

The Symmetry of the Benzene Molecule

V. Deitz and D. H. Andrews

Citation: [The Journal of Chemical Physics](#) **1**, 62 (1933); doi: 10.1063/1.1749221

View online: <http://dx.doi.org/10.1063/1.1749221>

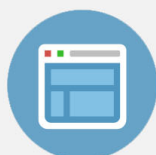
View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/1/1?ver=pdfcov>

Published by the [AIP Publishing](#)



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



The Symmetry of the Benzene Molecule*

V. DEITZ AND D. H. ANDREWS, *Chemistry Laboratory, Johns Hopkins University*

(Received November 4, 1932)

The melting points of various isomeric organic compounds indicate that molecular symmetry has an important effect on physical properties. With R. H. Fowler's statistical treatment of the crystal state, the symmetry number has been calculated for benzene and cyclohexene. The data employed are the vapor pressure, the heat

capacity of the crystal, the heat capacity of the vapor as calculated from Raman spectra, the heat of sublimation and the moments of inertia. According to this calculation the symmetry number for benzene has the value 6 ± 0.5 indicating that the molecule is not plane. The symmetry number for cyclohexene is 2 ± 0.2 as is to be expected.

RECENT developments in statistical mechanics and quantum mechanics have made clear the importance of the symmetry of the molecule in various physical and chemical processes. This property must be ranked as of equal influence with mass and energy in many instances where the process in question involves molecular orientation. For example, one finds great differences among the melting points of certain series of organic compounds which have approximately the same mass, thermal energy, and differ only in shape or symmetry. One of the most striking cases is the series of hydrogenated benzene derivatives: benzene, cyclohexadiene, cyclohexene, and cyclohexane.

We may define the symmetry of these compounds in the manner of Ehrenfest and Trkal¹ who were the first to point out the role of symmetry in statistical mechanics. These authors assign to each type of molecule a symmetry number which is defined as the number of equivalent positions which the molecule may assume when it executes all possible rotations in space. Thus with benzene, if we assume a flat molecule, we may rotate the ring in its own plane and find six equivalent positions, and by turning the ring over six more, giving a total symmetry number of twelve. The same is true of cyclohexane. Ordinary cyclohexadiene and cyclohexene have both a symmetry number of two. Cyclohexadiene with the double bonds in the 1-2 and 4-5 position has a

symmetry number of four. As is shown in Table I, the melting points of these compounds vary over a hundred degree range and appear to be related to the molecular symmetry. Thus, the removal of the first double bond presumably lowers the symmetry of the ring from 12 to 2 and we get a drop in melting point from 5.5 to -95°C . The removal of still another double bond causes no change in symmetry and little in melting point. The last step, however, which restores the symmetry to something like that of benzene, raises the melting point to within a tenth of a degree of its original value.

We can form a qualitative idea of the reason for this influence of symmetry on melting point by observing the distinction between the processes of liquid forming from crystal and of crystal forming from liquid. The melting point is the temperature at which these two processes are in equilibrium. In the first case, crystal to liquid, the factors which fix the rate are the mass, thermal energy, and intermolecular force. If these are the same, a symmetrical or unsymmetrical molecule have both the same chance of escaping from the crystal.

In the reverse process, however, if we consider a symmetrical and an unsymmetrical molecule under exactly the same conditions, the former has the greater chance of orienting itself properly to fit into the crystal lattice. Freezing therefore takes place at a higher temperature. This rule is verified qualitatively in dozens of series of organic isomers.

As contrasted with the melting points, the boiling points of this series lie within a very narrow range of temperature. The processes of going

* From the dissertation submitted by V. Deitz to the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ Ehrenfest and Trkal, *Proc. Roy. Soc. (Amsterdam)* **23**, 162 (1920).

TABLE I.

	C_6H_6	C_6H_8	C_6H_{10}	C_6H_{12}
	Benzene	Cyclohexadiene	Cyclohexene	Cyclohexane
M.P.	+5.48°C	-95.°C	-103.7°C	+6.4°C
B.P.	+80.2°	+81.°	+81.6°	+80.0°
Mol. Wght.	78.04	80.06	82.08	84.10

from liquid to vapor and from vapor to liquid do not, of course, involve molecular orientation, so it is to be expected that molecular symmetry will have little influence. The fact that boiling points do lie so close together is evidence that the other factors such as thermal energy and intermolecular force vary only slightly throughout the series, at least in the region of the boiling point.

These qualitative evidences of the influence of symmetry on melting point made it appear worth while to look for a really quantitative measure of the effect of symmetry on physical properties in general. For this purpose the vapor pressures of crystals appear more promising than their melting points. As may be seen from the discussion which follows, symmetry may be regarded as influencing the behavior of a molecule through its effect on the entropy of the molecule. To determine the absolute entropy of the vapor state we may calculate the change in entropy as the system proceeds by various paths from a state of zero entropy, the crystal at absolute zero, to the vapor state. Thus it may pass from the ordered crystal phase to the chaotic vapor phase either directly by sublimation, or by melting to liquid and vaporization. Consequently one may infer that symmetry will play a part in determining the absolute entropy and therefore the vapor pressure of either crystal or liquid.

The first step in solving this problem is to set up the vapor pressure equation for a crystal, using the various terms, found in statistical mechanics, one of which involves a factor directly measuring the molecular symmetry. Fowler² has

² R. H. Fowler, *Statistical Mechanics*, Cambridge University Press, Cambridge, 1929.

given the most thorough discussion of the background of statistical mechanics needed for this problem and we shall use his treatment as the basis for discussion.

We take as a starting point the following equation (Fowler, Eq. (436)) which may be derived on the basis of classical thermodynamics:

$$\ln p = -\frac{\lambda_0}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T (C_{vap.} - C_{sol.}) dT + i, \quad (1)$$

where λ_0 is the molal heat of sublimation at $T=0$, and i is a chemical constant defined by this equation. $C_{vap.}$ and $C_{sol.}$ are the heat capacities per mole of the vapor and crystal at constant pressure.

We now let $(C_p)_0$ represent the constant part of $C_{vap.}$ i.e., the part which has already attained its classical value, and we let $(C_p)_1$ represent the variable part of $C_{vap.}$ Eq. (1) may then be put in the form

$$\ln p = -\frac{\lambda_0}{RT} + \frac{(C_p)_0}{R} \ln T + \int_0^T \frac{dT}{RT^2} \int_0^T \{(C_p)_1 - C_{sol.}\} dT + i. \quad (2)$$

It is possible to express statistically rather than thermodynamically the part of this which depends on the variable specific heats. Using the partition functions developed by Fowler we may write (Fowler, Eq. (438))

$$\ln p = -\frac{\lambda_0}{RT} + \frac{(C_p)_0}{R} \ln T + \ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} + \ln R(T) V(T) - \ln K(T) + \ln R(0) V(0) - \ln K(0), \quad (3)$$

where $R(T)$ =rotational vapor partition function at temperature T , $V(T)$ =vibrational partition function at temperature T , $K(T)$ =crystal partition function at temperature T , $R(0)$ =rotational vapor partition function at temperature 0°K , $V(0)$ =vibrational partition function at temperature 0°K , $K(0)$ =crystal partition function at temperature 0°K . The value of the partition function at $T=0^\circ\text{K}$ must remain in our equation because by definition the partition functions have been constructed to start out with a constant term.

We may now apply this equation to the case of crystalline benzene in the temperature range of 100° – 298°K . Under these special conditions we may make the following changes in Eq. (3):

(1) In the case of a polyatomic molecule like benzene with moments of inertia as large as 10^{-38} , the rotational degrees of freedom are fully excited at temperatures above 10°K . Then $(C_p)_0=4R$ and the rotational partition function is then identical with the classical value:

$$R(T)=8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}/h^3.$$

(2) Vibration is contributing to the heat capacity but has not attained the classical value and must be calculated from

$$V(T)=\sum_1^f \frac{1}{1-\exp(-h\nu_f/kT)}$$

where the summation is over the f modes of vibration having $(3n-6)$ degrees of freedom.

(3) The crystal partition function, $K(T)$ is to be discussed from thermodynamic relationships. It has been shown by Fowler (page 128) that any crystal containing the average number \bar{P} molecules with a partition function $K(\theta)$ and average energy \bar{E} , contributes to the entropy of the crystal by the following amount:

$$S_{(s)}=k[\bar{P} \ln K(\theta) - \bar{E}_{(s)} \ln \theta].$$

We may change the independent variable θ to T (the absolute temperature) by the known relationship between the two, $\theta=e^{-1/kT}$. Then for a mole of the crystal:

$$S_{(s)}=R[\ln K(T) + \bar{E}_{(s)}/T]$$

or

$$\ln K(T)=S_{(s)}/R - \bar{E}_{(s)}/RT.$$

By definition

$$\begin{aligned}\bar{E}_{(s)} - \bar{E}_s^0 &= \int_0^T C_{v(s)} dT \\ \frac{\bar{E}_{(s)}}{RT} &= \frac{1}{RT} \int_0^T C_{v(s)} dT + \frac{E_{(s)}^0}{RT}.\end{aligned}$$

But $E_{(s)}^0/RT$ is the first term in the crystal partition function and therefore equal to $\ln K(0)$. Hence

$$\ln K(T) = -\frac{1}{RT} \int_0^T C_{v(s)} dT + \frac{S_{(s)}}{R} - \ln K(0).$$

(4) Fowler has shown that if we ignore electronic structure and treat the atoms as structureless mass points, then: $K(0)=V(0)=1$.

(5) $R(0)=\bar{\omega}_0\delta/\sigma$.

It is assumed that the energy in the lowest rotational state is equal to zero so that both $\bar{\omega}_0$ and δ will have the value of unity.

With these expressions for the partition functions we obtain:

$$\begin{aligned}\ln p &= -\frac{\lambda_0}{RT} + \frac{4R}{R} \ln T + \ln \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \\ &+ \ln \left[\sum_1^f \frac{1}{1 - \exp(-h\nu_f/kT)} \right] \\ &+ \ln \frac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{h^3} \\ &+ \frac{1}{RT} \int_0^T C_{v(s)} dT - \frac{S_{(s)}}{R} + \ln \frac{\bar{\omega}_0\delta}{\sigma}.\end{aligned}\quad (4)$$

Our problem, then, is to substitute in this equation the experimentally determined values of the vapor pressure and other physical constants and to solve for the values of the symmetry number contained in the last term.

We may take as the first step the calculation of the vibrational contribution of the specific heat. It is necessary to know this, first, in order to extrapolate the specific heat curve of the solid to 0°K , and second, in order to calculate the specific heat of the vapor, for which experimental measurements are not available.

The best source of data for this calculation lies in the frequencies observed in the Raman spectra. With the help of the mechanical models of molecules developed by Kettering, Shutts and An-

TABLE II.

Benzene Ring vibration	Degrees of freedom	Cyclohexene Ring vibration	Degrees of freedom	Degrees of freedom
400 cm ⁻¹	2	171 cm ⁻¹	1	1263
605	1	282	1	1426
849	2	390	1	1443
991	6	445	1	1650
1178	1	487	1	C-H
C-H		635	1	stretching
bending		656	1	2635
1584	6	821	1	2660
1605	6	873	1	2833
C-H		904	1	2856
stretching		963	1	2873
2947	1	1034	1	2908
3047	2	C-H		2934
3060	2	bending		2986
3185	1	1062	1	3020
		1134	1	
	30	1218	1	42
		1238	1	

draws³ it is possible to assign values for the number of degrees of freedom associated with each Raman frequency. Table II gives the values so assigned, the frequencies being those observed by Wood and Collins.⁴ The specific heat term associated with each frequency at various temperatures can be calculated with the help of the Einstein specific heat function. When multiplied by the appropriate factors to take into account the number of degrees of freedom associated with each frequency, the sum of these results gives the

³ C. F. Kettering, L. W. Shutts and D. H. Andrews, Phys. Rev. [2], 36, 531 (1930).

⁴ Wood and Collins, Phys. Rev. [2], 42, 386 (1932).

total contribution of vibration to the heat capacity of the molecule. These assignments of degrees of freedom are not exact but it is believed that they give the correct order of distribution of frequencies with an accuracy sufficient for this calculation.

In extrapolating the heat capacity curve of the solid to 0°K it is also necessary that one know the characteristic temperature, θ_m , for the molecules vibrating as units in the crystal lattice, i.e., excluding internal molecular vibration. This frequency when substituted in the modified Debye equation for the heat capacity of a solid yields the so-called Debye contribution to the heat capacity. This frequency may be calculated most conveniently by the Lindemann melting point formula. The modifications necessary to apply this treatment to a molecular crystal lattice have been discussed by Andrews.⁵ From the Lindemann formula it is found that for benzene, $\theta = 159$, and for cyclohexane, $\theta = 133$. With these values, C_p has been calculated for the lattice vibrations in the temperature range below available experimental values.

The difference of $C_p - C_v$ for the solid was calculated according to Andrews' modifications of Nernst's formula:

$$C_p - C_v = (C_v)^2 (T/T_m) (0.0214)$$

where (C_v) is the specific heat at constant volume arising from the Debye terms mentioned above,

⁵ D. H. Andrews, Chem. Reviews 5, 533 (1928).

TABLE III. Benzene.

<i>T</i>	Einstein (Solid and vapor) <i>C_v</i>	<i>C_p</i> (Vapor)	Debye (Solid) <i>C_v</i>	Expansion (Solid)	Calc. <i>C_v</i>	Condensed Phase Experimental <i>C_p</i>	<i>S</i>	<i>H</i>
10	0	8.0	0.24	0	0.24	0.3	0.01	0.8
20	0	8.0	1.67	0	1.7	1.7	0.57	9.9
30	0	8.0	4.00	0.05	4.1	4.5	1.68	40.0
40	0	8.0	6.06	0.11	6.2	6.6	3.27	95.0
50	0.02	8.02	7.54	0.22	7.8	8.0	4.92	169.0
60	0.06	8.06	8.56	0.34	9.0	9.4	6.51	257
80	0.26	8.26	9.86	0.6	10.8	11.1	9.41	465
100	0.64	8.64	10.54	0.85	12.0	12.0	11.95	695
120	1.1	9.1				13.30	14.25	947
140	1.70	9.7				14.80	16.42	1227
160	2.4	10.4				16.33	18.52	1538
180	3.0	11.0				18.04	20.54	1881
200	4.0	12.0				20.10	22.50	2556
220	4.6	12.6				22.34	24.48	2680
250	6.1	14.1				26.15	27.59	3402
280	7.6	15.6				31.44	39.39	6652
300	8.7	16.7				32.33	41.59	7290
350	11.6	19.6				35.9	46.84	8993

TABLE IV. *Cyclohexene*.

<i>T</i>	Einstein (Solid and vapor) <i>C_v</i>	<i>C_p</i> (Vapor)	Debye (Solid) <i>C_v</i>	Expansion (Solid)	Calc. <i>C_v</i>	Condensed Phase		
						Experimental <i>C_p</i>	<i>S</i>	<i>H</i>
10	0	8.0	0.4	0	0.4		0.05	1.0
20	0	8.0	2.6	0	2.6		0.79	13.0
30	0	8.0	5.3	0.08	5.4		2.18	52.0
40	0.2	8.2	7.3	0.2	7.9		3.90	119
50	0.4	8.4	8.6	0.4	9.4		6.58	205
60	0.7	8.7	9.4	0.6	10.7		7.42	306
80	1.4	9.4	10.4	1.0	12.9		10.61	535
100	2.30	10.3	10.9	1.2	14.2	13.2	13.5	787
120	3.29	11.3				14.85	16.06	1067
140	4.28	12.3				21.4	25.50	2360
160	5.35	13.35				24.3	28.7	2815
200	7.67	15.7				28.0	39.3	4674
250	10.87	18.9				30.8	45.9	6141
300	14.35	22.35				34.3	51.7	7763
350	18.51	26.7				37.7	57.15	9560

T is the temperature at which computations are being made, and *T_m* is the melting point of the crystal.

Tables III and IV give the heat capacity, entropy and relative heat content values which are based on the recent work of Parks and Huffman,⁶ and the extrapolated values calculated in the manner described above. It may be seen that the calculated values of the heat capacity of the solid check the experimental values fairly well at the temperatures below which it is necessary to use calculated values for extrapolation.

In regard to the moments of inertia of the two substances under consideration, it seems best to use calculated values, as the values that might be obtained from a study of band spectra are very uncertain. For benzene the plane hexagonal model is assumed with the distance between the carbon atoms equal to 1.42Å. This is done in view of the fact that for graphite the C-C distance is 1.44Å, and for hexa-methyl benzene 1.42Å. The hydrogens are considered to be on the extension of the diagonal line, 1.2Å away from the carbon atoms. There is no existing x-ray data as to these dimensions determined directly from benzene itself. The calculated results are given in Table V.

For cyclohexene a plane hexagon is also taken as the basis of calculation, five sides being 1.54Å long and the sixth side 1.35Å, the latter being the carbon-carbon separation in double bonds. The hydrogens are assumed to be 1.2Å from the

TABLE V. *Moments of inertia*.

	Benzene	Cyclohexene
<i>A</i>	154×10^{-40}	197×10^{-40}
<i>B</i>	154×10^{-40}	213×10^{-40}
<i>C</i>	308×10^{-40}	395×10^{-40}
(<i>ABC</i>)	7.42×10^{-114}	16.59×10^{-114}

carbons. While it is probable that benzene and cyclohexene are not representable by a plane model a calculation on this assumption is not too far from the actual state of affairs and the difference in the numerical values obtained in either case is small.

The values of the vapor pressure are taken from the work of Deitz⁷ which was carried out in order to make these calculations possible.

The only other values necessary to complete the calculation are those of *V(T)*. These values as calculated from $V(T) = [1 - \exp(-h\nu/kT)]^{-1}$ are given in Table VI.

With the aid of the above data calculations for the value of the symmetry number have been made from Eq. (4), and are given in Table VI.

In examining the results of these calculations we may note in the first place that the symmetry number stays reasonably constant over a wide range of temperature. This is a test of the accu-

⁷ V. Deitz, J. Am. Chem. Soc. (1933). Shortly to be published. The values of the heat of sublimation (λ_0) at 0°K were calculated as 12,302 cal for benzene; 11,333 cal for cyclohexene. These values are based on the heats of vaporization reported by Mathews, J. Am. Chem. Soc. **48**, 562 (1926), the heats of fusion reported by Parks (reference 6), and the heat capacities in the above table.

⁶ G. S. Parks and H. M. Huffman, J. Am. Chem. Soc. **52**, 1032 (1930).

TABLE VI.

Substance	Temp.	$\ln V(T)$	Sym. number
Benzene (s)	100°K	0.0000	5.4
" (s)	200°	0.0901	6.0
" (s)	250°	0.1503	6.3
" (s)	278.5	0.1972	6.9
" (l)	278.5	0.1972	6.5
" (l)	298	0.2466	5.5
Cyclohexene (s)	100°	0.0493	1.8
" (l)	298°	0.6316	2.2

racy of the estimates of the heat capacities, and indicates that these values are satisfactory for the present purpose.

In order to extend the temperature range as far as possible, two calculations for liquid benzene and one for liquid cyclohexene have been included. Over this large temperature range one might expect considerable change in the conditions which affect the validity of the various assumptions upon which Eq. (4) is based. The fact that the symmetry numbers remain so constant is an indication that these assumptions are justified to a considerable extent, and that the results secured are not fortuitous.

In order to illustrate the sensitivity of the value of symmetry number to changes in the experimental data, the following calculation was made with the data at 200°K. If the value of ABC , the product of the three moments of inertia, is in error by 10 percent, the error in the

symmetry number, $\Delta\sigma$, is 0.2. If the entropy of the solid is in error by 2 percent, $\Delta\sigma$ is 1.2. If the temperature is in error by 2°, $\Delta\sigma$ is 1.0. If λ_0 is in error by 2 percent, $\Delta\sigma$ is 1.0. Again if $V(T)$ is in error by 10 percent, $\Delta\sigma$ is 0.2. Finally if the vapor pressure data are off by 10 percent, $\Delta\sigma$ is 0.3.

The absolute value of the symmetry numbers suggests immediately that we are dealing not with a plane hexagon but with a puckered ring. It is true that the majority of the evidence from dipole measurements and x-rays has been in favor of a flat benzene ring. We are dealing here, however, with a property that may well be much more sensitive than either of the above in detecting lack of symmetry of the ring. The value six seems to show that there are but three rather than six equivalent positions on one side of the ring. It is impossible to say whether this is due to a staggering of the hydrogens or to a puckering of the ring. It seems significant however, that the number six should be indicated so definitely. The result of a symmetry number of two for cyclohexene tends to confirm the validity of the conclusion.

In conclusion it may be pointed out that this provides a method for calculating the absolute vapor pressure from the thermal and statistical properties of the molecule. It appears that symmetry may play an important part in determining the physical properties of a molecule and perhaps the chemical behavior as well.