic Hydrocarbons

		Critical Constants (*13*)			Constants Calculated from Comprehensive Analysis of Vapor Pressure Data			From T_b and T_c	
	T_b, ° K.	T_c, ° K.	P_c, mm. Hg.	$D_{\text{calcd.}}$[a]	B	C	$B_{\text{calcd.}}$[b]	$A_{\text{calcd.}}$	$C_{\text{calcd.}}$
Benzene	353.265	562.2	36,936	1.56738	−2457.12	−5.28840	−2457.12	23.36128	−5.31165
Toluene	383.790	593.5	31,586	2.04294	−2690.80	−5.45371	−2711.79	24.27652	−5.54949
Ethylbenzene	409.351	616.1	27,748	2.50619	−2991.85	−6.05908	−2966.49	25.43516	−5.86460
o-Xylene	417.576	632.1	27,991	2.61456	−3040.72	−5.94175	−3040.89	25.82849	−5.98184
m-Xylene	412.268	625.1	27,292	2.62296	−2997.10	−5.91474	−3001.48	25.99177	−6.05781
p-Xylene	411.516	618.2	26,608	2.63119	−2979.00	−5.89868	−2982.88	25.65800	−5.94421
n-Propylbenzene	432.382	640.1	24,457	3.06882	−3223.79	−6.36370	−3221.13	27.03537	−6.34224
Isopropylbenzene	425.557	623.7	23,917	2.97980	−3163.62	−6.34609	−3108.08	25.89683	−5.98145
1-Methyl-2-ethylbenzene	438.318	651.5	24.928	3.11982	−3296.98	−6.41766	−3295.56	27.50441	−6.47943
1-Methyl-3-ethylbenzene	434.470	645.1	24,366	3.12873	−3254.62	−6.32870	−3256.15	27.44422	−6.47527
1-Methyl-4-ethylbenzene	435.154	638.7	23,818	3.13747	−3244.88	−6.30517	−3237.55	26.86236	−6.27373
1,2,3-Trimethylbenzene	449.249	646.8	24,335	3.14935	−3351.05	−6.19472	−3337.82	25.97083	−5.90845
1,2,4-Trimethylbenzene	442.516	644.1	24,062	3.15835	−3301.19	−6.21412	−3271.76	26.23930	−6.03840
1,3,5-Trimethylbenzene	437.881	629.6	23,157	3.13569	−3315.01	−6.41273	−3263.63	26.34108	−6.06487
n-Butylbenzene	456.435	662.0	21,858	3.67311	−3528.43	−6.86872	−3475.80	28.19716	−6.66120
Isobutylbenzene	445.924	652.7	21,911	3.56118	−3366.20	−6.62042	−3366.20	28.04813	−6.65549
sec-Butylbenzene	446.470	656.9	22,321	3.54099	−3387.26	−6.70668	−3387.26	28.34121	−6.75040
tert-Butylbenzene	442.284	647.3	22,184	3.45977	−3352.49	−6.68195	−3352.49	28.12571	−6.68194
1-Methyl-2-propylbenzene	457.965	672.5	22,230	3.72760	−3625.69	−7.35252	−3550.23	29.38364	−7.05196
1-Methyl-3-propylbenzene	454.965	666.6	21,782	3.73702	−3518.89	−6.84421	−3510.82	29.20373	−7.00530
1-Methyl-4-propylbenzene	456.465	660.7	21,341	3.74652	−3499.60	−6.76275	−3492.22	28.50280	−6.76281
1-Methyl-2-isopropylbenzene	451.315	657.3	21,789	3.63162	−3371.83	−6.40553	−3437.18	28.34744	−6.72985
1-Methyl-3-isopropylbenzene	448.305	651.4	21,348	3.64095	−3406.98	−6.71892	−3397.77	28.15770	−6.67961
1-Methyl-4-isopropylbenzene	450.265	645.7	20,923	3.65037	−3379.72	−6.52512	−3379.17	27.33951	−6.39448
1,2-Diethylbenzene	456.588	669.6	22,458	3.65759	−3558.01	−6.97056	−3550.23	29.40080	−7.05304
1,3-Diethylbenzene	454.267	663.6	21,994	3.66709	−3553.62	−7.00359	−3510.82	29.09871	−6.96300
1,4-Diethylbenzene	456.917	657.6	21,546	3.67642	−3493.97	−6.65794	−3492.22	28.16762	−6.63844
1,2-Dimethyl-3-ethylbenzene	467.075	665.1	21,972	3.68907	−3620.05	−6.76723	−3592.49	27.93846	−6.51049
1,2-Dimethyl-4-ethylbenzene	462.915	662.6	21,751	3.69857	−3538.35	−6.52925	−3526.43	27.75662	−6.47949
1,3-Dimethyl-2-ethylbenzene	463.175	665.1	21,972	3.68907	−3550.70	−6.59583	−3592.49	28.67111	−6.77003
1,3-Dimethyl-4-ethylbenzene	461.575	662.6	21,751	3.69857	−3524.42	−6.55955	−3526.43	28.00667	−6.56812
1,3-Dimethyl-5-ethylbenzene	456.915	649.1	21,006	3.67439	−3466.93	−6.43917	−3518.30	28.15547	−6.61238
1,4-Dimethyl-2-ethylbenzene	460.075	662.6	21,751	3.69857	−3487.09	−6.50125	−3526.43	28.28374	−6.66633
1,2,3,4-Tetramethylbenzene	478.205	665.8	21,310	3.81118	−3713.52	−6.77416	−3699.66	27.43238	−6.27990
1,2,3,5-Tetramethylbenzene	471.165	665.8	21,310	3.81118	−3667.92	−6.79703	−3699.66	28.83863	−6.77798
1,2,4,5-Tetramethylbenzene	469.965	663.3	21,098	3.82060	−3624.49	−6.61148	−3633.60	28.10277	−6.55052
Naphthalene	491.120	749.7	29,792	3.45604	−3824.42	−7.07715	−3824.42	29.18743	−6.88557
1-Methylnaphthalene	517.807	764.3	26,212	4.08291	−3885.74	−6.23405	−4121.35	30.10442	−7.10196
2-Methylnaphthalene	514.217	764.3	26,212	4.08291	−3817.97	−6.06333	−4055.29	29,88115	−7.05450
1-Ethylnaphthalene	531.835	774.9	23,530	4.67498	−4324.13	−7.62202	−4376.02	32.11873	−7.71242
2-Ethylnaphthalene	531.065	774.9	23,530	4.67498	−4225.40	−7.21188	−4309.96	31.46921	−7.51712

[a] $D = a/2.303\ R^2$, where a is the pressure van der Waals constant, $(\text{cc./g. mole})^2$ atm. Values of a calculated for above alkyl aromatic hydrocarbons are presented elsewhere (*14*).
[b] Values of vapor pressure constant B were calculated from group contribution values of Table II.

and the established constant *D*. This treatment, when applied to the data of benzene, produced the straight-line relationship presented in Figure 1. The slope and intercept of this line were $B = -2457.12$ and $C = -5.28840$. To produce consistency in this analysis, the data of each investigator were referred to a reliable vapor pressure point occurring within his set of data. For all the aromatic hydrocarbons included in this study, relationships similar to Figure 1 were obtained, from which the *B* and *C* values were calculated. In Figure 1 the plotted critical points for benzene do not coincide, but are displaced along the straight line. This results from the use of different reference points for the evaluation of *Y* and *X*. Both values *B* and *C* established from the experimental data of the alkyl aromatic hydrocarbons considered are reported in Table I.

Several methods of correlation for constants *B* and *C* have been attempted in which the physical properties of these compounds were considered as variables. The results of these attempts point to a correlation for *B* which indicates the existence of an additive contribution resulting from the replacement of hydrogen by a methyl group. Thus, using benzene as the base group, values of *B* can be produced for an alkyl aromatic hydrocarbon in the successive addition of group contribution values, ΔB, associated in the replacement of hydrogen by a methyl group. The group contribution values, ΔB, depended on the nature of the carbon atom involved in the substitution and on the nature of the carbon atoms adjacent to it. To differentiate between the types of carbon atoms involved in these studies, the following classification proposed by Andersen, Beyer, and Watson (*1*) was adopted and was applied to the carbon atoms of the alkyl side chains.

Type				
1	2	3	4	A
$\overset{\vert}{-CH_3}$	$\overset{\vert}{-CH_2}$	$\overset{\vert}{\underset{\vert}{-CH}}$	$\overset{\vert}{\underset{\vert}{-C-}}$	C atom in aromatic ring

The position and sequence of substitutions on the aromatic nucleus influenced the final value of *B*. The results of contribution values, ΔB, produced from the alkyl aromatic compounds investigated are presented in Table II. With the values of this table, it becomes possible to evaluate constant *B* for an alkyl aromatic hydrocarbon. To illustrate the use of the group contribution values, ΔB, the vapor pressure constant *B* for 1,3-dimethyl-4-ethylbenzene is calculated as follows

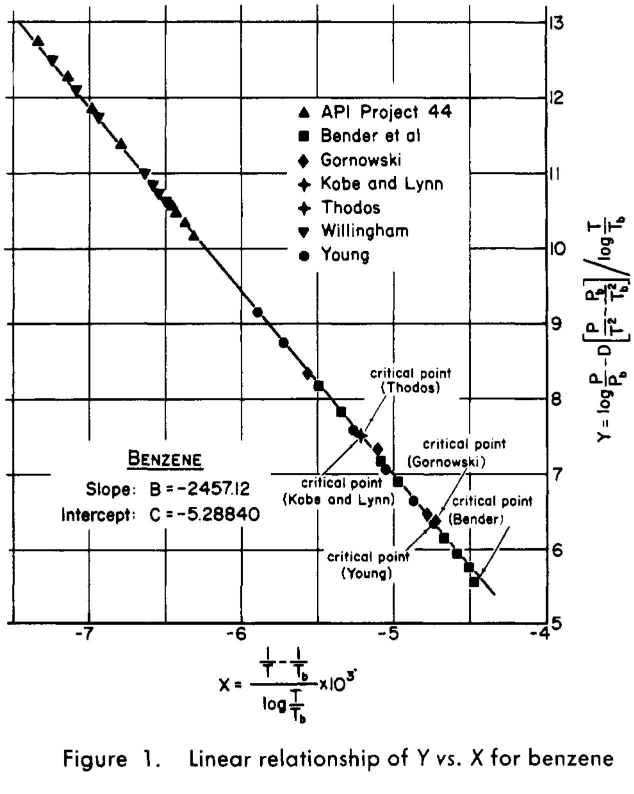
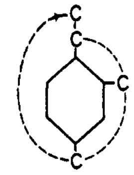


Figure 1. Linear relationship of *Y* vs. *X* for benzene

Table II. Group Contribution Values, ΔB, in the Replacement of Hydrogen by Methyl Groups for the Aromatic Alkyl Hydrocarbons

	B	ΔB
A. Base Groups		
Benzene	−2457.12	
Naphthalene	−3824.42	
B. First methyl substitution on base group		−254.67
C. Second methyl substitution on base group		
ortho		−329.10
meta		−289.69
para		−271.09
D. Third methyl substitution on base group		
1,2,3		−296.93
1,2,4		−230.87
1,3,5		−262.15
E. Fourth methyl substitution on base group		−361.84
F. Methyl substitutions on alkyl side chains[a]		
A −← 1		−254.67
2 −← 1		−254.67
A −← 2 →− 1		−141.62
A −← 2 →− 2		−166.13
2 −← 2 →− 1		−145.07
A −← 3 →− 1 ↓ 1		−244.41

[a] Arrows point away from type of carbon atom on which the methyl substitution is made and toward the types of carbon atoms adjacent to it.



Base group - benzene	−2457.12
Substitution	
First methyl	−254.67
Second methyl (ortho)	−329.10
Third methyl (1, 2, 4)	−230.87
Side chain (A −← 1)	−254.67
	$B = -3526.43$

Following a similar procedure, constants *B* were calculated for all the alkyl aromatic hydrocarbons included in this study. These values of *B* are also presented in Table I. A comparison of calculated constants *B* with the values obtained from the comprehensive treatment of the vapor pressure data shows good agreement and on this basis the evaluation of these constants from a knowledge of the structure of the hydrocarbon has been considered reliable.

Vapor Pressure Constants A and C. Several attempts to reproduce the vapor pressure constant *C* were made and included correlations with the structure of the hydrocarbon. None of these correlations proved satisfactory. Correlations of constant *B* and constant *C* with the normal boiling point as a parameter produced consistent relationships but were not sufficiently precise to define exactly the actual vapor pressure function over the entire range. Consequently, the possibility of evaluating *C* from structural considerations and readily available physcial properties was abandoned, thus necessitating the use of two vapor pressure points for the establishment of constants *A* and *C*.

Although any two reliable vapor pressure measurements suffice to establish *A* and *C*, it is preferable that these two points cover the extremes of the range included between the triple point and the critical point. The normal boiling point is not only readily available but also fairly reliable. Well established normal boiling points are reported in the literature (*12*) and have been accepted as reliable enough to use in this study. The critical point has been arbitrarily selected as the other value necessary along with the normal boiling point, to define, these constants. The selection of the critical point produces constants that properly define the vapor pressure function in the high pressure region. Because experimental critical values for all the hydrocarbons treated in this analysis are not available, critical constants for these substances were calculated (*13*) and were used in this study. As a result, constants A and C for each of these alkyl aromatic hydrocarbons have been established from the calculated critical point, the normal boiling point, and the calculated vapor pressure constants B and D. these calculated constants are presented in Table I and complete the requirements for the definition of the vapor pressure constants necessary to establish Equation 4 for the alkyl aromatic hydrocarbons included in this study.

Comparison of Results. The calculated constants B and D resulting from the structure of the alkyl aromatic hydrocarbons, and the values of A and C calculated from the critical point and the normal boiling point, were used to define the generalized vapor pressure function, Equation 4, for the alkyl aromatic hydrocarbons. In this connection, several selected vapor pressures for each compound were calculated and covered the available experimental pressures ranging from 10 mm. to the critical point. Calculated and experimental values have been compared for the 41 hydrocarbons studied and show an absolute average deviation of less than 1%, with a maximum average deviation of 5.0% for 1,2,3,4-tetramethylbenzene and a minimum average of 0.07% for 1,3-dimethyl-4-ethylbenzene. In Table III are included the calculated results of some representative hydrocarbons which are compared with the vapor pressures reported in the literature.

Table III. Comparisons of Literature and Calculated Vapor Pressures for Some Aromatic Hydrocarbons

	Temp., ° K.	Vapor Pressure, Mm. Hg. Lit.		Vapor Pressure, Mm. Hg. Calcd.	% Dev.
		Benzene			
	280.715	40.00	(*11*)	40.24	0.61
	312.243	175.89	(*15*)	175.79	−0.06
	340.300	500.69	(*15*)	500.33	−0.07
	368.863	1200	(*11*)	1200.5	0.04
	383.165	1739	(*16*)	1759.2	1.16
	423.165	4331	(*6*)	4385.8	1.26
	453.165	7630	(*16*)	7747.5	1.52
	513.165	19425	(*6*)	19696	1.91
	533.165	25329	(*16*)	27733	1.59
Crit.	562.165	36936	(*8*)	36922	−0.04
					0.83
		Toluene			
	279.525	10.0	(*11*)	9.976	−0.24
	319.898	80.0	(*11*)	79.34	−0.82
	363.832	402.43	(*15*)	401.53	−0.22
	393.735	1000	(*11*)	1000.6	0.06
	409.585	1500	(*11*)	1502.2	0.15
Crit.	593.965	31616	(*8*)	31764	0.47
					0.33
		o-Xylene			
	305.305	10.0	(*11*)	10.123	1.23
	336.625	47.66	(*15*)	47.77	0.24
	348.022	77.28	(*15*)	77.45	0.22
	385.605	300.0	(*11*)	300.49	0.16
	414.497	700.0	(*11*)	700.22	0.03
	445.235	1500	(*11*)	1496.0	−0.27
Crit.	631.565	28044	(*8*)	27818	−0.80
					0.42
		1,2,4-Trimethylbenzene			
	338.555	20.00	(*11*)	20.00	0.00
	370.640	80.00	(*11*)	79.70	−0.38
	426.699	500.0	(*11*)	499.6	−0.07
	453.655	1000	(*11*)	1000.7	0.07
	471.365	1500	(*11*)	1502.3	0.15
					0.13
		1,3-Dimethyl-4-ethylbenzene			
	353.865	20.00	(*11*)	19.98	−0.08
	387.165	80.00	(*11*)	79.92	−0.10
	445.165	500.0	(*11*)	499.5	−0.09
	473.115	1000	(*11*)	1000.1	0.01
	491.465	1500	(*11*)	1500.7	0.05
					0.07
		1,2,3,4-Tetramethylbenzene			
	352.665	10.00	(*11*)	8.808	−11.92
	401.565	80.00	(*11*)	74.07	−7.43
	461.335	500.0	(*11*)	491.97	−1.61
	490.075	1000	(*11*)	1010.9	1.09
	508.965	1500	(*11*)	1542.4	2.82
					4.97

NOMENCLATURE

a = pressure van der Waals constant, (cc. per gram mole)^2 atm.
A, B, C, D = vapor pressure constants
b = volume van der Waals constant, cc. per gram mole
C_{pl} = specific heat of liquid at constant pressure
C_{pg} = specific heat of vapor at constant pressure
P = vapor pressure
R = gas constant, 62,360 (mm. Hg.) (cc.) per (gram-mole) (° K.)
t = temperature, ° C.
T = absolute temperature, ° K.
X = temperature modulus, $\left(\frac{1}{T} - \frac{1}{T_b}\right) \Big/ \log \frac{T}{T_b}$
Y = vapor pressure modulus, $\left[\log \frac{P}{P_b} - D\left(\frac{P}{T^2} - \frac{P_b}{T_b^2}\right)\right] \Big/ \log \frac{T}{T_b}$
Δ = difference

Subscripts

b = any arbitrary reference point
r = reduced state

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