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SIGNIFICANT STRUCTURE THEORY OF MOLECULES HAVING
HINDERED INTERMOLECULAR ROTATION IN THE
CONDENSED PHASES*

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Communicated March 25, 1966

Significant structure theory leads to a partition function which accounts for all three phases of simple substances and in particular describes rather accurately the liquid and dense gas regions.¹ In the case of polyatomic molecules, additional degrees of freedom not possessed by monatomic molecules must be taken into account, and for light molecules like hydrogen, quantum effects must be considered.² We present here a modification of the basic partition function to account for hindered intermolecular rotation.

The Significant Structure Model (refs. 1 and 2).—The problem of describing a condensed system is really the problem of determining the distribution of the normal modes of motion of the molecules. This distribution follows from our liquid model, according to which all the molecules vibrate much as in a solid except for molecules jumping into vacancies. The result is that a vacancy surrounded by molecules converts three vibrational degrees into translations, and in so doing the vacancy behaves as a gas molecule. Since vacancies are of molecular size, the number of moles of vacancies in a mole of liquid is $V - V_s/V_s$, where V is the molar volume of the liquid and V_s is the molar volume of the solid at the melting point. A vacancy surrounded by other vacancies is without dynamic properties, but when it is completely surrounded by other molecules, it acts like a gas molecule. Since the fraction of the positions next to a vacancy filled by molecules is V_s/V , we write $(V_s/V) \cdot (V - V_s/V_s) = (V - V_s/V)$ for the fraction of gaslike molecules, with the remaining fraction V_s/V being solidlike. Accordingly, for simple molecules like liquid argon, our model leads to the partition function

$$f = \left(f_s \left(1 + 10.7 e^{\frac{-0.0052 E_s V_s}{(V - V_s) RT}} \right) \right)^{NV_s} f_g^{\frac{N(V - V_s)}{V}},$$

where the numerical value of all parameters is calculated from the model.

This formula should apply equally well for polyatomic molecules if proper account is taken of hindered rotation and of the internal vibrations. The internal vibrations are practically unchanged by any phase change so that they offer no difficulty.

A Simplified Partition Function for Hindered Rotation.—Some solids show higher-order transitions below the melting point which have been interpreted to be due to the onset of molecular rotation.³ Some members of series of similar compounds do not show any transitions below the melting point but do have large entropies of

fusion approximately equal to the sum of the entropies of transition and fusion of those compounds that begin rotating below the melting point.^{4a} Thus it appears that some molecules are able to realize their rotational degrees of freedom while still in the condensed phase.^{4b} Also it would seem likely that this rotation would not be completely uninhibited, except for perhaps the most spherical molecules. In order to describe this situation quantitatively, it is useful to choose a useable partition function for hindered rotation. For a linear molecule the hindered rotational partition functions f_{hr} is well represented by the classical expression

$$f_{hr} = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{P_{\phi}=-\infty}^{\infty} \int_{P_{\theta}=-\infty}^{\infty} \frac{e^{-H/kT} d\theta d\phi dP_{\theta} dP_{\phi}}{\sigma h^2} \quad (1)$$

Here H , the Hamiltonian, is

$$H = T + U = \frac{1}{2}I(\dot{\theta}^2 + \sin^2\theta \dot{\phi}^2) + U \quad (2)$$

and the generalized momenta are

$$P_{\theta} = \frac{\partial T}{\partial \dot{\theta}} = I\dot{\theta} \quad (3)$$

and

$$P_{\phi} = \frac{\partial T}{\partial \dot{\phi}} = I \sin^2 \theta \dot{\phi}. \quad (4)$$

Here T and U are the kinetic and potential energy, respectively. Substituting (4) and (3) into (2) and using the resulting H in (1) and integrating gives:

$$f_{hr} = \frac{4\pi^2 I k T}{\sigma h^2} \int_{\theta=0}^{\pi} e^{-U/kT} \sin \theta d\theta. \quad (5)$$

For a linear heteropolar molecule $\sigma = 1$ and $U = E_0 (\cos \theta + 1)$. Substituting these results into (5) yields

$$f_{hr} = \frac{8\pi^2 I k T}{h^2} \frac{kT}{E_0} e^{-\frac{E_0}{kT}} \sinh \left(\frac{E_0}{kT} \right). \quad (6)$$

For a homopolar linear molecule $\sigma = 2$ and $U = E_0 (\cos 2\theta + 1)$. This leads to

$$f_{hr} = \frac{4\pi^2 I k T}{2h^2} \int_{\theta=0}^{\pi} e^{-\frac{E_0 (\cos 2\theta + 1)}{kT}} \sin \theta d\theta = \frac{4\pi^2 I k T}{2h^2} \int_{\theta=0}^{\pi} e^{-\frac{E_0 (2\cos^2\theta)}{kT}} \sin \theta d\theta. \quad (7)$$

If we substitute $X = \cos \theta$ in (7), we obtain

$$f_{hr} = \frac{4\pi^2 I k T}{2h^2} \int_{X=-1}^1 e^{-\frac{2E_0 X^2}{kT}} dX. \quad (8)$$

The integral in (8) can be integrated numerically by using tables of the error function or by using a series expansion of the integrand. For the nonlinear molecule we have for hindered rotation the partition function

$$f_{3hr} = \frac{(8\pi^3 ABC)^{1/2} (kT)^{3/2}}{\sigma h^3} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{\psi=0}^{2\pi} e^{-\frac{U}{kT}} \sin \theta d\theta d\phi d\psi. \quad (9)$$

Here θ , ϕ , and Ψ are Euler's angles. For a molecule like CH_3CCl_3 it should be a fair approximation to take $U = E_0 (\cos \theta + 1)$ and $\sigma = 1$. Substituting these values into (9) gives

$$f_{3nr} = \frac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{h^3} \frac{kT}{E_0} e^{-\frac{E_0}{kT}} \sinh \frac{E_0}{kT}. \quad (10)$$

Similarly for ethane, we have $V_2 = E_0 (\cos 2\theta + 1)$ and $\sigma = 2$, giving

$$f_{3nr} = \frac{4\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{2h^3} \int_{X=-1}^1 e^{-\frac{2E_0X^2}{kT}} dX. \quad (11)$$

In many other cases U takes a more general form.

The above classical expressions are useful and will be employed in subsequent calculations of hindered rotation, but we will here be concerned with a simple quantized approximation. Suppose that for all energies less than some value E in the rotational degrees of freedom a molecule behaves as an oscillator while for higher energies it rotates, then approximately

$$f_{nr} = f_v + e^{-\frac{E}{kT}} (f_{\text{rot}} - f_v'). \quad (12)$$

For the simple one-dimensional oscillator $f_v = f_v'$. In general, the term $e^{-E/kT} f_v'$ subtracts out the vibrational states which have been replaced by rotational levels. The value of the energy E preventing rotation must fall off sharply as the density of the liquid drops off. Accordingly, we expect a dependence of the barrier height E , hindering rotation, of the form

$$E = \frac{BV_s}{V - V_0}.$$

The proportionality constant, B , called the barrier height constant, is a characteristic constant for each substance. For lightly hindered rotation we make the approximation $f_v = f_v' = 1$. The final form of the hindered rotational partition function then becomes

$$f_{nr} = 1 + e^{-\frac{BV_0}{(V_s - V_0)RT}} (f_{fr} - 1). \quad (13)$$

Note that below the transition point $V \approx V_0$ and no rotation occurs and that at high temperatures or large volumes the rotation becomes free. Also, if rotation begins at the melting point, $V_s = V_0$. Here V_s is the volume of the solid at the melting point.

The hindered rotational partition function is used to replace the free rotational partition function in the "solidlike" part of the total partition function. In the "gaslike" part, a free rotational partition function is used since these molecules which are "gaslike" are assumed to rotate freely. The complete partition function for polyatomic molecules now becomes

$$f = \left[\frac{e^{E_s/RT}}{(1 - e^{-\theta/RT})^3} \left[1 + n \left(\frac{V - V_s}{V_s} \right) e^{-\frac{\alpha E_s V_s}{(V - V_s)RT}} \right] \right. \\ \left. \times \left[1 + e^{-\frac{BV_s}{(V_s - V_0)RT}} (f_{fr} - 1) \right] \right]^{\frac{NV_s}{V}} \cdot \left(\frac{(2\pi mk)^{3/2}}{h^3} \frac{eV}{N} f_{fr} \right)^{\frac{N(V - V_s)}{V_s}} \\ \times \left(\prod_{i=1}^r \frac{1}{1 - e^{-\frac{h\nu_i}{kT}}} \right), \quad (14)$$

where the ν_i are the frequencies of the vibrational degrees of freedom. For linear molecules

$$f_{fr} = \frac{8\pi^2 I k T}{\sigma h^2}, \quad (15)$$

and for nonlinear polyatomic molecules

$$f_{fr} = \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{\sigma h^3}. \quad (16)$$

In this case r in (14) is the total number of degrees of freedom minus 5 for linear and minus 6 for nonlinear molecules, where I , A , B , and C are principal moments of inertia and sigma is the symmetry number.

Application to Selected Examples.—Methane, carbon tetrachloride, and nitrogen exhibit second-order transitions well below their melting points, indicating the introduction of hindered rotation in the solid phase (cf Table 1). Methyl chloride and chlorine, while similar to the above molecules in some respects, do not have any transitions below their melting points. They do, however, have exceptionally large volume expansions and entropy changes on melting, indicating the introduction of hindered rotation at the melting point (cf. Table 1).

TABLE 1
OBSERVED PROPERTIES AND PARAMETERS OF CH₄, CCl₄, N₂, CH₃Cl, AND Cl₂

	CH ₄	CCl ₄	N ₂	CH ₃ Cl	Cl ₂
T_{fr} (°K)	20.6 ⁸	225.1 ¹⁰	35.61 ¹⁵	—	—
S_{fr} (e.u.)	0.89 ⁸	4.86 ¹⁰	1.54 ¹⁵	—	—
V_o (cm ³ /mole)	30.6 ⁹	80 ¹¹	28 ¹⁶	—	—
T_m (°K)	90.65 ⁸	250.41 ¹²	63.14 ¹⁵	175.43 ¹⁷	171.4 ⁵
S_m (e.u.)	2.48 ⁵	2.40 ¹⁰	2.73 ¹⁵	8.76 ¹⁷	8.90 ¹⁸
V_s (cm ³ /mole)	30.94 ⁵	87.1 ¹³	29.31 ⁵	37.3 ¹¹	34.34 ⁵
E_s (cal/mole)*	2200 ¹⁵	7296 ¹⁴	1448 ¹⁵	6453 ¹⁷	4586 ¹⁸
θ (°K)†	75 ⁵	52 ¹⁰	51 ¹⁵	—‡	86 ¹⁸

* Calculated from vapor pressure equations.

† Calculated as $\theta_R = 3/4 \theta_D$.

‡ Not reported in ref. 17.

In the past the application of significant structure theory made a simplifying approximation that either the molecules rotate freely in the "solidlike" part of the liquid as in the case of methane and nitrogen,⁵ or that the rotational degrees of freedom are not realized in the liquid state, as in the case of chlorine.⁶ Such approximations made it necessary to replace 10.7, the number of nearest neighbors, with an unrealistically large value and to replace our calculated value 0.0052 by a quantity chosen to fit the data. By introducing the hindered intermolecular rotation partition function, it is possible to maintain n and a in (14) at the theoretical values for argon,⁷ given in equation (1), and still reproduce the experimental data satisfactorily. To compare results obtained, first assuming free rotation and second hindered rotation, the parameters were adjusted until certain observed data were reproduced. In the case of CH₄ and N₂, when they were assumed to rotate freely, and in the case of Cl₂, when it was assumed not to rotate in the bound state, n , a , V_s , E_s , and θ were obtained according to the technique developed by Fuller.^{5, 6} In the case of CCl₄, when it was assumed to rotate freely, and in the case of CH₃Cl,

when it was assumed not to rotate in the "solidlike" state, these parameters were obtained by systematic adjustment until the following conditions were met simultaneously: the calculated vapor pressure and entropy of vaporization were taken equal to their observed values at the boiling point; the calculated pressure at the observed melting point temperature equaled 1 atm (giving a value for a), and the calculated entropy of fusion equaled the observed value (in the case of CCl_4) or the calculated entropy of the liquid at the melting point equaled the observed values (in the case of CH_3Cl), giving a value for n . Values of the necessary observed data used in these procedures are given in Tables 1 and 3, and the values of the parameters obtained are listed in Table 2 under the heading NHR (nonhindered rotation).

In the case of hindered rotation, for all molecules, n and a were chosen equal to the theoretical values for argon. The remaining parameters, V_s , E_s , θ , B_0 , and V_0 , were obtained in an analogous way to that described above except in the case of CH_3Cl and Cl_2 . In these cases V_0 was arbitrarily chosen equal to 0.9000 V_s (the approximate value for the remaining molecules which have a transition below the melting point). Values of these parameters are listed in Table 2 under the heading HR (hindered rotation).

TABLE 2
CALCULATED VALUES OF THE PARAMETERS FOR CH_4 , CCl_4 , N_2 , CH_3Cl , AND Cl_2

		CH_4	CCl_4	N_2	CH_3Cl	Cl_2
n	NHR*	13.3	17.0	12.9	11.0	14.3
	HR†	10.70	10.70	10.70	10.70	10.70
a	NHR	0.002960	0.001361	0.003430	0.000082	0.001298
	HR	0.005200	0.005200	0.005200	0.005200	0.005200
V_s (cm ³ /mole)	NHR	30.94	87.7701	29.31	45.5440	39.1757
	HR	31.8417	84.1771	28.6338	42.0772	37.6874
E_s (cal/mole)	NHR	2200.	8615.47	1529.9	5733.61	6075.9
	HR	2249.67	9255.27	1616.03	6359.93	6250.45
θ (°K)	NHR	75.33	57.4668	55.94	70.5081	41.48
	HR	74.6266	59.5427	64.9213	92.1619	84.0983
B_0 (cal/mole)	HR	3.3751	69.9531	4.5209	40.8390	39.7348
	V_0/V_s	HR	0.9513	0.8808	0.9092	0.9000‡

* NHR = assuming free rotation in the bound state for CH_4 , CCl_4 , and N_2 ; assuming no rotation in the bound state for CH_3Cl and Cl_2 . The values for CH_4 and N_2 are taken from ref. 5; those for Cl_2 are from ref. 6.

† HR = assuming hindered rotation in the bound state.

‡ Chosen arbitrarily.

Values of selected calculated and¹⁹ observed properties at the melting, boiling, and critical points are given in Table 3. Also, a plot of the reduced densities and the rectilinear diameter versus reduced temperature for CCl_4 is given in Figure 1, and a plot of the logarithm of the reduced pressure versus the reciprocal of the reduced temperature for CCl_4 is given in Figure 2. (The results for CCl_4 are representative of all the molecules studied, when expressed in this manner.)

Discussion.—A comparison of observed and calculated values first assuming and second not assuming free rotation is made in Table 3. This shows that in general the results improve when the hindered intermolecular partition function is used. Since the observed melting and boiling temperatures, entropy of fusion and vaporization, and equilibrium molar volumes at the boiling point were used to obtain the parameters, one would expect these values to agree closely. The calculated molar liquid volumes at the melting point improve slightly in every case when hindered rotation is included. Of more interest is the fact that while the calculated entropies of fusion for CH_4 , CCl_4 , and N_2 agree with experiment whether free or hindered rota-

TABLE 3

CALCULATED AND OBSERVED PROPERTIES AT THE MELTING POINT, BOILING POINT, AND CRITICAL POINT FOR CH₄, CCl₄, N₂, CH₃Cl, AND Cl₂

		CH ₄	CCl ₄	N ₂	CH ₃ Cl	Cl ₂
T_m (°K)	NHR	90.66	250.17	63.16	175.43	187.44
	HR	90.65	250.41	63.14	175.76	171.40
	Obs	90.65	250.41	63.14	175.43	171.40
V_{1m} (cm ³ /mole)	NHR	34.106	93.988	32.641	46.314	41.967
	HR	35.241	92.341	32.157	45.913	40.695
	Obs	35.42	91.75	31.95	45.487	41.145
S_{1m} (e.u.)	NHR	13.601	44.789	14.558	25.126	27.287
	HR	16.104	47.367	16.367	28.140	26.102
	Obs	16.13	46.192	16.346	27.237	25.799
S_{sm} (e.u.)	NHR	10.838	42.180	11.626	—	—
	HR	13.634	44.968	13.637	—	—
	Obs	13.66	43.792	13.617	18.477	16.904
P_b (atm)	NHR	0.98	1.01	0.99	1.00	0.98
	HR	1.00	1.00	1.00	1.00	1.00
	Obs	1.00	1.00	1.00	1.00	1.00
V_{1b} (cm ³ /mole)	NHR	36.07	103.39	34.52	50.58	44.82
	HR	37.77	103.19	34.63	49.86	44.45
	Obs	37.79	103.59	34.70	50.71	45.32
V_{ob} (cm ³ /mole)	NHR	9170.	27880.	6220.	20077.	19650.
	HR	8930.	28044.	6127.	20003.	19237.
	Obs	9163.	27263.	6346.	19747.	19616.
S_{1b} (e.u.)	NHR	19.018	56.584	19.641	33.385	31.205
	HR	19.044	56.498	19.059	33.065	30.803
	Obs	18.83	56.72	19.074	33.476	31.030
S_{ob} (e.u.)	NHR	36.567	77.108	36.291	59.056	52.458
	HR	36.512	77.118	36.256	54.047	51.423
	Obs	36.34	77.22	36.31	54.16	51.44
T_c (°K)	NHR	212.7	581.1	134.4	450.4	463.6
	HR	207.5	575.8	129.0	441.4	421.6
	Obs	191.1	556.4	126.2	416.3	417.
V_c (cm ³ /mole)	NHR	103.9	297.0	98.5	149.7	131.4
	HR	107.1	294.3	97.1	145.7	130.6
	Obs	99.0	276.	90.1	143.	124.
P_c (atm)	NHR	60.8	58.1	40.5	89.2	104.7
	HR	57.5	58.1	39.4	90.0	95.9
	Obs	45.8	45.0	33.5	65.9	76.1

tion is assumed, nevertheless the calculated liquid entropies agree better when hindered rotation is assumed. This is especially marked in the case of CH₄. Also, the calculated values for the liquid molar entropy at the melting point of CH₃Cl and N₂ (molecules that do not rotate in the solid state) improve when hindered rotation

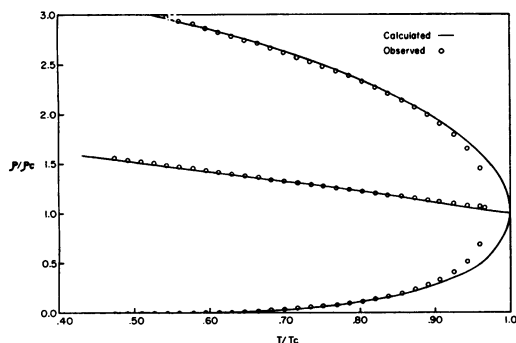


FIG. 1.—Reduced densities and rectilinear diameter vs. reduced temperature for carbon tetrachloride.

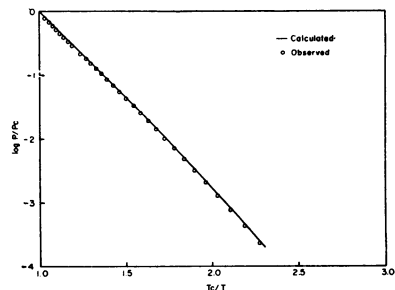


FIG. 2.—Reduced pressure vs. reciprocal reduced temperature for carbon tetrachloride.

is included. Assuming observed hindered rotation improves the calculated values of the critical properties.

Finally, it is seen that adopting values for n and a equal to the theoretical values for argon is possible when hindered rotation is included. This means that simple polyatomic molecules can be treated successfully with significant structure theory by considering them to behave essentially like inert gases with the appropriate modifications necessary to account for intermolecular rotation.

Summary.—The significant structure theory is applied to the hindered intermolecular rotation of polyatomic molecules in the condensed phase. The modification makes it possible to treat the translational degrees of freedom as they were treated for argon. A comparison of results shows that our treatment of hindered intermolecular rotation is an improvement on previous calculation of thermodynamic properties, particularly near the critical point.

* This is an essential portion of a thesis submitted by Don R. McLaughlin to the Chemistry Department, University of Utah, in partial fulfillment of the requirements for a Doctor of Philosophy degree.

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