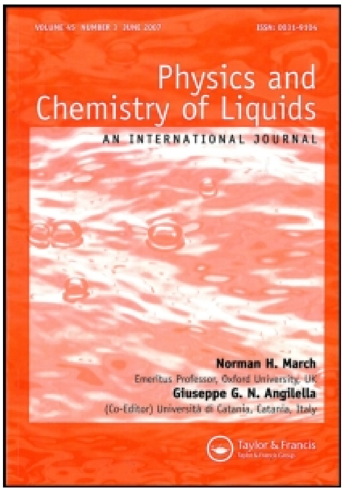

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The Significant Structure Theory Applied to Halobenzenes

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Abstract—Just as molecular structure, as revealed by X-ray diffraction, can be interpreted in terms of intuitive models, so liquid structure can be interpreted in terms of a model which leads to a partition function giving the Helmholtz free energy in terms of volume, temperature, and composition. From this explicit expression for the Helmholtz free energy all thermodynamic properties are calculable and can be compared with experiment. Absolute Rate Theory permits the prediction of transport properties from this same model, providing still further insight into liquid structure. Here, Significant Liquid Structure Theory has been applied to twelve substituted benzenes and the results compared with experiment. A single equation is derived for the twelve substances differing in ten of the cases only in three parameters having to do with the solid-like part of the liquid. For simple liquids these properties are those of the solid at the melting point. These properties are the energy of sublimation, molar volume of the solid, and the Einstein characteristic temperature, θ. Hindered rotation is explained in terms of a barrier to rotation of one tenth the energy of sublimation.

1. Introduction

The significant structure theory of liquids is applied to twelve halobenzenes. According to this theory, there are the fractions $(V - V_s)/V$ gas-like and V_s/V solid-like degrees of freedom, where V and V_s are the molar liquid volume at a given temperature and the molar solid volume at the melting point, respectively. For the solid-like degrees of freedom, the Einstein partition function is generally used, while the ideal gas partition function is employed for the gas-like degrees of freedom. Utilizing these ideas, the partition function for a liquid is obtained, and from it the thermodynamic properties of the liquid are calculated.

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2. The Partition Function for Liquid Halobenzenes

For spherical molecules there is little or no force restricting molecular rotation. For highly nonspherical molecules the rotational motion is totally hindered. For such cases the partition function of the solid-like molecules contains no rotational term and the resulting libration is described by an oscillational partition function.

Halobenzenes are an intermediate case requiring a partition function with partially hindered rotation as follows:

$$f_i = \left\{ \frac{\mathrm{e}^{E_s/\mathrm{RT}}}{(1-\mathrm{e}^{-\theta/T})^3} \cdot f_{\mathrm{HR}} \cdot \prod_{i=1}^{30} \frac{1}{1-\mathrm{e}^{-h\nu i/kT}} \times \left[1 + \frac{n(V-V_s)}{V_s} \mathrm{e}^{-aE_sV_s/(V-V_s)\mathrm{RT}} \right] \right\}^{N(V_s/V)} \times \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{eV}{N} \cdot \frac{8\pi^2(8\pi^3\mathrm{ABC})^{1/2}(kT)^{3/2}}{\sigma h^3} \times \prod_{i=1}^{30} \frac{1}{1-\mathrm{e}^{-h\nu i/kT}} \right\}^{N(V-V_s/V)}. \tag{1}$$

$$f_{\mathrm{HR}} = \left\{ \frac{1}{1-\mathrm{e}^{-\theta/T}} + \mathrm{e}^{-lE_s/\mathrm{RT}} \left[\left(\frac{8\pi^2(8\pi^3\mathrm{ABC})^{1/2}(kT)^{3/2}}{\sigma h^3} \right)^{1/3} - \frac{1}{1-\mathrm{e}^{-\theta/T}} \right] \right\}^3. \tag{2}$$

where f_i is the partition function for a mole of halobenzene in the liquid state; f_{HR} is the hindered rotation partition function; E_s is the energy of sublimation; θ, the Einstein characteristic temperature; ν_i, the ith internal vibrational frequency; A, B, C are the moments of inertia along the three principal axis; σ, the symmetry number; n and a are dimensionless parameters; N, h, and k are Avogadro's number, Planck's constant, and Boltzmann's constant, respectively. lE_s is the potential barrier. When lE_s becomes large, corresponding to strongly hindered rotation, the term $\mathrm{e}^{-lE_s/\mathrm{RT}}$ becomes very small and the principal contribution to f_{HR} is librational in nature.

The molecular constants, such as molecular weight, moments of inertia, vibrational frequencies, and the symmetry number are known or can be obtained from the literature.(2–19) In some compounds the moments of inertia are not available but can be calculated from bond angles and bondlength.

3. Results and Discussion

The thermodynamic properties of twelve liquid halobenzenes were calculated. The Helmholtz free energy, A, is related to the partition function f_L by

$$A = -kT \ln f_L. \tag{3}$$

The other thermodynamic properties can be found by taking derivatives with respect to volume and temperature.

The liquids were investigated from the melting point to the critical point. The computer calculations for each property are compared to the experimentally observed results for that property. The data referred to as observed were obtained from the literature as referenced.$^{(5-25)}$ The results are compared graphically when sufficient data are available.

The parameters used are listed in Table 1. The energy barrier for hindered rotation increases in the order of F, Cl, Br and I. This is reasonable because the larger the substitute atoms, the more restricted the rotation. The effect of the number of substituted halogen is not apparent in fluorine compounds but is appreciable in chlorine and bromine substituted compounds. This is because the size of the fluorine atom is small compared with the whole molecule. The Einstein characteristic temperature, θ, for molecular displacement is approximately inversely proportional to the square root of

TABLE 1 Summary of Parameters Used in Calculation 1

	n	a	E_s	θ	V_s	
C_6H_5F	21.0	0.000534	11623.14	80.54	82.98	0.1
o-$C_6H_4F_2$	21.0	0.000534	12100.00	76.82	88.58	0.1
m-$C_6H_4F_2$	21.0	0.000534	11505.8	72.35	87.50	0.1
C_6HF_5	21.0	0.0016	12140.8	65.75	97.48	0.1
C_6F_6	21.0	0.0016	11518.0	62.76	102.04	0.1
C_6H_5Cl	21.0	0.000534	12951.53	71.42	92.42	0.1
p-$C_6H_4Cl_2$	21.0	0.000534	14350.0	66.0	110.0	0.1
m-$C_6H_4Cl_2$	21.0	0.000534	14620.0	66.0	108.04	0.1
o-$C_6H_4Cl_2$	21.0	0.000534	14830.0	66.50	108.90	0.1
C_6H_5Br	21.0	0.000534	13810.81	61.82	97.56	0.1
o-$C_6H_4Br_2$	21.0	0.000534	16620.0	56.50	114.73	0.1
C_6H_5I	21.0	0.000534	14932.64	56.76	104.81	0.1

the mass of the compound, and decreases as the molecular weight of the compound increases.

THE VAPOR PRESSURES AND THE MOLAR VOLUMES

The molar volumes and the equilibrium vapor pressure are found from a line of double tangency on a plot of the Helmholtz free energy against volume at a fixed temperature. The points of tangency fix the liquid and vapor molar volumes and the slope of the tangent is the vapor pressure since $P = -(\partial A/\partial V)_T$. As shown in Figs. 1 and 2, the calculated values agree with the observed data⁽²⁾ very well in the range from the melting to the boiling point.

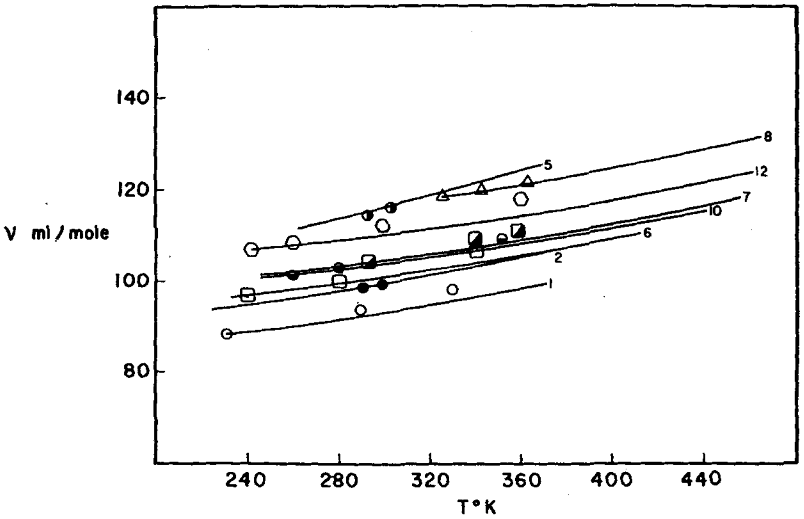

Figure 1. Molar volumes versus temperature.

KEY TO ALL FIGURES

○	*1* C_6H_5F	◑	*5* C_6F_6	⊗	*9* *o*–$C_6H_4Cl_2$
●	*2* *o*–$C_6H_4F_2$	□	*6* C_6H_5Cl	◒	*10* C_6H_5Br
▲	*3* *m*–$C_6H_4F_2$	◪	*7* *m*–$C_6H_4Cl_2$	⬓	*11* *o*–$C_6H_4Br_2$
◩	*4* C_6HF_5	△	*8* *p*–$C_6H_4Cl_2$	⬡	*12* C_6H_5I

THE ENTROPIES

The entropy is calculated by using the equation $S = -(\partial A/\partial T)_V$. Most of the calculated values and the observed values are within 5%. For chlorobenzene, near the melting point, the deviation is

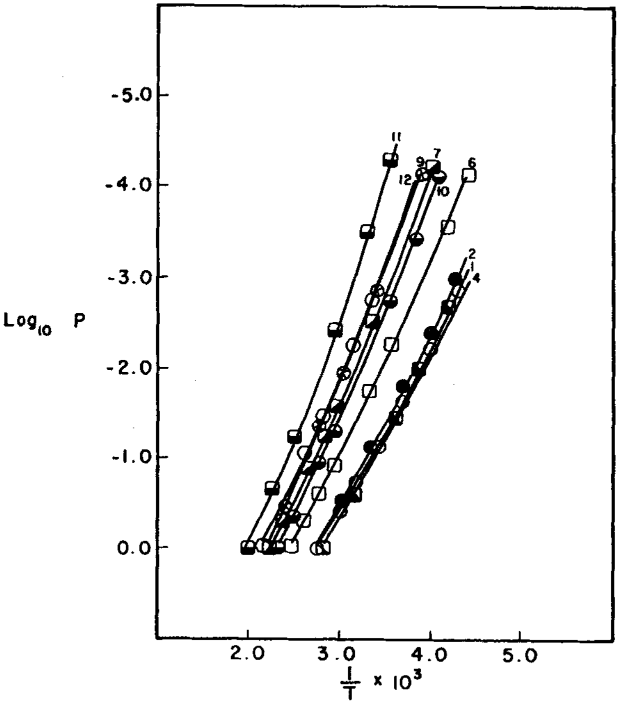

Figure 2. Log of vapor pressures versus $1/T$.

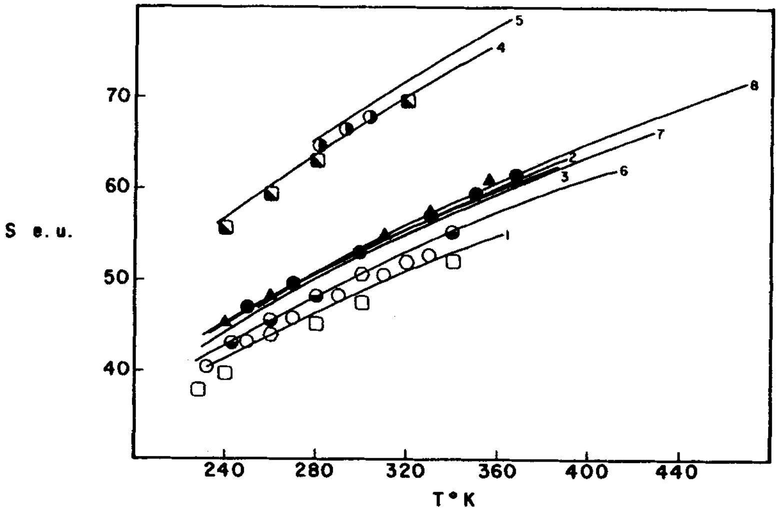

Figure 3. Entropies versus temperature.

about 9%. The results are plotted in Fig. 3. In Table 2, entropy changes of melting and vaporization are listed and the calculated and the observed values are in good agreement.

TABLE 2 Entropy Changes of Melting and Vaporization

	ΔS_f		ΔS_v	
	obs.	calc.	obs.	calc.
C_6H_5F	10.75	11.61	21.68	21.50
o-$C_6H_4F_2$	11.68	11.91	20.98	21.25
m-$C_6H_4F_2$	10.04	11.73	—	20.90
C_6HF_5	11.53	13.93	21.41	21.28
C_6F_6	9.98	12.80	21.44	21.27
C_6H_5Cl	10.02	10.08	20.75	21.11
p-$C_6H_4Cl_2$	13.32	12.17	20.80	21.22
m-$C_6H_4Cl_2$	—	11.47	20.70	21.15
o-$C_6H_4Cl_2$	11.70	10.84	20.90	21.29
C_6H_5Br	10.48	9.95	20.45	21.18
o-$C_6H_4Br_2$	10.72	11.16	20.45	21.55
C_6H_5I	9.62	8.67	20.42	21.42

THE HEAT CAPACITIES

The heat capacity is calculated by using the equation

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V \tag{4}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V}\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial p}{\partial V}\right)_T^{-1} \tag{5}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \left(-\frac{V\partial^2 A}{\partial V^2}\right)^{-1} \tag{6}$$

and

$$C_p = C_v + \frac{\alpha^2 VT}{\beta}. \tag{7}$$

Here α and β are the coefficient of thermal expansion and the compressibility, respectively. The results of C_p are shown in Fig. 4. Near the melting point the calculated values of C_p are somewhat high because the temperature and pressure dependence of V_s are neglected. This approximation is less important at higher temperatures. The observed values for C_p for ΦF, ΦCl, ΦBr and ΦI are rather imprecise

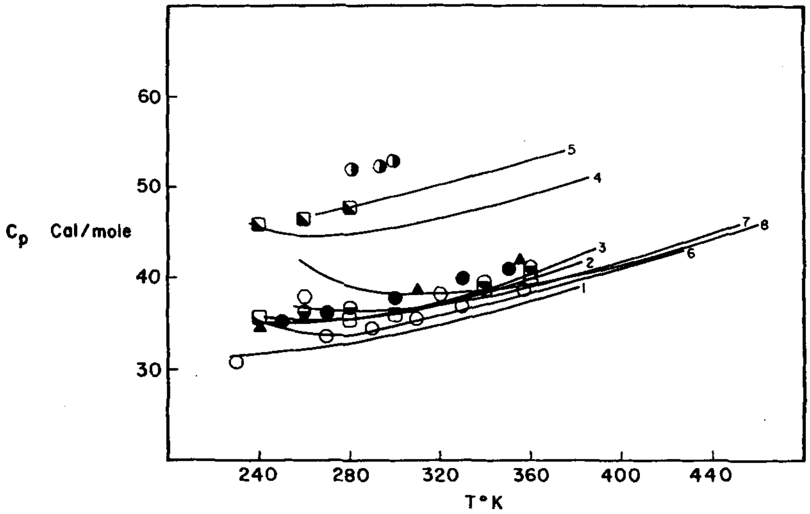

Figure 4. Heat capacities versus temperature.

and involve Debye extrapolations to 90°. However, in the case of ΦF, much better experimental determinations of C_p to 10 °K shows that the older work is in error by as much as 2.3 e.u. with respect to entropy and shows no s-shaped curve in C_p.

THE CRITICAL PROPERTIES

The critical temperature, T_c, critical volume, V_c, and critical pressure, p_c, are calculated in the usual way by using the two conditions:

$$\left(\frac{\partial p}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0. \tag{8}$$

The critical properties thus obtained are given in Table 3 as calculation 1, and are compared with experiment. We find the calculated molar volumes in good agreement with the experimental values. The calculated T_c for most compounds are 6 to 8% high. The calculated p_c values for calculation 1 are high by about 40%. This deviation in the critical pressure is principally due to the use of an ideal gas partition function for the gas-like degrees of freedom. This neglects

TABLE 3 Critical Properties of Halobenzenes

	T °K			V_c(ml)			p_c(atm)		
	Obs.	Calc.		Obs.	Calc.		Obs.	Calc.	
		(1)	(2)		(1)	(2)		(1)	(2)
C_6H_5F	559.71	529.45	551.59	271.48	284.21	278.00	44.60	61.90	58.85
o–$C_6H_4F_2$	—	605.33	—	—	303.56	—	—	59.24	—
m–$C_6H_4F_2$	—	590.64	—	—	299.78	—	—	58.53	—
C_6HF_5	531.95	575.87	—	—	334.26	—	34.70	51.18	—
C_6F_6	516.72	560.15	—	—	349.80	—	32.61	47.57	—
C_6H_5Cl	632.36	682.68	633.74	308.38	315.91	309.00	44.60	64.17	60.83
m–$C_6H_4Cl_2$	683.95	740.93	—	358.70	367.40	—	38.30	59.88	—
o–$C_6H_4Cl_2$	697.25	752.32	—	360.00	369.40	—	40.53	60.52	—
p–$C_6H_4Cl_2$	684.75	738.73	—	371.94	373.60	—	38.55	58.72	—
C_6H_5Br	670.16	723.98	672.24	342.83	331.82	324.27	44.60	64.85	61.49
o–$C_6H_4Br_2$	759.57	825.63	—	365.68	390.20	—	41.57	62.84	—
C_6H_5I	721.16	770.97	716.80	351.14	356.17	348.39	44.60	64.28	61.03

the presence of dimers, trimers, etc. which become increasingly abundant near the critical point.

Finally, in Table 3 we also list the results of calculation 2 for the critical properties. In calculation 2 we decrease n from 21 to 12.5 and take a equal to 0.00534, the theoretical and experimental values for argon with all the other parameters unchanged from their values in calculation 1. The critical properties are considerably improved, especially T_c.

This decrease with increasing volume in the appropriate value for n in the critical region was to be expected since n is a measure of how much an increase in volume contributes to both the translational and rotational entropy and the latter contribution disappears when free rotation sets in. With free rotation n and a should approximate argon-like values. At the melting point both translation and rotation are facilitated by the volume increase and, at roughly equal rates, measured in terms of increments to the degeneracy. At the critical point, on the other hand, the molecules are approaching free rotation and additions to the rotational degeneracy with increasing volume is minimal and n has dropped almost to the theoretical value of argon, i.e., almost to 10.7 from 21.

It should be clear that applying significant structure theory to liquids allows one to draw conclusions about liquid structure, such for example as the degree of restriction in molecular rotation, much as X-ray analysis allows deductions with respect to molecular structure. Like X-ray analysis it also offers the possibility of almost unlimited refinement as one requires that the model reproduce the values of more and more properties with increasing precision.

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REFERENCES

1. Eyring, H. and Jhon, M. S., *Significant Liquid Structures*, John Wiley and Sons, Inc., New York, 1969.
2. McCulloh, K. E. and Pollnow, G. F., *J. Chem. Phys.* **22**, 1144 (1954).

3. Dreisbach, R. R., *Physical Properties of Chemical Compounds*, American Chemical Soc., Washington, D.C. (1959).
4. Scott, D. W., McCullough, J. P., Wood, W. D., Messerly, J. F., Pennington, R. E., Kincheloe, T. C., Hossenlopp, I. A., Douslin, D. R. and Waddington, G., *J. Am. Chem. Soc.* **78**, 5457 (1956).
5. Scott, D. W., Messerly, J. F., Todd, S. S., Hossenlopp, I. A., Osborn, A. and McCullough, J. P., *J. Chem. Phys.* **38**, 532 (1963).
6. Green, J. H. S., Kynaston, W. and Paisley, H. M., *J. Chem. Soc.* **473** (1963).
7. Messerly, J. F. and Finke, H. L., *J. Chem. Thermodynamics* **2**, 867 (1970).
8. Counsell, J. F., Hales, J. L. and Martin, J. F., *J. Chem. Soc.* (*A*) 2042 (1968).
9. Doraiswamy, S. and Sharma, S., *Proc. Indian Acad. Sci. Sect.* (*A*) **68** (2) 53 (1968).
10. Steele, D. and Whiffen, D. H., *Spectrochimica Acta* **16**, 368 (1960).
11. Evans, F. D. and Tiley, P. E., *J. Chem. Soc.* (*B*) 134 (1966).
12. Patrick, C. R. and Prosser, G. S., *Trans. Fara. Soc.* **60**, 700 (1964).
13. Counsell, J. F., Green, J. H. S., Hales, J. L. and Martin, J. F., *Trans. Fara. Soc.* **61**, 212 (1965).
14. Whiffen, D. H., *J. Chem. Soc.* 1350 (1956).
15. Tobin, M. C., *J. Phys. Chem.* **61**, 1392 (1957).
16. Schmid, E. W. and Brandmiller, J., *Z. Electrochimie*, **64**, 940 (1960).
17. Scherer, J. R., *Spectrochemica Acta* **20**, 345 (1964).
18. Weissberg, A., *Organic Solvents, Technique of Organic Chem.*, *VII*, Interscience Pub., Inc., New York, 1955.
19. Shurvell, H. F., Dulaurens, B. and Pesteil, P., *Spectrochimica Acta* **22**, 333 (1966).
20. Stull, D. R., *J. Am. Chem. Soc.* **59**, 2726 (1937).
21. Schiemann, G. and Pillarsky, R., *Ben.* **62**, B. 3035 (1929).
22. Patrick, C. R. and Prosser, G. S., *Trans. Fara. Soc.* **60**, 700 (1964).
23. Ambrose, D., *J. Chem. Soc.* (*A*) 1381 (1968).
24. Stull, D. R., *Ind. Eng. Chem.* **39**, 517 (1947).
25. Griffing, V. and Cargyle, M. A., *J. Phys. Chem.* **58**, 1054 (1954).