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Determination of Barrier Heights from Low-Temperature Heat-Capacity Data

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A method is presented by which barrier heights, in potential functions hindering the internal rotation of methyl groups, or spectroscopically inactive vibrational frequencies, can be obtained solely from thermal data for the solid phase. The observed heat capacities are analyzed in terms of contributions from the lattice vibrations, the internal vibrations, the expansion of the lattice, and the internal rotation. At low temperatures, the hindered rotation can be treated as torsional oscillation with a frequency related to the barrier height. It is shown that barrier heights derived by this method are in accord with those estimated from comparison of gas-phase entropies, but can be determined with greater precision than such values.

INTRODUCTION

THERMAL data have been used previously to determine barrier heights, in potential functions hindering internal rotation, by comparison of experimental and statistically calculated values of the vapor-phase heat capacity and/or third-law entropy values for the vapor. The lack of gas-phase heat-capacity data for many substances has made the entropy comparison the more common method of barrier-height evaluation. The experimental determination of the third-law entropy of a gas requires that the low-temperature solid-phase heat capacity be augmented by: enthalpies of vaporization (or sublimation), vapor-pressure measurements, and equation of state data for the vapor. The advantages and feasibility of determining barrier heights exclusively from low-temperature solid-phase heat capacities is demonstrated.

The third-law entropies in the ideal gas state are computed as the sums of four terms. These are: (1) the entropy of the condensed phase,

$$S_T^\circ = \int_0^T C_p d \ln T,$$

obtained by integration of the low-temperature heat capacity data; (2) the entropy of vaporization (or sublimation), $\Delta S v_T = \Delta H v / T$; (3) the entropy change upon compression of the vapor from its equilibrium vapor pressure, p_T°, to one atmosphere, $\Delta S_T = R \ln p_T^\circ$; and (4) a correction for the nonideality of the vapor, dependent upon the equation of state. The third-law entropies for the ideal gas state usually lie between 50 and 80 cal/(mole °K) and in the most favorable cases, where the contributions from (2) and (3) above are measured concomitantly with the heat capacities, carry a precision index of 0.15 to 0.30 cal/(mole °K). These uncertainties are assigned by the experimentalists on the basis of sample purity, phase complexity, availability of *PVT* data and cryogenic technique.

The statistically determined entropies are usually computed assuming the separability of contributions arising from translation, vibration, over-all rotation, and internal rotation. The entropy contributions are calculated using well-known methods and are based upon the gram molecular weight, the frequency and degeneracy assignments for the normal vibrations, the moments of inertia (based upon the molecular geometry) and the temperature. The internal rotation entropy contribution is computed for free rotation, i.e., the barrier height V_0 is set equal to zero.

If, upon comparison of the two entropy values, the experimental value is less than the calculated one, a nonzero barrier height may be assumed. If the hindering potential is assumed to take the form $V = \frac{1}{2} V_0 (1 - \cos n\phi)$, the entropy difference between free rotation and hindered rotation, $S_f - S$, can be related to a barrier height by recourse to the tables of Pitzer and Gwinn.[1] The quantity $S_f - S$ is the small difference between two large values but retains the original uncertainty of 0.15 to 0.30 cal/(mole °K). The tables of Pitzer and Gwinn indicate that an uncertainty of 0.2 cal/(mole °K) in the entropy due to internal rotation would encompass values of V_0 between 0 and 900 cal/mole for a methyl group affected by a low-potential barrier, at 300°K. For higher potential barriers, the same uncertainty would be consistent with V_0's between 2600 and 3600 cal/mole. This large uncertainty in the barrier heights derived from precise thermal data has relegated the use of such data to a confirmatory, rather than a definitive, method of barrier-height evaluation.

Comparison between experimental and calculated values of the low-temperature heat capacities of the crystalline phases might permit more precise evaluation of barrier heights. The heat capacity contribution of a hindered rotor at 100°K is comparable to the magnitude of $S_f - S$ at 300°K, but the experimental uncertainty in the heat capacity of a typical organic substance is about 0.02 cal/(mole °K). This uncertainty corresponds to an uncertainty of only 10 cal/mole for $V_0 \simeq$

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[1] K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942).

TABLE I. The parameters for Eq. (3).

Substance	θ_D	a	b	m	θ_E	Source of C_p (obs)	Source of spectral data
toluene	125	0.0090	0	1	171	a	a
o-xylene	139	0.0118	0	2	500	b	b
m-xylene	118	0.0083	0	2	141	b	b
p-xylene	142	0.0110	0	2	220	b	b
mesitylene	112	0.0065	0.0065	3	160	c	b
1,1-dichloroethane	124	0.0080	0.0020	1	350	d	e
1,1,1-trifluoroethane	110	0.0108	0.0108	1	340	f	f

[a] D. W. Scott, G. B. Guthrie, J. F. Messerly, S. S. Todd, W. T. Berg, I. A. Hossenlopp, and J. P. McCullough, J. Phys. Chem. **66**, 911 (1962).
[b] K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. **65**, 803 (1943).
[c] R. D. Taylor and J. E. Kilpatrick. J. Chem. Phys. **23**, 1232 (1955).
[d] J. C. M. Li and K. S. Pitzer, J. Am. Chem. Soc. **78**, 1077 (1956).
[e] L. W. Daasch, C. Y. Liang, and J. P. Neilsen, J. Chem. Phys. **22**, 1293 (1954).
[f] H. Russell, D. R. V. Golding, and D. M. Yost, J. Am. Chem. Soc. **66**, 16 (1944).

500 cal/mole. In the absence of an *a priori* method of "calculating" the heat capacity of a crystalline phase, an empirical method relying on parameters derived from the heat-capacity data is needed to permit the determination of barrier heights. To this end the following approach is used.

CONTRIBUTIONS TO THE HEAT CAPACITY

The degrees of freedom, $^\circ/F$, contributing to the heat capacity at constant pressure C_p of a crystalline phase are the following: the intermolecular vibrations (lattice vibrations), corresponding to the translational and over-all rotational contributions for the gas; the intramolecular vibrations; internal rotations; and C_p-C_v, a term resulting from the expansion of the lattice as effected by the anharmonicities of the vibrations. The contribution of the intramolecular vibrations can be calculated, to the harmonic oscillator approximation, by a combination of Einstein functions based upon the observed spectrum. No *a priori* method exists for determining the remaining contributions. The lattice vibrations and the C_p-C_v term are treated in the manner described by Lord, Ahlberg and Andrews[2] and amplified by Lord,[3] whose conclusions are briefly presented below.

Lattice Vibrations

The contributions to the lattice heat capacity arising from the "translational" and "rotational" effects can be treated together or combined. The "translational" modes are usually represented by a Debye function for $3^\circ/F$ with a empirically chosen θ_D. The "rotational" modes are best represented by an Einstein function for $3^\circ/F$ with a second empirically chosen characteristic temperature θ_E. However, except at the lowest temperatures (usually below 30°K), the heat capacity represented by an Einstein function can equally well be represented by a Debye function with a different characteristic temperature. Moreover, the combination of an Einstein function and a Debye function (or two Debye functions) can be treated as a single Debye function for $6^\circ/F$, with an intermediate value of θ_D. Since the characteristic temperatures are chosen empirically, and are assigned no theoretical significance, it is, perhaps, advantageous to choose a single $6^\circ/F$ Debye function to represent the lattice contribution to the heat capacity, C_v^L. What is thus sacrificed in accuracy at the lowest temperatures is compensated for by reduction of the number of empirical parameters. As was pointed out by Lord,[3] however, for molecules with molecular weights large relative to their moments of inertia, such as methane, the combination of a Debye and an Einstein term gives a closer representation of the heat capacity.

C_p-C_v

Heat capacities calculated from Debye and Einstein functions are harmonic vibration contributions to C_v. The experimental heat capacity is determined as C_s, but calorimetric technique makes the difference between C_s and C_p negligible for crystalline phases at low temperatures. The difference between C_p and the calculated contributions to C_v is given by the thermodynamic relation $C_p-C_v=\alpha^2VT/\beta$, in which α is the coefficient of thermal expansion, β the compressibility, and V the molar volume. In the (usual) absence of thermal expansion and compressibility data, recourse is made to the quasithermodynamical result of Lord's[3] work, i.e., he showed that C_p-C_v could be reduced to the form

$$C_p-C_v \simeq [aC_v^L+bC_v^I]^2T, \qquad (1)$$

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[2] R. C. Lord, J. E. Ahlberg and D. H. Andrews, J. Chem. Phys. **5**, 649 (1937).

[3] R. C. Lord, J. Chem. Phys. **9**, 700 (1941).

TABLE II. Contributions to the heat capacity.

a. Toluene

T	C_p	C_v^L	C_v^I	C_p-C_v	Δ	$E(\theta_E/T)$
°K	cal/(mole °K)					
25	4.60	4.40	0.01	0.04	0.15	0.10
30	6.00	5.71	0.02	0.08	0.19	0.22
35	7.28	6.80	0.04	0.13	0.31	0.36
40	8.40	7.65	0.06	0.19	0.50	0.52
45	9.38	8.33	0.12	0.25	0.68	0.67
50	10.23	8.89	0.20	0.32	0.82	0.81
60	11.64	9.69	0.44	0.46	1.05	1.05
70	12.73	10.19	0.73	0.59	1.22	1.24
80	13.60	10.58	1.08	0.73	1.21	
90	14.35	10.84	1.47	0.86	1.18	
100	15.01	11.04	1.90	0.99	1.08	
120	16.40	11.30	2.86	1.25	0.99	
140	17.91	11.46	3.92	1.48	1.05	

b. *o*-Xylene

T	C_v^L	C_v^I	$2E(\theta_E/T)$	C_p-C_v	C_p (cal)	C_p (obs)	Δ
°K	cal/(mole °K)						
30	4.95	0.11	0.00	0.10	5.16	5.19	0.03
40	6.97	0.43	0.01	0.27	7.68	7.60	−0.08
50	8.33	0.92	0.02	0.48	9.75	9.63	−0.12
60	9.23	1.48	0.06	0.71	11.48	11.41	−0.07
70	9.86	2.07	0.16	0.94	13.03	12.98	−0.05
80	10.30	2.68	0.30	1.18	14.46	14.43	−0.03
90	10.62	3.28	0.48	1.41	15.79	15.82	0.03
100	10.85	3.85	0.68	1.64	17.02	17.13	0.11
120	11.16	5.11	1.10	2.07	19.44	19.59	0.15
140	11.35	6.41	1.52	2.51	21.79	21.86	0.07
160	11.48	7.80	1.87	2.93	23.98	24.03	0.05
180	11.57	9.28	2.16	3.35	26.36	26.32	−0.04
200	11.63	10.86	2.41	3.76	28.66	28.65	−0.01
220	11.68	12.55	2.62	4.18	31.03	31.13	0.10

c. *m*-Xylene

T	C_p	C_v^L	C_v^I	C_p-C_v	Δ	$2E(\theta_E/T)$
°K	cal/(mole °K)					
15	1.74	1.72	0.00	0.00	0.02	0.03
20	3.28	3.28	0.00	0.01	−0.01	0.17
25	5.08	4.77	0.00	0.04	0.27	0.44
30	6.80	6.13	0.01	0.08	0.58	0.80
35	8.43	7.15	0.05	0.12	1.11	1.20
40	9.86	8.00	0.12	0.17	1.57	1.56
45	11.06	8.67	0.25	0.23	1.91	1.88
50	12.04	9.16	0.40	0.29	2.19	2.14
60	13.25	9.89	0.86	0.40	2.10	
70	14.54	10.38	1.40	0.52	2.24	
80	15.54	10.74	2.02	0.63	2.16	
90	16.49	10.95	2.70	0.74	2.10	
100	17.41	11.13	3.38	0.85	2.05	
120	19.15	11.36	4.78	1.06	1.95	
140	21.03	11.50	6.30	1.27	1.96	
160	22.96	11.60	7.81	1.47	2.08	

TABLE II (*Continued*)

d. *p*-Xylene

T °K	C_p	C_v^L	C_v^I	C_p-C_v	Δ	$2E(\theta_E/T)$
	cal/(mole °K)					
15	1.03	1.04	0.00	0.00	−0.01	0.00
20	2.25	2.21	0.00	0.01	0.03	0.01
25	3.72	3.52	0.01	0.04	0.15	0.04
30	5.17	4.80	0.04	0.08	0.25	0.14
35	6.50	5.90	0.10	0.15	0.35	0.30
40	7.76	6.82	0.19	0.22	0.53	0.50
45	8.94	7.57	0.34	0.31	0.72	0.72
50	10.07	8.21	0.51	0.41	0.94	0.93
60	12.05	9.13	0.97	0.60	1.35	1.43
80	15.27	10.22	2.15	1.01	1.89	
100	17.96	10.80	3.60	1.41	2.15	
120	20.26	11.13	5.05	1.81	2.27	
140	22.34	11.33	6.54	2.17	2.30	
160	24.28	11.45	8.05	2.53	2.25	
200	28.13	11.62	11.22	3.25	2.04	
240	32.28	11.72	14.61	3.99	1.96	
280	36.83	11.76	18.17	4.68	2.12	

e. Mesitylene

T °K	C_v^L	C_v^I	$3E(\theta_E/T)$	C_p-C_v	C_p (cal)	C_p (obs)	Δ
	cal/(mole °K)						
20	3.62	0.00	0.13	0.01	3.76	3.77	0.01
25	5.31	0.01	0.40	0.04	5.76	5.67	−0.09
30	6.48	0.02	0.84	0.07	7.41	7.48	0.07
35	7.50	0.07	1.31	0.12	9.00	9.09	0.09
40	8.29	0.17	1.81	0.18	10.45	10.49	0.04
45	9.01	0.29	2.27	0.25	11.82	11.77	−0.05
50	9.39	0.45	2.70	0.33	12.87	12.97	0.10
60	10.07	0.89	3.40	0.53	14.89	15.16	0.27
70	10.52	1.38	3.92	0.74	16.56	16.59	0.03
80	10.82	1.92	4.31	0.98	18.03	18.18	0.15
90	11.07	2.52	4.61	1.26	19.46	19.55	0.09
100	11.20	3.01	4.84	1.55	20.70	20.76	0.06
120	11.41	4.32	5.15	2.21	23.09	23.12	0.03
140	11.55	5.52	5.36	2.98	25.41	25.39	−0.02
160	11.63	6.73	5.49	3.82	27.67	27.58	−0.09
180	11.70	7.95	5.58	4.83	30.06	29.78	−0.28

f. 1,1-Dichloroethane

T °K	C_v^L	C_v^I	$E(\theta_E/T)$	C_p-C_v	C_p (cal)	C_v (obs)	Δ
	cal/(mole °K)						
35	6.81	0.00	0.01	0.10	6.91	6.99	0.08
40	7.68	0.01	0.02	0.16	7.87	7.96	0.09
45	8.36	0.03	0.05	0.21	8.65	8.77	0.12
50	8.91	0.06	0.09	0.25	9.31	9.42	0.11
60	9.71	0.19	0.20	0.37	10.47	10.45	−0.02
70	10.23	0.38	0.34	0.48	11.43	11.42	−0.01
80	10.59	0.63	0.52	0.59	12.33	12.32	−0.01
90	10.86	0.94	0.64	0.71	13.15	13.12	−0.03
100	11.04	1.29	0.78	0.83	13.94	13.93	−0.01
110	11.19	1.63	0.91	0.95	14.76	14.72	−0.04
120	11.30	1.99	1.02	1.07	15.38	15.48	0.10

TABLE II (*Continued*)

g. 1,1,1-Trifluoroethane

T	C_v^L	C_v^I	$E(\theta_E/T)$	C_p-C_v	C_p (cal)	C_p (obs)	Δ
°K				cal/(mole °K)			
30	6.60	0.00	0.00	0.15	6.75	6.81	0.06
35	7.65	0.00	0.01	0.24	7.90	7.85	−0.05
40	8.38	0.00	0.03	0.33	8.74	8.69	−0.05
45	9.00	0.00	0.06	0.44	9.49	9.45	−0.04
50	9.46	0.01	0.10	0.53	10.10	10.09	−0.01
55	9.83	0.02	0.16	0.64	10.65	10.63	−0.02
60	10.13	0.04	0.22	0.76	11.15	11.12	−0.03
70	10.58	0.13	0.37	1.02	12.10	12.04	−0.06
80	10.87	0.25	0.53	1.28	12.93	12.94	0.01
90	11.07	0.44	0.68	1.58	13.77	13.77	0.00
100	11.23	0.69	0.82	1.90	14.64	14.66	0.02
110	11.34	0.98	0.95	2.28	15.55	15.61	0.06

where C_v^I is the summed contribution of the intramolecular vibrations. For atomic lattices, and simple ionic lattices, Nernst and Lindemann[4] showed that $a=(0.0214/T_m)^{\frac{1}{2}}$. Since a and b must, of necessity, be derived empirically, we sacrifice agreement with the Nernst–Lindemann prediction, if the expression for C_p-C_v can be simplified by setting $a=b$ or $b=0$. For molecules containing no groups undergoing internal rotation, the heat capacity of the solid phase is given by

$$C_p=C_v^L+C_v^I+(C_p-C_v) \qquad (2a)$$

$$=6D(\theta_D/T)+\sum g_iE(\theta_{Ei}/T)+[aC_v^L+bC_v^I]^2T, \qquad (2b)$$

where the summation extends over the normal vibrational frequencies, $\theta_{Ei}=hc\omega_i/k$, each with degeneracy g_i. Equation (2b) contains two or three empirically derived constants θ_D, a (and b if it is different from a or zero). The success of this representation has been demonstrated by the agreement of calculated and experimental heat capacities for a number of molecular lattices.[5]

Internal Rotation

The contribution to the heat capacity due to hindered internal rotation is dependent upon the form assumed for the hindering potential and upon the temperature. The most commonly assumed potential function is $V=\frac{1}{2}V_0(1-\cos n\phi)$, where V_0 is the height of the barrier to rotation and n is the number of maxima encountered in one complete revolution of the internal rotor. Three temperature ranges give rise to three different treatments for the heat-capacity contribution. Where the temperature is low, such that $kT\ll V_0$, the contribution can be treated as that of a torsional oscillator[6] with a harmonic frequency given by [7,8] $\nu=n/2(V_0/I_r)^{\frac{1}{2}}$, where I_r is the reduced moment of inertia. At high temperatures, $kT\gg V_0$, the heat capacity contribution approaches that of a free rotor and can be treated as such. The heat capacity at intermediate temperatures can be treated using the tabulated functions of Pitzer and Gwinn.[1] It has been observed[6] that the contribution calculated on the basis of a harmonic torsional oscillator can be extended into the range where kt is no longer small compared to V_0. To fit the heat capacity of a system containing one, or more, internal rotors, an additional parameter, corresponding to V_0, is necessary. Since hindered rotation is primarily effected by intramolecular forces, its contribution to C_p-C_v can be included in the C_v^I term. The heat capacity is given by

$$C_p=6D(\theta_D/T)+\sum g_iE(\theta_{Ei}/T)$$
$$+[aC_v^L+bC_v^I]^2T+f(V_0,n,T). \qquad (3)$$

APPLICATION OF THE PROCEDURE

The practical application of Eq. (3) to actual heat capacity data can be summarized in the following outline.

(1) Using the normal frequency assignment, the vibrational contributions may be calculated and their sum subtracted from the experimental heat capacity.

(2) At the lowest temperatures the C_p-C_v contribution can be estimated by a formula due to Nernst and Lindemann,[4] $C_p-C_v=0.0214\ C_p^2T/T_m$. This contribution can be computed and subtracted from the remainder of (1).

(3) If there is reason to believe that V_0 is high, the remainder from (2) will be C_v^L and can be used to deduce θ_D. If the barrier is low, or unknown in magnitude, the remainder from (2) must be fitted, by trial and error, to the form $6D(\theta_D/T)+mE(\theta_E/T)$, where m is the number of hindered rotors present.

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[4] W. Nernst and F. A. Lindemann, Z. Elecktrochem. **17**, 817 (1911).

[5] W. F. Brucksch and W. T. Zeigler, J. Chem. Phys. **10**, 740 (1942).

[6] J. O. Halford, J. Chem. Phys. **15**, 364 (1947).

[7] J. O. Halford, J. Chem. Phys. **16**, 560 (1948).

[8] W. H. Stockmayer, J. Chem. Phys. **27**, 321 (1957).

TABLE III. Barrier heights derived from thermal data. References b–f correspond to those in Table I.

Substance	I_r10^{40} (g cm^2)	Source of I_r	n	θ_E °K	V_0 (cal/mole)	V_0 (lit) (cal/mole)	Source of V_0 (lit)
toluene	5.008	a	6	171	200±25	0–300[a]	a
o-xylene	5.41	b	6	500	1850±75	2000–2500	b
m-xylene	5.41	b	3–6	141	300±75	0–1000	g
p-xylene	5.32	b	6	220	350±25	0–900	g
mesitylene	5.46	b	6	160	190±25	0–900	g
1,1-dichloroethane	5.20	d	3	350	3490±200	3100–4000	d
1,1,1-trifluoroethane	5.125	f	3	340	3250±200	3040–3950	f

[a] Estimated from data given by Ref. a, Table I.

[g] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, J. Res. Natl. Bur. Std. (U.S.) **37**, 95 (1946).

(4) Once θ_D is known, the lattice heat capacity may be computed and, together with the vibrational contribution, subtracted from the experimental C_p. The remainder can now be fitted, by trial and error again, with a C_p-C_v term and a hindered rotor contribution. The former can often be simplified by setting $b=0$. In general $f(V_0, n, T)$ can be fitted by an Einstein function for the entire temperature range or by an Einstein function at low temperatures and by $mR/2$ (the contribution of "free rotation") at higher temperatures.

Except at the lowest temperatures, where the lattice heat capacity is not adequately described by a single $6^\circ/F$ Debye function, and in the regions of transition and fusion, where the harmonic oscillator approximation becomes impossible, it should be possible to fit the heat capacity to within 1% over the entire temperature range.

The above procedure has been applied to toluene (methylbenzene), *o*-, *m*-, and *p*-xylene (1,2-, 1,3-, and 1,4-dimethylbenzene), mesitylene (1,3,5-trimethylbenzene), 1,1-dichloroethane and 1,1,1-trifluoroethane. Table I, below, presents the parameters used in applying Eq. (3) to each of these substances; $f(V_0,n,T)$ was represented by $mE(\theta_E/T)$ for all substances at low temperatures, and for *o*-xylene, mesitylene and the substituted ethanes at higher temperatures. Table II presents the actual heat capacity analyses for the above substances. The presentation is a comparison of C_p(calc) with C_p(obs) for *o*-xylene, mesitylene and the substituted ethanes. For the remaining substances, all contributions other than that due to hindered rotation are subtracted from C_p(obs) and the remainder is compared with $mE(\theta_E/T)$ at low temperatures and with $mR/2$ at higher temperatures.

DISCUSSION

The frequency derived for the torsional oscillation of the methyl group can be related to a barrier height by

$$V_0=0.04935I_r10^{40}\theta_E^2/n^2. \quad (4)$$

The numerical factor in Eq. (4) is a combination of physical constants and conversion factors, and V_0, I_r, n, θ_E are as before. In Table III, barrier heights computed from Eq. (4) are tabulated for the substances studied. The precision indices are based upon an uncertainty of about 10°K in θ_E. For comparison, values of the barrier heights obtained from gas-phase entropies are also tabulated.

It is evident that the barrier heights obtained in this study are in accord with those computed from gas-phase entropies, and that the precision is substantially greater, particularly for low barriers. The values of n are unambiguous with the exception of those of *o*- and *m*-xylene. For *o*-xylene, the assignment of $n=6$ is in accord with a meshed arrangement of the two methyl groups, or alternatively, with complete independence. For *m*-xylene a more complex potential form must be considered. The methyl group rotation is hindered by the ring, as in toluene, and by the other methyl group, as in mesitylene. The best potential is probably of the form

$$V=\tfrac{1}{2}V_3(1-\cos 3\phi)+\tfrac{1}{2}V_6(1-\cos 6\phi), \quad (5)$$

where V_3 is the barrier effected by the methyl group and V_6 by the ring. The maximum value of V (the true potential barrier) is approximately one-half the value that would be calculated for a simple threefold potential, 600 cal/mole. The maximum potential barrier in *m*-xylene is 300 cal/mole and V_3 and V_6 are each about 200 cal/mole, in accord with the barriers in toluene and mesitylene.

Criticism of the method can be made both with respect to the parameters used and with respect to the uniqueness of the derived barrier heights. The vibrational contributions to the heat capacities were calculated from gas-phase spectral data. These frequencies may be shifted somewhat on transition to the solid phase. However, a discrepancy of 5 cm^{-1} in the lowest frequency encountered (146 cm^{-1}) would change the

TABLE IV. Apparent θ_E for toluene.

T °K	θ_D ($a=0.009$) °K			T °K	a ($\theta_D=125$°K)		
	123	125	127		0.008	0.009	0.010
30	214	176	156	30	173	176	182
40	185	173	164	40	170	173	178
50	179	170	162	50	162	170	179
60	180	171	163	60	158	171	185
70	181	172	165	70	153	172	192

heat capacity contribution by only 0.03 cal/(mole °K) at 100°K and by 0.04 cal/(mole °K) at 50°K. A gain in accuracy, over the high-temperature gas-phase comparison, results from the inclusion of the anharmoncity contribution in the calculations. The effect of a 3°K inaccuracy in the evaluation of θ_D would contribute an uncertainty of 0.04 cal/(mole °K) in the heat capacity at 100°K. The effect is greater at lower temperatures, and accounts for some of the larger discrepancies observed, i.e., *m*-xylene. This same situation was also encountered in the analyses of Brucksch and Zeigler.[5] It should also be noted that the third-law value of the gas-phase entropy contains a contribution based upon θ_D (extrapolation of the heat-capacity measurements to 0°K). An uncertainty of 3°K in the θ_D would be reflected by an uncertainty of 0.035 cal/(mole °K) in the entropy at 300°K.

The precision with which θ_E can be determined can be estimated from the effect of a variation in either θ_D or a. A variation of as little as 2°K in θ_D causes a pronounced trend in the apparent θ_E as a function of temperature. Similar trends are occasioned by variations in a. Table IV illustrates these trends for toluene for which a $\theta_E = 171 \pm 10$°K was chosen.

After the contributions of the lattice and vibrational parts of the heat capacity have been subtracted from the experimental values, the remainders must still be divided between $C_p - C_v$ and the hindered rotor contribution. We have no independent means of evaluating either term, except that a may be estimated by the approximate relation of Nernst and Lindemann. However in the cases of low-potential barriers (toluene, *m*- and *p*-xylene), where the high-temperature contribution can be expected to approach that of "free" rotation, we can confirm the choice of the $C_p - C_v$ expression. Applying the same argument to mesitylene, one would expect its hindered rotation contribution to approach that of "free" rotation at high temperatures. Assuming that the heat-capacity increment between *m*-xylene and mesitylene is the same as that between toluene and *m*-xylene (both involve the addition of a methyl group in the *meta* position), results in a discrepancy of almost 1 cal/(mole °K) at 100°K. Since the heat-capacity contribution of a torsional oscillator is greater than that of free rotation (for $\theta_E = 160$°K at 100°K), the calculated persistence of torsional oscillation is in agreement with the observed data. Mesitylene might also be undergoing gradual order–disorder transition at low temperatures (there is a "hump" in the heat capacity at 60°K). Such a phenomenon would tend to make the vibrations more anharmonic and require the use of a b term in the heat-capacity fit which is not needed for the other methyl benzenes. That the same parameters fit the heat capacity both below and above the anomaly indicates(as would be expected for a rearrangement of the molecule as a whole) that the environment effecting the hindered rotation is little changed by such a transition. For the cases of a high-potential barrier (*o*-xylene and the substituted ethanes) the high-temperature limit is not realized, and the examination of uniqueness must rely on a comparison of the derived and estimated values of a. The Nernst–Lindemann relation predicts $a = 0.0093$, 0.011, and 0.011 for *o*-xylene, 1,1-dichloroethane and 1,1,1-trifluoroethane, respectively, in reasonable accord with the derived values. Since the hindered internal rotation is effected by the intramolecular forces, equating the value derived for the solid phases with that of the gas phase should have the same validity as equating the normal vibrational frequencies. The torsional frequency is usually low and will therefore be shifted more than other frequencies. The precision index of 10°K in θ_E corresponds to an uncertainty of 5 to 7% in the low frequencies. This uncertainty is comparable to an expected shift of zero to 5%.[9]

The application of this method is not restricted to the determination of barrier heights for internal rotation, but could equally well be used to determine the frequencies of spectroscopically inactive vibrations.

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Chemi-Ionization in Atomic O and N Mixtures*

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Saturation current methods have been used to measure ion-production rates with and without the addition of a nonreactive quenching compound (N_2O). These measurements strongly indicate that metastable molecules play a decisive role in chemi-ionization processes occurring in atomic O and N systems. Mobility measurements, derived from an analysis of transient currents resulting from pulsed operation of the ion-collection system, identify the predominant ion as NO^+. No change in this mobility occurs from 0.6 to 100 msec after a pulsed clearing field has removed ions previously created. This and other observations indicate that NO^+ is the initial ion formed by chemi-ionization processes. Only the reactions $N+N+NO^* \rightarrow N_2+NO^++e$ and $N_2^*+NO^* \rightarrow N_2+NO^++e$ are consistent with these observations.

INTRODUCTION

Exothermic chemical reactions generally result in products with excess internal energy. Seldom is a large fraction of the released energy immediately converted into kinetic energy of the products. Since these products are molecular, this excess energy may be in the form of vibrational and rotational energy, or electronic energy, or both.

In the absence of further interaction with its environment, this energy is dissipated by the unimolecular processes of radiation, dissociation, or auto-ionization. The occurrence and rates of these processes depend upon the state of the excited species. Radiation and dissociation of excited molecules have been studied in some detail. However, since few chemical reactions liberate sufficient energy to ionize the products formed in the initial reaction, few such processes have been studied.

Ions undergo chemical reactions like other reactants. Such reactions largely determine the equilibrium ionic species, which in turn governs the rate of charge removal.

Ionization processes have been most studied in rare gases.[1] In such systems metastable atomic species play an essential role in producing ionization when energy is supplied in "quanta" less than that corresponding to the atom ionization potential. These metastable species react with other ground-state atoms, forming molecules which stabilize by electron ejection. Apparently the rates of this type of reaction may be very large ($\approx 10^{-9}$/cc).

Nitrogen–oxygen afterglows, in which conspicuous ionization was observed 60 years ago,[2] contain metastable molecules which may participate in reactions similar to those causing ionization in the rare gases. Indeed all the excited states of molecular nitrogen and oxygen which can be initially populated by atomic recombination are metastable while several states of nitric oxide formed by atomic association are also metastable.

Recently Kunkel and Gardner have reported earlier measurements of electron densities in the nitrogen afterglow.[3] They showed that the amount of ionization depends upon the amount of nitric oxide or oxygen added. For conditions where charge loss was primarily due to volume recombination rather than ambipolar diffusion, they were able to estimate charge production rates ($\approx 10^{10}$/cc sec) from the observed electron densities

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