Entropies and Heat Capacities of Cyclic and Polycyclic Compounds

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Procedures are described for estimating gas phase entropies (298° K) and heat capacities (300° to 1500° K) of cyclic and polycyclic hydrocarbons from the corresponding well established thermodynamic properties of linear and branched hydrocarbons. The procedures used are extensions of group additivity methods for obtaining thermodynamic property estimates. Group value corrections useful in cyclic and polycyclic compound estimations are tabulated. Estimation methods are illustrated in detail for representative compounds. Estimates are accurate to about ±1.5 cal/mole -° K, in both $S°$ and C_p°. Estimates of the entropies and heat capacities of a large number of saturated and unsaturated cyclic and polycyclic hydrocarbons are also listed.

THE SYNTHESIS, chemistry, and thermal rearrangements of cyclic and polycyclic compounds have been the subjects of extensive study, particularly in the last decade. In spite of this effort, the thermodynamic properties, which are an essential prerequisite for the understanding of reaction equilibria, are in most cases not well established. Although heats of formation and ring strain data for cyclic compounds are now fairly extensive (*9*), entropy and heat capacity values are almost nonexistent. Lack of such data is not surprising. Third law entropies and heat capacities are obtained only through rather laborious experimental studies, while statistical thermodynamic calculations of $S°$ and C_p° require knowledge of all fundamental vibration frequencies of the molecules, which are at this time prohibitively difficult to determine.

Where entropies and heat capacities are not known, it is possible to estimate them with moderate accuracy—i.e., ~1.5 cal/ mole-° K in $S°$ and C_p°—by making "reasonable" structural and vibrational frequency "corrections" to the corresponding established thermodynamic properties of similar "reference" compounds. This procedure is known as the difference method (D.M.) and has been used by the authors to estimate the entropies and heat capacities of a large number of free radical species (*3*).

A suitable choice of reference compound—i.e., one similar in mass, size, and structure to the unknown assures that the external rotational and translational entropies and heat capacities of the reference and unknown compounds will be the same and that vibrational contributions to these quantities for the two will be similar. The basic assumption of the difference method is that $S°$ and C_p° differences between the reference and unknown are vibrational in nature, and that they may be closely estimated by considering only low frequency motions thought to be significantly changed in the unknown, relative to the reference compound. Fortunately, entropies and heat capacities of molecules are not excessively sensitive to the exact choice of their vibrational frequencies and estimates of moderate accuracy can be made with relative ease.

This paper presents methods for making D.M. estimates of entropies and heat capacities of cyclic and polycyclic hydrocarbons. First additivity "corrections" and the rules for their use in $S°$ and C_p° estimates are presented. Estimation methods are illustrated and comparisons of predictions with the established thermodynamic data in "known" systems are given. Then the rationale for the suggested D.M. correction values is discussed.

ADDITIVITY CORRECTIONS

Entropies of cycloalkanes up to cyclooctane and heat capacities of cycloalkanes up to cyclohexane have been reported. $S°$ and C_p° values are available for only three cycloalkenes (cyclobutene, cyclopentene, and cyclohexene) and four cyclounsaturates (cyclopentadiene, benzene, 1,3,5-cycloheptatriene, and 1,3,5,7-cyclooctatetraene). The data (*3*) are summarized in Table III.

Also shown in Table III are the entropy and heat capacity estimates obtained by using the additivity corrections of Tables I and II, according to the difference method estimation procedures. The reference compounds for these $S°$ and C_p° estimates are the linear alkanes.

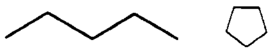
The difference method and use of the additivity corrections for making the thermodynamic estimates of Table III are illustrated below.

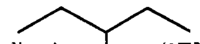
Linear Alkanes → Cycloalkanes. Starting with the $S°$ and C_p° data for the linear alkanes, two kinds of corrections are required, in order to obtain the corresponding values for the cycloalkanes: cyclization corrections (Table I), and extra $X°$ ($S°$ and C_p°) corrections (Table II).

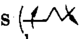
Cyclization corrections allow for normal frequency changes in transforming the linear hydrocarbons to cyclic compounds. These are mainly $S°$ and C_p° losses due to internal rotation restrictions. Extra $S°$ corrections allow for abnormal (relative to a standard ring), out of plane, ring vibrations. In Example 1 the intrinsic entropy, S_{int}°, is related to the observed entropy, $S°$ by the relation, $S_{\text{int}}^\circ = S° + R\ln(\sigma/n)$, where σ is the total symmetry number (internal and external) for the molecule, and n is the number of optical isomers.

Four internal rotations are lost in the cyclization of

EXAMPLE 1. *n*-Pentane → Cyclopentane



σ		$S°$	$S°_{int}$	$C_p°$						
				300	400	500	600	800	1000	1500
18		83.5	89.3	28.8	36.5	43.6	49.6	59.3	66.6	77.9
Cyclization	+(2EM)$_c$		−9.3	−4.6	−4.6	−5.0	−5.2	−6.0	−6.6	−7.9
	+2(LG)$_c$		−9.8	−1.7	−1.3	−1.1	−0.6	0.0	+0.3	1.3
10	 (standard C$_5$ ring)		70.2	22.5	30.6	37.5	43.8	53.3	60.3	71.3
Extra $X°$	+($X°$)		3.9	−0.8	−0.9	−0.9	−0.9	−1.0	−1.0	−1.0
10		69.5	74.1	21.7	29.7	36.6	42.9	52.3	59.3	70.3
	 Observed	70.0	74.6	20.0	28.4	36.1	42.6	52.4	59.8	70.7

n-pentane: two end methyl groups rotating against *n*-butyl groups (), and two ethyl groups rotating against *n*-propyl groups (). The former are accounted for in one single correction, (2EM)$_c$, and the latter are considered here as large group corrections, (LG)$_c$. A large group cyclization correction refers to any internal rotor involving linear allyl groups larger than methyl.

Cyclopentane has abnormal looseness in one of its out-of-plane vibrations (a pseudorotation); hence the extra $X°$ correction.

Entropies and heat capacities of other saturated rings have been made as above, starting from the linear compounds.

Cycloalkanes → Cycloalkenes. Starting from the entropies and heat capacities of cycloalkanes (Table III), the entropies and heat capacities of the various cycloalkenes can be estimated by again making two kinds of additivity corrections: ring tightness corrections (T_i, Table II), and unsaturation corrections ($-2H$, Table I). The former allow for the tightening in out-of-plane bending frequencies due to the π bond; the latter allow for $X°$ losses due to the six vibrational degrees of freedom and other associated vibrational changes resulting from the removal of the two H atoms to form the π bond. Specifically, ring tightness corrections are given individually—i.e., for each double bond. Thus for the tightness correction of a diene, both T_1 and T_2 must be added, while for a triene, the tightness is $T_1 + T_2 + T_3$, etc.

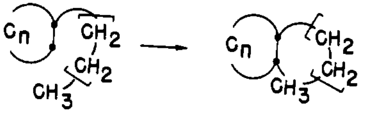
Table I. Additivity Corrections

A. Cyclization of Alkyl Side Chain Corrections

1. Methyl Group Cyclization (M)$_c$

$S°$ (300)	$C_p°$ 300	400	500	600	800	1000	1500
−5.2	−3.3	−3.9	−4.5	−5.1	−6.1	−7.1	−8.5

2. Large Group (Internal Rotor) Cyclization Correction (LG)$_c$



$S°$ (300)	$C_p°$ 300	400	500	600	800	1000	1500
−4.9	−0.83	−0.65	−0.55	−0.30	0.00	0.14	0.66

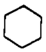
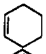
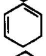
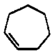
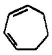
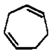
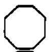
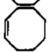
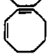
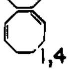
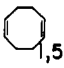
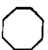
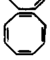
3. Two End Methyl Groups Cyclizations (2—EM)$_c$

$S°$ (300)	$C_p°$ 300	400	500	600	800	1000	1500
−9.3	−4.6	−4.6	−5.0	−5.2	−6.0	−6.6	−7.9

B. Removal of 2 H Atoms to Give Double Bond in a Cyclic Compound ($-2H$)$_c$

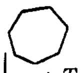
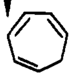
Type	$S°$ (300)	$C_p°$ 300	400	500	600	800	1000	1500
$-(2H)_c$	−0.4	−1.4	−2.7	−3.8	−4.8	−6.3	−7.5	−9.3

Table II. Double Bond Tightness Corrections

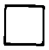
			C_p°, Gibbs/Mole						
		S°	300	400	500	600	800	1000	1500
Cyclopropane									
Extra X°		0	0	0	0	0	0	0	0
T_1 1st		0	0	0	0	0	0	0	0
Cyclobutane									
Extra X°		1.9	0.2	0.1	0.1	0.1	0	0	0
T_1 1st		−1.9	−0.2	−0.1	−0.1	−0.1	0	0	0
T_2 2nd		−1.4	−0.7	−0.4	−0.3	−0.2	−0.1	−0.1	0
Totally tight C_4[a]		−3.3	−0.9	−0.5	−0.4	−0.3	−0.1	−0.1	0
Cyclopentane									
Extra X°		3.9	−0.8	−0.9	−0.9	−0.9	−1.0	−1.0	−1.0
T_1 1st		−3.9	0.8	0.9	0.9	0.9	1.0	1.0	1.0
T_2 2nd		−2.8	−1.4	−0.8	−0.6	−0.4	−0.2	−0.2	0
Totally tight[a]		−6.7	−1.4	−0.8	−0.6	−0.4	−0.2	−0.2	0
Cyclohexane									
Extra X°		0	0	0	0	0	0	0	0
T_1 1st		0	0	0	0	0	0	0	0
T_2(1,3); 2nd (1,3)		−1.4	−0.7	−0.4	−0.3	−0.2	−0.1	−0.1	0
T_2(1,4); 2nd (1,4)		0	0	0	0	0	0	0	0
T_3 3rd (1,3,5)		−2.8	−1.4	−0.9	−0.6	−0.5	−0.3	−0.2	−0.1
Totally tight		−4.2	−2.1	−1.3	−0.9	−0.7	−0.4	−0.3	−0.1
Cycloheptane									
Extra X°		2.5	0.3	0.2	0.1	0	−0.2	−0.5	−0.7
T_1 1st		−2.5	−0.3	−0.2	−0.1	0	0.2	0.5	0.7
T_2(1,3) 2nd (1,3)		−1.4	−0.65	−0.4	−0.3	−0.2	−0.1	−0.1	0
T_2(1,4) 2nd (1,4)		0	0	0	0	0	0	0	0
T_3 3rd (1,3,5)		−1.4	−0.65	−0.4	−0.3	−0.2	−0.1	−0.1	0
Totally tight[a]		−8.1	−2.9	−1.8	−1.3	−0.8	−0.2	0.1	0.7
Cyclooctane									
Extra X°		8.4	0.8	0.6	0.5	0.2	−0.4	−0.8	−1.4
T_1 1st		−3.2	−0.3	−0.2	−0.1	0.0	0.2	0.4	0.7
T_2(1,3 2nd-1,3)		−4.2	−0.4	−0.3	−0.3	−0.2	0.1	0.3	0.6
T_2(1,4)		−1.0	−0.1	−0.1	−0.1	0.0	0.1	0.1	0.1
		0.0	0	0	0	0	0	0	0
T_3(1,3,5; 3rd-1,3,5)		−1.0	−0.1	−0.1	−0.1	0	0	0.1	0.1
T_3(1,3,6) 1,3,6		−3.8	−1.3	−0.8	−0.6	−0.4	−0.2	0	0
T_4 4th 1,3,5,7		−3.4	−1.5	−1.0	−0.7	−0.5	−0.2	0	0
Totally tight[a]		−15.3	−4.1	−2.6	−2.0	−1.2	−0.1	0.8	1.4

[a] Totally tight values for C_n ring with maximum unsaturation and all in-plane and out-of-plane bending frequencies set equal to 550 cm^{-1}.

EXAMPLE 2. Cycloheptane → 1,3,5-Cycloheptatriene

	σ	S°	S°_{int}	C_p° 300	400	500	600	800	1000	1500
	1	81.5	81.5	32.1	43.4	53.0	61.9	75.2	84.6	99.2
+ T_1			−2.5	−0.3	−0.2	−0.1	0.0	0.2	0.5	0.7
+ $T_{2(1,3)}$	Tightness		−1.4	−0.65	−0.4	−0.3	−0.2	−0.1	−0.1	0.0
+ T_3			−1.4	−0.65	−0.4	−0.3	−0.2	−0.1	−0.1	0.0
+ $3(2H)_c$	Unsaturation		−1.2	−4.2	−8.1	−11.4	−14.4	−18.9	−22.5	−27.9
	1	75.0	75.0	26.3	34.3	41.0	47.1	56.3	62.4	72.0
	Observed		75.4				Not reported			

EXAMPLE 3. Cyclobutane → Cyclobutene

Compound	σ	S°	S°_{int}	C_p° 300	400	500	600	800	1000	1500
	8	63.2	67.3	18.0	24.2	29.7	34.8	42.2	47.6	55.1
+ T_1	Tightness		−1.9	−0.2	−0.1	−0.1	−0.1	0	0	0
+ $(2H)_c$	Unsaturation		−0.4	−1.4	−2.7	−3.8	−4.8	−6.3	−7.5	−9.3
	2	63.6	65.0	16.4	21.4	25.8	29.9	35.9	40.1	45.8
	Observed	63.0	64.4	16.0	21.6	26.4	30.3	36.2	40.5	46.7

The estimated values of Table III, obtained as described above, are in good agreement with the literature values where available—i.e., on the average, well within the expected error limits of ±1.5 cal/mole-°K. Estimates for compounds where data do not exist are probably of similar reliability.

Alkyl Monocyclics → Polycyclics. Convenient reference compounds for making polycyclic compound entropy and heat capacity estimates are the corresponding alkyl-substituted monocyclic compounds. [Entropies and heat capacities of all reference compounds can be obtained with good accuracy from group additivities (*3*).] Estimation procedures then involve the successive application of four additivity corrections.

Step 1. Cyclization correction, for cyclizing the alkyl side chains to the desired polycyclic compound.

Step 2. Extra X° corrections to the new ring, to allow for low frequency out-of-plane vibrations in the new ring.

Step 3. Reference ring tightness corrections, to adjust for tightening in the reference ring resulting from strains produced by the new ring.

Step 4. New ring tightness corrections, to adjust for tightening in the new ring produced by the reference ring.

Polycyclic ring tightness corrections pertinent to steps 3 and 4 are of two different kinds: shared side corrections and methylene bridge corrections. Both are related to the π bond tightness corrections (Table II) in a manner described in Table IV. The values suggested are rationalized below and seem to provide estimates to a probable accuracy of ±1.5 cal/mole-°K.

Shared Side Polycyclics. Estimation procedures for obtaining the thermodynamic properties (S° and C_p°) of polycyclic compounds are illustrated below for 1,1,0-bicyclobutane (*3*), naphthalene (*3*), 2,3,0-bicycloheptane, and Decalin ([4,4,0]-bicyclodecane) (*8*) (Example 4a).

Steps 2, 3, and 4 are not required in the above estimate, since $C_3(X^\circ)$ and $C_3(T_i)$ corrections are zero. A very similar result can be obtained starting from cyclobutane. Thus, in forming the (C—C) bridge, the H atoms must be removed, and as a result of the (C—C) bridge, something approximating total tightening of the C_4 ring should occur. See Example 4b. These two estimates are in very good agreement.

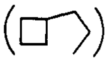
In Example 5a, the C_4 shared side tightness correction due to the C_5 ring is ⅔ the first π bond tightness correction in cyclobutane, and the C_5 shared side tightness correction due to the C_4 ring is ¾ the first π bond tightness correction in cyclopentene.

EXAMPLE 4a. Methylcyclopropane () → 1,1,0-Bicyclobutane ()

Compound	S°_{int}	C_p° (300)	C_p° (800)
	69.3	18.7	42.7
Cyclization -$(\text{M})_c$	−5.2	−3.3	−6.0
Looseness = 0			
Tightness = 0			
	64.1	15.4	36.7
Observed	63.8		

EXAMPLE 4b.

	Compound		S°_{int}	C_p° (300)	C_p° (800)
			67.3	18.0	42.2
Unsaturation		$-(2H)_c$	−0.4	−1.4	−6.3
			66.9	16.6	35.9
Tightness		$+(T_1 + T_2)_{C_4}$	−3.3	−0.9	−0.1
			63.6	15.7	35.8

EXAMPLE 5a. *n*-Propylcyclobutane () → 2,3,0-Bicycloheptane ()

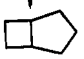
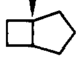
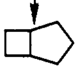
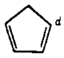
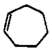
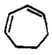
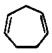
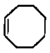
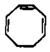
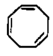
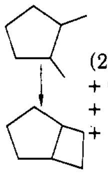
	Compound		S°_{int}	C_p° (300)	C_p° (800)
			95.0	34.2	75.6
Cyclization		$+ (M)_c$	−5.2	−3.3	−6.0
		$+ 2(\text{LG})_c$	−9.8	−1.7	0.0
			80.0	29.2	69.6
Extra X°		$+ C_5(X^\circ)$	3.9	−0.8	−1.0
			83.9	28.4	68.6
Tightness		$+ \frac{2}{3}(T_1)_{C_4}$	−1.3	−0.1	0.0
		$+ \frac{3}{4}(T_1)_{C_5}$	−3.0	+0.6	+0.8
			79.6	28.9	69.4

Table III. Comparison of Estimated and Observed Intrinsic Entropies and Heat Capacities of Monocyclic Compounds [a,b]

	S°_{int} (298)		C°_p (300)		C°_p (800)	
Rings	Est.	Obs.	Est.	Obs.	Est.	Obs.
	(60.9)	60.4	(13.3)	13.44	(31.1)	31.44
	60.5	59.8	11.9		24.8	
	(67.3)	67.6	(18.0)	17.4	(42.2)	42.4
	65.0, 65.3[b]	64.4	16.4, 15.8[b]	16.0	35.9, 36.1[b]	36.2
	63.2		14.3		29.5	
	(74.1)	74.6	(21.7)[c]	20.0	(52.3)	52.4
	69.8, 70.3[b]	70.6	21.1, 19.4[b]	18.1	46.9, 47.0[b]	45.8
	67.0, 67.5[b]	67.0	18.3, 16.6[b]	17.8	40.5, 40.6[b]	40.6
	(74.5)	74.9	(27.2)[c]	25.6	(64.4)	66.8
	74.1, 73.7[b]	(74.3)	25.8, 24.2[b]	25.3	58.0, 60.4[b]	59.5
	72.3		23.7		51.6	
	73.7	(73.1)	24.4		51.7	
	69.1, 68.7[b]	69.3	21.0, 19.3[b]	19.7	45.1, 47.5[b]	45.1
	(81.5)	81.8	(32.1)[c]		(75.2)	
	78.9		30.5		69.1	
	77.1		28.4		62.7	
	78.5		29.1		62.8	
	75.3, 75.6[b]	75.4	26.3		56.3	
	(91.8)	91.8	(36.6)[c]		(86.5)	
	88.2		34.9		80.4	
1,3- 	83.6		33.1		74.2	
1,4-  or 1,5-	86.8		33.5		74.2	
1,3,5- 	82.2		31.6		67.9	
1,3,6- 	79.4		30.4		67.7	
1,3,5,7- 	78.4	78.4	28.7		61.4	

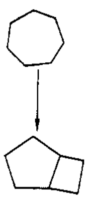
[a] All units cal/mole-° K, based on the 1-atm standard state. [b] Reference compounds for all estimates are linear hydrocarbons. Cycloolefin thermodynamics estimated, starting from cycloalkane values in parentheses. Estimates for cycloolefins, starting from reported thermodynamics of cycloalkanes are (on average) somewhat more accurate in cases (indicated by [b]) where comparisons can be made. [c] Heat capacities of cyclic alkanes obtained by difference method estimates based on linear hydrocarbons appear systematically too high at lower temperatures. More reliable estimates for rings C_5 and larger can probably be realized by making following extra reductions: C°_p (300), −1.6 cal/mole-° K; C°_p (400), −1.2 cal/mole-° K; C°_p (500), −0.8 cal/mole-° K; C°_p (600), −0.4 cal/mole-° K; C°_p (800), no correction. The general agreement illustrated in examples (for which the above extra corrections were not made) suggest that these corrections do not necessarily give better results in the more complex systems. [d] Cyclopentadiene ring best represented as totally tight.

EXAMPLE 5b.



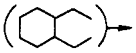
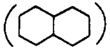
Compound	$S°$	$S°_{int}$	$C_p°$ (300)	$C_p°$ (800)
	87.8	92.2	32.4	76.0
$(2EM)_c$		-9.3	-4.6	-6.0
+ $C_4(X°)$		1.9	0.2	0.0
+ $\frac{2}{3}(T_1)_{C_4}$		-1.3	-0.1	0.0
+ $\frac{3}{4}(T_1)_{C_5}$		-3.0	+0.6	+0.8
		80.5	28.5	70.8

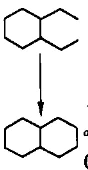
EXAMPLE 5c.



	$S°$	$S°_{int}$	$C_p°$ (300)	$C_p°$ (800)
	81.8	81.8	(32.1)	(75.2)
- $C_7(X°)$		-2.5	-0.3	+0.2
+ $C_4(X°)$		+1.9	+0.2	0.0
+ $C_5(X°)$		+3.9	-0.8	-1.0
- $(2H)_c$		-0.4	-1.4	-6.3
+ $\frac{2}{3}(T_1)_{C_4}$		-1.3	-0.1	0.0
+ $\frac{3}{4}(T_1)_{C_5}$		-3.0	+0.6	+0.8
		80.4	30.3	69.2

Again, all three estimates are in good agreement.

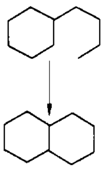
EXAMPLE 6a. 1,2-Diethylcyclohexane ()→ cis or trans Decane ()



	Compound	$S°_{int}$	$C_p°$(300)	$C_p°$ (800)
		111.2	48.7	109.1
Cyclization	+ $2(ME)_c$	-9.3	-4.6	-6.0
Looseness = 0	+ $2(LG)_c$	-9.6	-1.7	0.0
Tightness = 0	[a]	92.3	42.4	103.1
	Observed (cis)	91.7	40.1	103.4
	Observed (trans)	90.9	40.0	103.4

[a] Extra $X°$ and tightness (T_1) corrections in the C_6 ring system are zero.

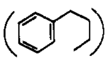
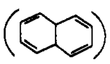
EXAMPLE 6b.

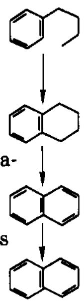


	$S°_{int}$	$C_p°$ (300)	$C_p°$ (800)
	111.6	48.9	108.9
$1(ME)_c$	-5.2	-3.3	-6.0
$3(LG)_c$	-14.7	-2.5	0.0
	91.7	43.1	102.9

The two methods of calculation are in good agreement with each other, but in poor agreement on C_p at 300° K.

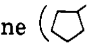
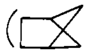
EXAMPLE 7.

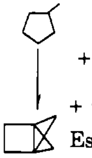
n-Butylbenzene () ——→ Naphthalene ()



	Compound	$S°_{int}$	$C_p°$ (300)	$C_p°$ (800)
		108.6	42.1	89.4
Cyclization	+ $(M)_c$	-5.2	-3.3	-6.0
	+ $3(LG)_c$	-14.7	-2.5	0.0
		88.7	36.3	83.4
Unsaturation	+ $2(-2H)_c$	-0.8	-2.8	-12.6
		87.9	33.5	70.8
Tightness	+ $(T_1 + T_2 + T_3)_{C_6}$	-4.2	-2.0	-0.7
		83.7	31.5	70.1
	Observed	83.3		

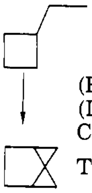
Methylene-Bridged Polycyclics. The procedure for estimating $S°$ and $C_p°$ values of methylene-bridged polycyclics is simpler than that of the shared side compounds. The only correction required, other than that for methylcyclization to form the bridge itself, is the tightness correction to the reference ring resulting from the methylene bridge (Table IV).

EXAMPLE 8a. Methylcyclopentane ()→ [2,1,1]Bicyclohexane ()



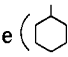
	Compound	$S°_{int}$	$C_p°$ (300)	$C_p°$ (800)
		83.0	26.9	63.5
Cyclization	+ $(M)_c$	-5.2	-3.3	-6.0
Tightness	+ $\frac{3}{4}(T_1 + T_2)_{C_5}$	-4.0	-0.1	0.7
	Estimated	73.8	23.5	58.2

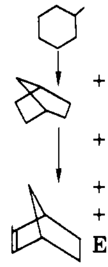
EXAMPLE 8b. Ethylcyclobutane → Bicyclohexane (2,1,1)



Compound	$S°_{int}$	$C_p°$ (300)	$C_p°$ (800)
	85.8	28.1	64.7
$(EM)_c$	-5.3	-3.4	-6.3
$(LG)_c$	-4.9	-0.8	0.0
$C_4(T_1)$	-1.9	-0.2	0
Totals	73.7	23.7	58.4

Agreement is excellent.

EXAMPLE 9. Methylcyclohexane ()→ Norbornene ()

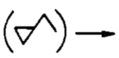


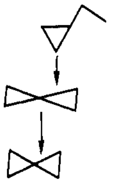
	Compound	$S°_{int}$	$C_p°$ (300)	$C_p°$ (800)
		83.4	32.4	75.7
Cyclization	+ $(M)_c$	-5.2	-3.3	-6.0
		78.2	29.1	69.7
Unsaturation	+ $(-2H)_c$	-0.4	-1.4	-6.3
Tightness	+ $(T_1 + T_2)_{C_6}$	-1.4	-0.6	-0.1
	+ $\frac{1}{2}(T_3)_{C_6}$	-1.4	-0.7	-0.2
	Estimated	75.0	26.4	63.1

In the above, the tightness corrections applied to the C_6 ring are guesses. An increase in ring tightness in the series norbornane, norbornene, norbornadiene is expected; therefore, corrections of $\frac{3}{4}(T_1 + T_2)$, $(T_1 + T_2 + \frac{1}{2}T_3)$, and $(T_1 + T_2 + T_3)$, respectively, for these compounds seem reasonable.

Spirocompounds. The thermodynamic properties of spiropentane are known (*3*). They can be estimated starting from ethylcyclopropane as reference (Example 10).

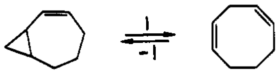
The agreement between the estimated and observed values is within the expected error limits. However, the D.M. estimates can be improved by correcting for the unusual low frequency rock, wag, and twist frame vibrations in spiropentane: 305, 305, and 272 cm^{-1}, respectively. Since the D.M. assumes all three vibrations to be 400 cm^{-1} (see below), an extra $X°$ correction in spiropentane (and very likely all other spiro compounds) contributes to the extent indicated by Example 10 and Table IV. Given the spectral data, D.M. estimates can always be improved, but in such cases D.M. estimates are not needed. It is also evident that unusual vibrational frequencies must occur in many other compounds for which data are not available. Nevertheless, in the absence of data, if spiropentane is typical, it is apparent that estimates of acceptable accuracy can be made

Example 10. Ethylcyclopropane () ⟶ Spiropentane()

Compound			S°_{int}	C_p° 300	400	500	600	800	1000	1500
Cyclization			78.7	24.2	32.2	39.2	45.0	53.8	60.2	70.0
		$-(M)_c$	−5.3	−3.4	−4.0	−4.7	−5.3	−6.3	−7.2	−8.6
		$-(LG)_c$	−4.9	−0.8	−0.7	−0.6	−0.3	0	0.1	0.7
		Estimated	[68.5	20.0	27.5	33.9	39.4	47.5	52.9	60.7]
		Extra X°(spiro)	1.4	0.7	0.4	0.3	0.2	0.1	0.1	0.0
		Estimated	69.9	20.7	27.9	34.2	39.6	47.6	53.0	60.7
		Observed	70.2	21.2				47.9		

by the difference method. It is well to emphasize the term "acceptable accuracy" by noting that heats of formation for complex ring compounds are seldom known to better than ±1 kcal per mole. Therefore, errors in calculated equilibrium constants for reactions involving polycyclic compounds are more likely to result from errors in their measured heats of formation than from errors in their estimated entropies of up to ±1.5 cal/mole-° K.

Example 11. Kinetic and equilibrium constant measurements provide several additional tests of the D.M. estimates. An equilibrium constant of $K_{eq} = 37$ has been obtained for the reaction (*4*) 5,1,0-bicycloocta-2-ene → 1,4-cyclooctadiene at 475° K. There was essentially no temperature variation of this equilibrium constant.

$\sigma = 1, n = 2$  $\sigma = 1, n = 2$

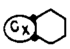
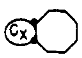
5,1,0-Bicyclooct-2-ene 1,4-Cyclooctadiene

D.M. Estimates

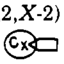
	5,1,0-Bicyclooct-2-ene	1,4-Cyclooctadiene
S° (real)	82.3 gibbs/mole	89.2 gibbs/mole
$C_p^\circ(300)$	31.6 gibbs/mole	33.5 gibbs/mole
$C_p^\circ(500)$	51.4 gibbs/mole	52.8 gibbs/mole
$< \Delta C_p^\circ >$	~ 1.8 gibbs/mole (300–475°)	$\Delta(\Delta S^\circ)_{300\text{-}475} = 0.8$ gibbs/mole

Table IV. Corrections

A. Shared Side Polycyclic Ring Tightness Corrections

Compound	Shared Ring	Tightness Correction in C_X Ring
	 C_3	Same as double bond tightness
	 C_4	¾ double bond tightness
	 C_5	⅔ double bond tightness
	 C_6	½ double bond tightness
	 C_7	⅓ double bond tightness
	 C_8	No correction

B. Methylene Bridge Ring Tightness Corrections for C_X Ring

(1,1,*X*-2) 	—(CH_2)-bridge	Tightness = ¾ (1st + 1,3) double bond tightness
(1,2,*X*-2) 	—(CH_2)-bridge	Tightness = (1st + 1,3) double bond tightness

C. Spiro compounds

	S°	C_p° 300	400	500	600	800	1000	1500
Extra X°	1.4	0.7	0.4	0.3	0.2	0.1	0.1	0

($\Delta H^\circ \cong 0.5$ kcal/mole; therefore, $\Delta S^\circ \cong 8.2$ gibbs/mole. We see that D.M. estimates give $\Delta S^\circ_{475} \cong 7.7$ gibbs/mole, in good agreement.

Example 12. The reaction kinetics of the Diels-Alder dimerization of cyclopentadiene to *endo*-dicyclopentadiene and the reverse decomposition kinetics have been measured. The Arrhenius parameters reported in the two studies of the dissociation reaction are in excellent agreement and therefore appear to be well established:

$$\log k_1 = 13.0 - 33.7/\theta\ (5);\ \log k_1 = 13.01 - 33.97/\theta\ (1)$$

where $\theta = 2.303\ RT$ in kcal per mole. By contrast, the three studies of the dimerization kinetics have yielded three different sets of Arrhenius parameters:

$$\begin{aligned} \log k_{-1}\ (\text{l/mole-sec.}) &= 4.93 - 14.9/\theta\ (5) \\ &= 6.1\ - 16.7/\theta\ (1) \\ &= 6.8\ - 16.9/\theta\ (14) \end{aligned}$$

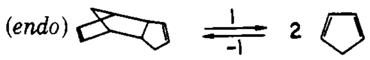
Converting the back reaction *A*-factor to the 1-atm pressure standard state, and using $A_1 = 10^{13.0}$ sec^{-1}, one obtains reaction entropies from the above of

$$\Delta S^\circ = 46.3,\ 41.0,\ 37.8 \text{ gibbs/mole, respectively}$$

D.M. estimates of S° and C_p° for cyclopentadiene are given in Table III; those for dicyclopentadiene are shown at top of next page.

endo ($\sigma = 1$, $n = 2$) (Values in parentheses are obtained starting with *n*-pentylcyclopentane.)

Thus, for the reaction,



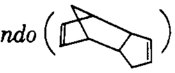
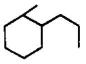
S° (298)	86.7 gibbs/mole	2 × 65.6 gibbs/mole
C_p° (300)	35.1 gibbs/mole	2 × 17.8 gibbs/mole
C_p° (500)	59.0 gibbs/mole	2 × 29.5 gibbs/mole

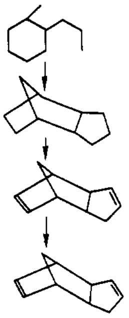
$$< \Delta C_p^\circ >_{300\text{-}500} = +\ 0.25 \text{ cal/mole-}^\circ\text{K}$$

and $\Delta S^\circ_{500} = 44.6 \pm 1.5$ cal/mole-° K.

The kinetic parameters of Kistiakowsky *et al.* (*5*) are the only ones in reasonable agreement with the reaction thermodynamics. The others are outside what we believe are the limits of error and should accordingly be considered suspect.

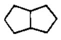
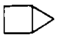
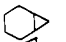
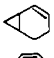
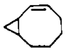
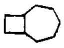
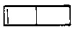
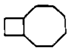
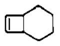
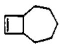
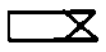
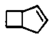
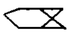
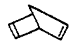
Entropies and heat capacities of a number of polycyclic compounds obtained by the difference method are given in Table V. In a forthcoming paper we will show that the thermodynamic estimates for most of these compounds, and for their transition states in various unimolecular reaction processes, are in good agreement with the observed kinetic parameters of their reactions.

endo () Reference.  (based on linear hydrocarbon)



		$S^\circ_{298\ \text{int}}$	C°_p (300)	C°_p (500)
Cyclization	(trans)	111.5	48.7	77.4
	$-\ 2(M)_c$	−10.4	−6.6	−8.6
	$-\ 2(LG)_c$	−9.8	−1.7	−1.1
		91.3	40.4	67.7
Looseness	$+\ C_5L$	3.9	−0.8	−0.9
Unsaturation	$-\ 2(2H)_c$	−0.8	−2.8	−7.6
		94.4	36.8	59.2
Tightness	$C_6(T_1 + T_2 + T_3)$	−4.2	−2.1	−0.9
	$C_5(T_1 + \frac{2}{3}T_2)$	−4.9	+0.4	+0.7
		$85.3(85.5)_{C_5}$	$35.1(35.7)_{C_5}$	$59.0(59.5)_{C_5}$

Table V. Estimated Entropies and Heat Capacities of Some Polycyclic Compounds[a,b]

Compound	σ	S°_{int}	S°	C°_p (300)	C°_p (800)	Compound	σ	S°_{int}	S°	C°_p (300)	C°_p (800)
[1,1,0] 	2	64.1	62.7	15.3	36.7	cis[3,3,0] 	2	86.5	85.1	32.3	80.2
[2,1,0] 	1	68.8	68.8	18.8	47.4		2	82.4	81.0	29.0	73.6
[3,1,0] 	1	74.4	74.4	22.7	58.7		2	75.3	73.9	22.3	58.1
[4,1,0] 	1	78.5	78.5	27.5	72.1		1	76.7	76.7	24.0	63.9
[5,1,0] 	1	83.0	83.0	33.8	80.7		1	67.8	67.8	17.1	41.2
[6,1,0] 	1	91.0	91.0	39.0	91.5		1	72.7	74.1	20.3	50.5
cis[2,2,0] 	2	73.9	72.5	23.4	56.5		1	76.7	78.1	25.5	65.7
cis[3,2,0] 	1	79.5	79.5	28.1	69.5		1	81.2	82.6	31.7	74.3
cis[4,2,0] 	1	83.5	83.5	33.0	80.9		1	86.7	88.1	36.7	85.4
cis[5,2,0] 	1	89.1	89.1	37.9	92.0		1	72.4	72.4	21.8	52.1
cis[6,2,0] 	1	97.8	97.8	43.1	102.7		1	81.5	81.5	31.2	74.5
[1,1,1] 	6	68.9	64.7	18.7	47.5		1	86.9	86.9	36.0	85.6
[2,1,1] 	2	74.2	72.8	22.3	57.2		1	77.4	78.8	25.4	63.3
[2,2,1] 	2	77.1	75.7	26.9	71.9		1	75.1	75.1	24.6	65.5
[3,1,1] 	2	77.6	76.2	27.1	71.9		2	74.0	72.6	24.1	65.4

[a] Reference compounds alkyl-substituted monocyclic compounds, thermodynamic properties obtained from additivity relations. [b] Units cal/mole-° K based on 1-atm standard state.

RATIONALE

In Table VI the intrinsic entropies $[S^\circ_{\text{int}} = S^\circ + R\ln(\sigma/n)]$ of the linear alkanes are compared with the intrinsic entropies of their cyclic counterparts. Entropies of the linear compounds are considerably higher, mainly because of the significant contributions of their hindered internal rotations. The cyclization of a C_n linear hydrocarbon transforms $(n - 1)$ internal rotations into ring vibrations. From the entropy differences between the linear and cyclic compounds one finds entropy losses of from 3.6 to 4.9 cal/mole-° K-internal rotor (column 3). It is easy to show that this value is not constant, primarily because of differing degrees of "looseness" in the out-of-plane ring vibrations for the various cyclic alkanes. For example, the single out-of-plane vibration of cyclobutane is a low frequency, double minimum motion which contributes 3.8 cal/mole-° K to the room temperature entropy (*13*). Also, one of the two out-of-plane vibrations of cyclopentane has been described as a pseudorotation (or alternate puckering of CH_2 groups) and contributes an exceptional 5.8 cal/mole-° K to that structure (*2*, *7*). Further, although normal mode frequencies of alkane rings larger than cyclohexane have not been reported (their entropies having been determined by third law methods), Dreiding models strongly suggest extensive freedom of motion in their structures. The latter resemble concerted partial rotations of the ring methylene groups. By contrast, cyclopropane with no out-of-plane vibrations, and cyclohexane with three in-plane and three out-of-plane vibrations are both relatively rigid molecules. [In-plane and out-of-plane vibrations on cyclohexane are 2 × 426, 522 cm^{-1}, and 2 × 231, 382 cm^{-1}, respectively (*2*).] If we now define (as a useful artifice for making thermodynamic estimates) standard out-of-plane and in-plane vibrations as 225 and 550 cm^{-1}, respectively, it is possible to calculate the excess entropy in the out-of-plane ring motions of cycloalkanes (column 4, Table VI) and also the entropies of their hypothetical standard cyclic forms (column 5). The entropy losses on cyclization per internal rotation (column 6) are now seen to be nearly constant (ΔS° cyclization $\rightarrow$ standard ring $\cong 4.8 \pm 0.15$ cal/mole-rotor).

Rapid and reliable estimates of the standard ring entropies can, therefore, be made from the established entropies of the corresponding linear compounds by subtracting 4.8 cal/mole-° K for each internal rotation lost in cyclization. To obtain real entropies, one must add the excess entropies of the out-of-plane ring vibrations to those of the standard rings.

The empirical 4.6 cal/mole-° K cyclization correction can be derived from the difference method in a straightforward manner by considering the vibrational changes which occur when a linear alkane is changed to a cycloalkane. The difference method also provides the corrections needed for estimating the heat capacities of cyclic compounds from those of the linear alkanes.

Cyclization Corrections via Difference Method. In the cyclization of a normal $\mathrm{C}_n\mathrm{H}_{2n+2}$ alkane to a cyclic $\mathrm{C}_n\mathrm{H}_{2n}$ alkane, the important vibrational changes are: loss of six H-atom vibrations—i.e., there are two less H atoms in the cyclic compound—replacement of the two internal rotations of the end methyl groups with two methylene rocks, replacement of $n - 2(\mathrm{C}\diagup^{\mathrm{C}}\diagdown\mathrm{C})$ skeletal bends with $n - 3$ in-plane bends and one (C—C) stretch, and transformation of $n - 3$ large group—i.e., bigger than methyl—internal rotations into out-of-plane ring vibrations.

Although there are a few other minor changes, most other vibrations have their counterparts in both linear and cyclic systems, and may be assumed to undergo negligible, or at least compensating, frequency changes. After examination of the normal mode frequencies observed for linear and cyclic alkanes, we have assigned standard frequencies to the various bond and group motions involved. These assigned frequencies (Table VII-A) do not differ significantly from those recommended elsewhere, for similar kinds of estimations (*11*). As an illustration of the thermodynamic accuracy of these assignments, calculated heat capacity contributions at 300° and 800° K of two end methyl groups $2[\mathrm{C}\text{—}(\mathrm{C})(\mathrm{H})_3]$, as in ethane and of an internal methylene group $\{[\mathrm{C}\text{—}(\mathrm{C})_2(\mathrm{H})_2]\}$ are compared in Table VII-B with their respective experimental group additivity values (*3*). The agreements at both temperatures for both groups are good, in fact, superior to those obtained using the group frequencies suggested by Pitzer (*12*).

The vibrational changes occurring in cyclization of a linear alkane are detailed in Table VIII-A,B. The loss in entropy from each methyl rotor is about −4.7 cal/mole-° K. These two values combine to give excellent agreement with the empirical value of -4.8 ± 0.15 cal/mole-rotor required for the standard cyclization.

Table VI. Intrinsic Entropies[a] of Some Linear and Cyclic $\mathrm{C_3}$-$\mathrm{C_8}$ Alkanes

Compound	S°_{int}	$\Delta S^\circ/i$ Rot	Extra $S^{\circ b}$	S°_{int} (Std)	ΔS° (st)/i Rot
Propane	70.26	4.93			4.93
Cyclopropane	60.40		0.0	60.4	
Butane	79.87	4.10			4.70
Cyclobutane	67.57		1.9	65.7	
Pentane	89.29	3.68			4.66
Cyclopentane	74.57		3.9	70.67	
Hexane	98.58	4.75			4.75
Cyclohexane	74.84		0	74.84	
Heptane	108.0	4.37			4.78
Cycloheptane	81.8		2.5	79.3	
Octane	117.3	3.64			4.84
Cyclooctane	91.8		8.4		
Ethane	60.7	5.4		83.4	
Ethene	55.3		−0.6		
Ethyl alcohol	69.7	5.1			4.90
Ethylene oxide	59.5				

[a] Units are cal/mole-° K, based on 1-atm standard state. [b] Extra S° refers to entropy in out-of-plane bending modes in excess of that of standard ring (see text).

Table VII. Frequency Assignments

A. Frequency Assignments for Group and Bond Motions in Hydrocarbons

Vibrations	ω, Cm^{-1}	Vibrations	ω, Cm^{-1}
(C—H)	3000	$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\mathrm{C})$	1050
$(\mathrm{CH_3})$ rock	1100	(C=C)	1650
$(\mathrm{CH_2})$ rock	800	(C—C)	900
$(\mathrm{CH_2})$ wag, twist	1200	$(\mathrm{C}\diagup^{\mathrm{C}}\diagdown\mathrm{C})$	400
$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\mathrm{H})$ in $\mathrm{CH_3}$	1450	$(\mathrm{C}\diagup^{\mathrm{C}}\diagdown\!\!\diagdown\mathrm{C})$	400
$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\mathrm{H})$	1350	In-plane (standard)	550
$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\mathrm{H})$ in $\mathrm{CH_2}$	1450	Out-of-plane (standard)	225
$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\!\!\diagdown\mathrm{C})$	1050		

B. Predictions of Frequency Assignments Compared to Observed Group Additivities[a]

1. Two end $(\mathrm{CH_3})$ groups —i.e., ethane

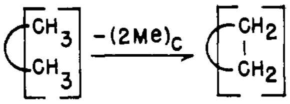
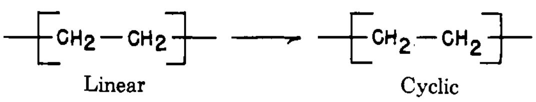
Vibrations	No.	ω, Cm^{-1}	C_p° (300)	C_p° (800)
(C—C)	6	3000	0.00	1.56
$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\mathrm{H})$	4	1450	0.32	4.72
$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\mathrm{H})$	2	1350	0.28	2.52
$(\mathrm{CH_3})$ rock	4	1100	1.16	5.80
(C—C)	1	900	0.51	1.60
$(\mathrm{CH_3}\overset{\curvearrowleft}{-}\infty)_{3.5}$[b]	1		2.10	1.70
Translation + rotation[c]	6		7.96	7.96
Totals	24		12.33	25.86
Observed			12.38	26.04

2. One methylene group $(\text{—}\mathrm{CH_2}\text{—})$

Vibrations	No.	ω, Cm^{-1}	C_p° (300)	C_p° (800)
(C—H)	2	3000	0.00	0.52
$(\mathrm{H}\diagup^{\mathrm{C}}\diagdown\mathrm{H})$	1	1450	0.08	1.16
$(\mathrm{CH_2})$ wag, twist	2	1200	0.42	2.74
$(\mathrm{CH_2})$ rock	1	800	0.66	1.68
$(\mathrm{C}\diagup^{\mathrm{C}}\diagdown\mathrm{C})$	1	400	1.48	1.90
$(\mathrm{LG}\overset{\curvearrowleft}{-}\infty)_{4.0}$[b]	1		2.30	1.90
(C—C)	1	900	0.51	1.60
Totals	9		5.45	11.50
Observed			5.50	11.06

[a] Units of heat capacities are cal/mole-deg. [b] $(\mathrm{CH_3}\overset{\curvearrowleft}{-}\infty)_{3.5}$. Internal rotation of methyl group against large mass with rotational barrier of 3.5 kcal per mole. LG. Group equal to, or larger than, an ethyl group. [c] Contribution of external rotation and translation to heat capacity (1-atm std. state) is $4R = 7.96$ cal/mole-° K.

Table VIII. Difference Method Corrections for Cyclization of Alkanes

			C_p°						
Vibrations	ω, Cm^{-1}	S°(298)	300	400	500	600	800	1000	1500
A. Two End Methyl Group Corrections									
$-2(C—H)$	3000	−0.00	−0.00	−0.00	−0.06	−0.08	−0.52	−1.02	−2.08
$-2(H \overset{C}{\wedge} H)$	1450	−0.02	−0.18	−0.61	−1.10	−1.58	−2.32	−2.80	−3.40
$-2(H \overset{C}{\wedge} H)$	1350	−0.03	−0.26	−0.74	−1.30	−1.78	−2.48	−2.92	−3.46
$-4(CH_3)r$	1100	−0.24	−1.16	−2.48	−3.68	−4.60	−5.80	−6.48	−7.24
$-(C \overset{C}{\wedge} C)$	400	−0.98	−1.47	−1.68	−1.78	−1.84	−1.90	−1.93	−1.96
$-2(CH_3 \not{-} \infty)_{3.5}$		−8.80	−4.20	−4.10	−4.00	−3.80	−3.40	−3.00	−2.50
$(C—C)$	900	0.14	0.51	0.89	1.17	1.37	1.60	1.73	1.87
$4(CH_2)w,t$	1200	0.16	0.84	2.04	3.20	4.16	5.48	6.24	7.12
$2(CH_2)r$	800	0.42	1.32	2.08	2.60	2.94	3.36	3.56	3.78
Totals	$(2Me)_c =$	−9.35	−4.60	−4.95	−5.21	−5.21	−5.98	−6.62	−7.87
B. Internal Large Group Cyclization Correction $(LG)_c$									
$-(C \overset{C}{\wedge} C)$	400	−0.98	−1.48	−1.68	−1.78	−1.84	−1.90	−1.93	−1.96
$-(LG \not{-} LG)_{V_0}$[a]		−6.4	−2.3	−2.3	−2.3	−2.1	−1.9	−1.70	−1.30
+(I.P.)	550	0.56	1.15	1.45	1.62	1.72	1.83	1.88	1.94
+(O.P.)	225	1.94	1.80	1.88	1.91	1.94	1.96	1.97	1.98
Total/rotor		−4.9	−0.83	−0.65	−0.55	−0.30	0.0	0.3	0.7
C. Methyl Group Cyclization Correction $(M)_c$									
$-(CH_3— \infty)_{3.5}$		−4.40	−2.10	−2.05	−2.00	−1.90	−1.70	−1.50	−1.25
$-(H \overset{C}{\wedge} H)$	1350	−0.01	−0.13	−0.37	−0.65	−0.89	−1.24	−1.46	−1.73
$-2(H \overset{C}{\wedge} H)$	1450	−0.02	−0.18	−0.60	−1.10	−1.58	−2.32	−2.80	−3.40
$-2(C—H)$	3000	−0.00	0.0	0.0	−0.06	−0.16	−0.52	−1.02	−2.08
$-2(CH_3)$ rock	1100	−0.12	−0.58	−1.24	−1.84	−2.30	−2.90	−3.24	−3.62
$-(C \overset{C}{\wedge} C)$	400	−0.98	−1.48	−1.68	−1.78	−1.84	−1.90	−1.93	−1.96
$2(H \overset{C}{\wedge} C)$	1050	0.16	0.68	1.36	1.96	2.40	2.98	3.30	3.65
$(C—C)$	900	0.14	0.51	0.89	1.17	1.37	1.60	1.73	1.87
Totals		−5.23	−3.28	−3.69	−4.30	−4.90	−6.00	−6.92	−8.52
The similar methyl cyclization		leads to almost identical results.							
Totals		−5.25	−3.44	−3.98	−4.67	−5.26	−6.30	−7.16	−8.64
The methyl cyclization correction of Table I is the average of these two									
D. Unsaturation Corrections $(-2H)_c$. Introduction of a Double Bond									
$-2(C—H)$	3000	0.00	0.00	0.00	0.00	−0.16	−0.52	−1.02	−2.08
$-2(H \overset{C}{\wedge} H)$	1450	−0.02	−0.18	−0.06	−1.10	−1.58	−2.32	−2.80	−3.40
$-2(CH_2)$ rock	800	−0.42	−1.32	−2.08	−2.60	−2.94	−3.36	−3.56	−3.78
$-4(CH_2)$ w,t	1200	−0.16	−0.82	−2.04	−3.20	−4.16	−5.48	−6.24	−7.12
$-(C—C)$	900	−0.14	−0.51	−0.89	−1.17	−1.37	−1.60	−1.73	−1.87
$4(H \overset{C}{\wedge} C)$	1050	0.32	1.36	2.72	3.92	4.80	5.96	6.60	7.30
$(C{=}C)$	1650	0.00	0.05	0.18	0.38	0.60	1.00	1.26	1.62
Totals		−0.42	−1.42	−2.71	−3.83	−4.81	−6.32	−7.49	−9.33

[a] S° and C_p° values for all internal rotations involving groups larger than CH_3 have been approximated by that of an $(Et \not{-} \infty)_{4.0}$ rotation. Since increased masses—i.e., larger rotational moments of inertia—are probably accompanied by higher rotational barriers (the two effects roughly canceling in order for group activities to hold), this seems a fair approximation.

The other methyl cyclization correction (Table I-A, used primarily in estimates for spiro and polycyclic compounds) also follows from D.M. considerations. Detailing of the appropriate frequency changes due to cyclization and the summing of their entropy and heat capacity contributions are shown in Table VIII-C. Origin of the unsaturation $(-2H)_c$ correction for the introduction of a π bond is shown (Table VIII-D).

The extra $S°$ and $C_p^°$ assigned to the out-of-plane bending motions in cycloheptane and larger rings and the tightness assigned to these motions under a variety of restrictive conditions (as in π bond formation and in polycyclic compounds) require clarification. First, there is no extra entropy in cyclohexane; thus the standard cyclic rings are, like cyclohexane, rather rigid structures. With the cyclohexane tightness as reference, a rough indication of the looseness and tightness can be made from Dreiding models of the compounds of interest. Although rather empirical, no other useful alternative for obtaining such estimates is available at this time. Our assignments, and the reasons for them, are therefore summarized below.

Ring Looseness. For rings from C_3 to C_6, the extra entropy and heat capacity have been calculated directly from their reported out-of-plane bending frequencies.

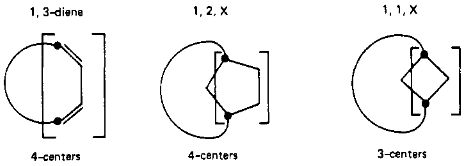
Cycloheptane and cyclooctane are very loose rings with torsional motions which strongly resemble internal rotations. We have, therefore, assumed an extra entropy of a C_7 ring equivalent to that of a $(CH_3 \circlearrowleft \infty)_{3.5}$ rotor. In cyclooctane, additional entropy, equivalent to that of two internal rotations (one methyl, one large group) has been assumed. We also suggest that the number of internal rotations, taken as measures of the extra entropy (and heat capacity), be given by the minimum number of double bonds which must be introduced into the ring in order to produce standard ring tightness: one in cycloheptane, two in cyclooctane, and three in cyclononane. The agreements between predicted and observed entropies in cycloheptane and cyclooctane using this procedure are good. Thus, such estimates of extra looseness do not seem to be much in error.

Ring Tightness Resulting from Double Bonds. A totally tight ring has been defined as one in which the out-of-plane vibrations have the same frequency as the standard in-plane ring vibrations—i.e., 550 cm^{-1}. The rationale for this assignment comes from a comparison of the intrinsic entropy of benzene ($S° = 69.3$) with the intrinsic entropy of cyclohexane less three unsaturation corrections ($S°$[⬡ − 3 $(-2H_c]$ = 73.6 cal/mole-°K). The magnitude of the difference between these quantities suggests an entropy loss of about 1.4 cal/mole-°K out-of-plane vibration. This is equal to the entropy (298°K) difference between the standard out-of-plane/in-plane ring vibrations.

Comparison of the entropies of cyclohexane and cyclohexene indicates only a minor change in entropy with the introduction of the first bond. The entropies of cyclopentene and of cyclobutene are both very close to those obtained from the standard C_5 and C_4 ring entropies (Table VI), less one saturation correction: $S°$ (⬠) = 70.6, $S°$ (⬠) $-(2H_c)$ = 70.3, $S°$ (□) = 64.4, $S°$(□ $-(2H_c)$) = 65.2, all in cal/mole-°K. It appears, therefore, that the first double bond removes the extra entropy (and heat capacity) residing in the lowest out-of-plane vibration of the cycloalkanes and reduces that motion to a frequency close to the standard value. With greater degrees of unsaturation, it is intuitive that ring tightness must increase with the addition of successive bonds, and that a minimum value close to that of the totally tight ring should probably be reached with complete unsaturation—e.g., benzene, 1,3,5,7-cyclooctatetraene. The cycloalkene tightness corrections of Table II have been made on this basis. The corrections suggested are mainly guesses based on Dreiding models. Errors will be greatest in the C_8 rings, since the difference between the totally unsaturated ring and cyclooctane is rather large—i.e., −13.4 cal/mole-°K.

Ring Tightness in Polycyclic Compounds. A. SHARED SIDE COMPOUNDS. It seems reasonable to assume that tightness in a reference ring, as a result of a second ring sharing a (C—C) bond, cannot exceed the tightness which would result by the simple introduction of a π bond between the same carbon centers. This follows from the fact that the torsional motions of neighboring carbon centers are undoubtedly most strongly coupled by a π bond. At the other extreme, when the second ring is very large, the primary or reference ring will not be strained and will be unable to distinguish that ring from two simple alkyl side chain substitutions. In this case the relative puckering and torsional motions of the shared carbons will be unrestricted and tightness corrections should be zero. Cyclooctene is the smallest floppy cycloolefin, so it seems reasonable to regard all secondary rings of $C_n \geqq C_8$ as large. The gradual gradation in tightness to the reference ring as the shared rings increase in size from C_3 to C_8 (Table II) therefore seems reasonable.

Tightness in Bridged Polycyclics. Models show that methylene bridges restrict the torsional motions of more than the two common carbon centers of the bridge with the reference ring. Considerable strain is also generally introduced. How much closer methylene bridging takes a reference ring toward its totally tight form than, for example, π bond formation, is a matter which cannot be resolved without data. However, it seems reasonable to assume that the methylene-bridged compounds are tighter than the corresponding cyclomonoolefins and that they have lower ring entropies and heat capacities. It also seems reasonable to assign the tightness in $[1,1,X]$ and $[1,2,X]$ bicyclics as 3/4 and 1 times the sum of the tightness produced by two neighboring double bonds in the reference ring, respectively. The fractions represent the number of carbon centers coupled in the reference ring. Thus,



In the last analysis, however, recourse to models is the most expedient method of estimating tightness, and probably the most reliable. The values of tightness corrections of Table II can then be used as reference points.

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