

AN ABSTRACT OF THE THESIS OF

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Title The Thermodynamics and Molecular Structure of Some  
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The details of construction of a type of cycling calorimeter, designed for the measurement of vapor heat capacities, are presented. A description of the procedure followed in operating the apparatus is included for the benefit of those who may later use the equipment.

Experimental values of the heats of vaporization and gaseous heat capacities of cis and trans 1,2-dimethylcyclohexane are discussed. Both types of data acquired are believed to be accurate to approximately  $\pm 0.3\%$ . Although there are no experimental data for the heat capacities of the compounds studied other than those presented in this paper, the heats of vaporization obtained compared favorably with values reported by other workers.

A review of the theoretical methods for calculating thermodynamic properties is given, emphasizing those of greatest applicability to hydrocarbons. It is demonstrated that the simple method for the calculation of the thermodynamic properties of alkylcyclohexanes proposed by Beckett, Pitzer and Spitzer produces results which deviate from experimental data by as much as 3%. A more detailed treatment of the problem using only those parameters discussed by the above authors is shown to result in even greater disparity between theoretically and experimentally determined heat capacities. While the agreement which is found by either treatment is sufficient for many practical purposes, means for improving the calculated results were sought.

Both the calculations mentioned in the last paragraph neglect the difference in entropy between polar and equatorial tautomers. This entropy change is calculated, assuming it to arise from an increased potential barrier for rotation of a polar methyl group. Upon repeating the more detailed calculation already developed in this paper, but using the newly determined entropy changes for the polar-equatorial contributions, the best correspondence to experimental values yet attained is found.

Finally, the entropy change is considered to be an adjustable parameter, the magnitude of which is taken to be that

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required to reproduce the experimental heat capacity for cis 1,2-dimethylcyclohexane at 400°K. When the figure evaluated in this manner is used to calculate the heat capacities of both cis and trans 1,2-dimethylcyclohexane at two temperatures, 400°K and 500°K, the computed values differ in no case by more than 0.6% from the experimental.

The results of this work are believed to provide important substantiation for some of the recently developed concepts of the molecular structure of hydrocarbons.



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THE THERMODYNAMICS AND MOLECULAR  
STRUCTURE OF SOME CYCLIC COMPOUNDS

by

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# THE THERMODYNAMICS AND MOLECULAR STRUCTURE OF SOME CYCLIC COMPOUNDS

## INTRODUCTION

### OBJECTS.

Adequate thermodynamic data are not available for any but the more common hydrocarbons. Because of this fact alone such data are desirable. The value of these data is greatly enhanced, however, in those cases where they also lead to a better understanding of the molecular structures of the compounds involved. Important generalizations may be drawn which permit the accurate calculation of the properties of a series of compounds based upon experimental data for a few of its members. The above statements explain the objects of the researches described in this paper, namely:

- i. to obtain thermodynamic data for a series of cyclic hydrocarbons,
- ii. to utilize such data in drawing a less ambiguous picture of the molecular structures of the compounds,
- iii. to demonstrate that the better structural knowledge thus arrived at permits a satisfactory calculation of thermodynamic data without recourse to experiment for



each compound.

The vapor heat capacity, together with other more readily obtainable data, provides sufficient information to accomplish the objects just outlined. Accurate values of the heat capacity of the ideal gas at one atmosphere pressure for hydrocarbon vapors may be obtained only by laborious experimental procedures. Nevertheless, in order to derive the various thermodynamic properties of a substance this quantity must be known. The heat capacities of the liquid and solid, the heats of phase changes, pressure-volume-temperature data, and the physical properties are, of course, equally important but may be more easily determined.

For the purpose of elucidating the molecular structure of a compound the heat capacity and entropy are the most valuable of the thermodynamic functions. As is well known, the usual sources of structural information, i.e., spectral data, electron diffraction measurements, dipole moments, etc., often fail to determine completely the structure of complex molecules. In cases where the latter types of data are adequate, the methods of statistical mechanics permit the derivation of thermodynamic properties

without the necessity for experimentation. It has been shown that the procedure may be, in a sense, reversed (2,10,11,12,20,22,23,41). Some of the ambiguities in the structures of hydrocarbons have been eliminated in varying degrees by utilizing thermodynamic data and statistical mechanical methods to augment other information.

It is apparent that a more thorough understanding of the structure of hydrocarbons in general and of the changes in structure from one member of a group of related substances to another should facilitate the estimation of the properties of those compounds for which no experimental data exist. For example, the similarity between members of an homologous series makes an approximation method based on fixed increments from member to member reliable (19). Further refinements to this and any other method may be made as a more complete picture of the molecular structure is obtained. A justification for one such method of estimation will be presented below.



# THE CALCULATION OF THERMODYNAMIC PROPERTIES BY STATISTICAL METHODS

## FUNDAMENTAL RELATIONSHIPS AND METHODS.

The use of statistical mechanics for the calculation of the thermodynamic properties of simple compounds from a knowledge of their molecular structures and vibration spectra has demonstrated its important practical value. It can be shown that the thermodynamic properties of a substance are related to its partition function,  $Q$ ,

$$\text{I. } Q = \sum_i g_i \exp \left( - \frac{\epsilon_i}{kT} \right),$$

where  $g_i$  is the degeneracy of the  $i$ -th energy level and  $\epsilon_i$  its energy,  $k$  is the Boltzman constant, and  $T$  the absolute temperature (6, page 355).

A fundamental postulate of statistical mechanics is that the entropy,  $S$ , is related to the statistical probability of a state. Since it has been found that the entropy of a system is represented by the sum of contributions from a number of sources, it is further postulated that this relation is of the form

$$\text{II. } S = k \ln W,$$

in which  $W$  is the probability as defined by statistical mechanics (6). If the expression for  $W$  from the classical distribution law,

$$\text{III. } \ln W = \sum_i (N_i \ln g_i - N_i \ln N_i + N_i),$$

is introduced, in which  $N_i$  represents the number of molecules in the  $i$ -th level, it is seen that the entropy thus defined has the additive properties required. Making use of the distribution law---

$$\text{IV. } N_i = g_i \exp(\alpha - \epsilon_i/kT) ,$$

where  $\alpha$  is an undetermined constant, the fact that the total energy of the system,

$$\text{V. } E = \sum_i N_i E_i ,$$

and the expression,

$$\text{VI. } \exp(\alpha) = Q/N ,$$

as obtained from equations I and IV, it is readily shown that

$$\text{VII. } S = E/T + R \ln Q/N + R.$$

Then from the definition of free energy,

$$\text{VIII. } F = E + RT - TS,$$

it is found that in terms of partition functions (6),

$$\text{IX. } F = -RT \ln Q/N.$$

All of the above equations and those to be derived later in this section are valid for the perfect gas only. Through use of equation IX other functions may be calculated by using customary thermodynamic relationships.

In general, the following equations may be obtained for the more important functions (41):

$$\text{X. } S = R \ln Q/N + RT \frac{\partial \ln Q}{\partial T}$$

$$\text{XI. } F/T = -R \ln Q/N$$

$$\text{XII. } H/T = RT \frac{\partial \ln Q}{\partial T}$$

$$\text{XIII. } C_v = RT^2 \frac{\partial^2 \ln Q}{\partial T^2} + 2 RT \frac{\partial \ln Q}{\partial T}$$

These expressions, together with the definition of the partition function, may be used to calculate the desired properties provided that each energy level of the substance involved is known. However, it is more convenient in practical work to use simplified formulas which may be developed. By separating the energy levels of a molecule into those which are



translational, rotational, electronic and vibrational in nature, the total energy being the sum of these, it may be seen that equation I becomes,

$$\text{XIV. } Q = Q_t Q_v Q_r Q_e,$$

in which the subscripts refer to the translational, rotational, electronic or vibrational energy levels which are included in the particular function.

Since equations X to XIII involve only the logarithm of the partition function, any of the thermodynamic functions may be regarded as the sum of contributions due to the various types of molecular energies.

Therefore, these contributions may be evaluated separately and their sum taken after a numerical value has been obtained for each.

#### Translational and Rotational Contributions:

The translational and rotational energy levels are spaced sufficiently close together that, except for hydrogen, their contributions are adequately represented by classical statistical methods at ordinary temperatures. For non-linear rigid molecules the translational and rotational parts of the thermodynamic functions are (41):

$$\text{XV. } S^{\circ} = 2.2875 \left[ 3 \log M - 8 \log T - 2 \log \sigma + \log(ABC) \right] - 7.659$$

$$\text{XVI. } (F^{\circ} - E_0^{\circ})/T = -S^{\circ} + 7.948$$

$$\text{XVII. } H^{\circ} - E_0^{\circ} = 7.948 T$$

$$\text{XVIII. } C_p^{\circ} = 7.948$$

In equations XV - XVIII,  $S^{\circ}$ ,  $F^{\circ}$ , and  $H^{\circ}$  refer to the standard entropy, free energy and heat content of one mol of the perfect gas at one atmosphere pressure. The terms A, B and C are the principal moments of inertia for the molecule, while M and  $\sigma$  are the molecular weight and symmetry number. The symbol,  $E_0^{\circ}$ , represents the energy of the perfect gas at absolute zero.

Electronic Contribution: The electronic contributions can be determined by equations X to XIII using the electronic energy levels for  $\epsilon_i$ . At ordinary temperatures, however, only the lowest energy level, for which  $g$  is normally unity, is important. Therefore, the electronic contributions become zero or negligible.

Vibrational Contributions: For vibrational

energy levels the partition function may be expanded to the form,

$$\text{XIX. } Q_v = \prod_i \left( 1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right)^{-1}$$

where  $\nu_i$  are the vibration frequencies in reciprocal centimeters and  $h$  is Plank's constant. Then the use of the general equations given above result in the following expression for each of the  $3N-6$  vibrational modes of a non-linear molecule:

$$\text{XX. } S = -R \ln (1 - \exp(-\mu)) + R\mu \frac{\exp(-\mu)}{1 - \exp(-\mu)}$$

$$\text{XXI. } F/T = R \ln (1 - \exp(-\mu))$$

$$\text{XXII. } H = RT \frac{\exp(-\mu)}{1 - \exp(-\mu)}$$

$$\text{XXIII. } C = \frac{\mu^2 R}{2 \cosh \mu - 1}$$

where:  $\mu = \frac{h\nu}{kT}$

The relationships whose development has been outlined above may be used to calculate the thermodynamic properties of simple molecules. In this treatment, however, the anharmonicity of vibrational modes has not been considered, and in general cannot be for lack of sufficient data. Mathematical treatments of



the anharmonicity of vibrations have been given (9,33) and it has been shown that the contribution of anharmonicity to the heat capacity of polyatomic molecules is given by,

$$\text{XXIV. } C \cong R \frac{\partial}{\partial T} \left[ T^2 \frac{\partial}{\partial T} \left( \sum_{i \leq j} f_{ij} \right) \right]$$

in which  $f_{ii} = g_i(g_i+1) X_{ii} (hc/kT) [\exp(\mu_i)-1]^2$

$$f_{ij} = g_i g_j X_{ij} (hc/kT) [\exp(\mu_i)-1][\exp(\mu_j)-1]$$

$$\mu_i = \frac{h\nu_i}{kT}$$

The anharmonicity constants,  $X$ , may be determined empirically from a knowledge of the overtones of the anharmonic fundamental in question. This procedure can seldom be carried out with certainty for complex molecules.

Nuclear Spin: The contribution of nuclear spin to the entropy,  $R \ln g_s$ , where  $g_s$  is the nuclear spin weight, is not usually included in the calculations where it occurs. As a result, the value calculated is the "virtual" entropy rather than the absolute entropy.

Data Required: For the numerical evaluation of the various contributions to the thermodynamic

functions, rather complete structural information must be available. Bond distances and angles, as determined from electron diffraction measurements, for example, are required to calculate the moment of inertia product appearing in equation XV. In addition, the complete vibration spectrum is necessary in order that the vibrational contributions may be obtained. The general structural configuration is also needed (and normally known where the above data are available) to determine the symmetry number,  $\sigma$ .

Method of Calculation: If all of these data may be obtained for a molecule, its thermodynamic properties are readily determined by use of the equations given above. The classical translational and rotational contributions are calculated by substitution of the appropriate values of the physical and molecular constants into equations XV to XVIII. In the case of polyatomic molecules, the direct evaluation of the vibrational contributions is more laborious. However, since these properties are functions of the variable  $h\nu/kT$  alone, tables are available in which the vibration contribution due a

single vibrational degree of freedom is given for particular values of  $\nu/T$  (36, page 654). Thus, it is necessary only to take the contributions of each vibrational frequency from the table, their sum representing the total value of the vibrational part of the particular thermodynamic function. Then the sum of the translational, rotational, vibrational and electronic contributions represents the value sought. Corrections to this value may be made for nuclear spin and anharmonicity affects where they occur and can be treated.

#### Theoretical Determination of Vibration

Spectrum: Unfortunately the method of calculation just described can be applied only to molecules for which sufficient spectral and structural data are available. The vibration spectra of complex molecules are never completely determined experimentally, and a knowledge of all fundamental frequencies is required for calculation of the thermodynamic functions. Not only is the analysis of complex spectra difficult to carry out, but, in general, certain frequencies are inactive both in the infra red and Raman spectra.



In such cases the calculation of the total vibrational contribution is impossible unless a theoretical treatment of the vibrational spectrum can be made. If a molecule is not so complex as to render the mathematical treatment unfeasible, normal coordinate or similar analyses may be made to complete the experimental spectrum (19,29,39,40). According to these methods a model is assumed for the molecule in question and force constants assigned to the various modes of vibration, usually by analogy to similar compounds. The mathematical treatment is then carried out in an attempt to duplicate the known vibrational frequencies. It is generally necessary to adjust the assumed force constants and recalculate until the desired agreement between experimental and calculated values is attained. The theoretical treatments then provide, in addition to those active frequencies, the frequencies of the vibrations which cannot be found experimentally. In this manner the complete spectrum may be estimated and the thermodynamic properties calculated exactly as before.

# RESTRICTED INTERNAL ROTATION IN HYDROCARBONS.

When attempts were made to use the above methods for the calculation of the entropy of ethane, it was found impossible to obtain adequate agreement with the experimental value derived from the Third Law. It was suggested by Kemp and Pitzer (10,11) that the discrepancy arose from considering the internal rotation about the carbon-carbon bond of this molecule to be completely unhindered. While this suggestion was contrary to the prior chemical evidence, such as the absence of cis- trans isomerism in 1,2 dichloroethane, it can be shown that the potential barrier to free rotation is too small to allow the molecule to be fixed in one or more positions (6, page 415).

Theoretical Formulation: The wave equation for the one dimensional restricted rotator has been transformed into an equation of the type of Mathieu by Nielson (14),

$$\text{XXV. } M'' + [a + 16 q \cos 2x] M = 0,$$

where,

$$q = \pi^2 I V / n^2 h^2,$$

$$a = \frac{32 \pi^2 I}{n^2 h^2} (E - \frac{1}{2} V_0).$$

Pitzer has provided a solution to this equation, using a potential function of the form,

$$V = \frac{1}{2} V_0 (1 - \cos 2x)$$

in which "n" is the number of potential maxima of height  $V_0$  through which the rotating group passes and  $x$  is the angle of rotation (17). Tables are now available (24,36 page 659) in which the difference between the various thermodynamic functions as calculated for free rotation and for restricted rotation are recorded. The value thus acquired, e.g.,  $S_{fr} - S_{rr}$ , is then used as a correction to the value calculated in the normal manner. In order to use the tables, it is necessary to know or assume the height of the potential barrier,  $V_0$ , and the moment of inertia of the rotating group about its axis of rotation. Conversely,  $S_{fr} - S_{rr}$  may be obtained from calculated values of  $S_{fr}$  and experimental values of the total entropy. With such information  $V_0$  may be determined by use of the tables (17,18,19).

Applicability of the Treatments for Restricted Rotation: Pitzer's treatment of restricted internal rotation is usually a good



approximation. However, the method gives the best results when  $V_0/RT$  is approximately 3 and the "n" maxima are nearly equal. If  $V_0/RT$  is less than about 1, the treatment for free rotation due to Edinoff and Aston (5) gives better results; while if  $V_0/RT$  is very large, as in a double bond, it is best to treat the problem as a vibration using the harmonic oscillator approximation (41). A more rigorous solution to the problem has been given by Crawford (3). In the event that the principal moments of inertia of the molecule are much larger than that for the rotating group, his treatment coincides with the solution of Pitzer. Such will be the case for the compounds to be considered here. Pitzer and Gwinn have treated restricted rotation in a more general fashion (24). They also provide, in addition to the equations required for calculation purposes, revised tables of easier applicability for obtaining the difference between functions with and without restricted rotation.

The validity of the restricted rotation concept has been adequately demonstrated for a number of hydrocarbons (18,20). Although the simple treatment applies strictly only to such compounds

as ethane, it has been shown to give good results for larger molecules. For many paraffins the value of  $V_0$  required to obtain agreement between calculated and experimental values ranges from 3000-4500 calories per mol.

#### STRUCTURAL USES OF THERMODYNAMIC DATA.

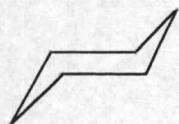
In the preceeding discussion it has been demonstrated that procedures are developed for the calculation of the thermodynamic properties of any compound provided sufficient spectral and structural information is available. However, for many of the hydrocarbons of practical importance such data are not easily obtained. Frequently information aside from thermodynamics does not determine the structure of a molecule unambiguously, for reasons which were presented above (page 11). In this event Pitzer and his co-workers, as well as others, have shown that thermodynamic data may be used to augment structural information from other sources (2,11,12,18). Essentially the method developed reverses the procedure for the theoretical calculation of thermodynamic properties. In those cases where spectral data are insufficient or assignments cannot be made with



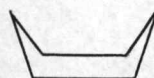
certainty, it is often possible to decide which is the proper assignment by this means. That is, those frequencies are chosen as correct which cause the calculated value to agree with the experimental (2). Missing vibrational frequencies may be estimated in the same way.

Another structural parameter which may be evaluated by the use of thermodynamic data is the potential barrier for restricted rotation in hydrocarbons. When all but this consideration can be accounted for in the customary manner, that value of  $V_0$  which is required to give agreement with experimental data is taken as correct.

In addition to the above information it is possible in some cases to obtain a more complete knowledge of the structural configuration of molecules. The cyclohexanes, for example, can exist in two ring formations, the so called chair and boat (trans and cis) forms.



CHAIR



BOAT



The tautomerism which occurs between the two forms affects such properties as the entropy and heat capacity, and its extent can be determined by methods which will be described in the next section (2). Furthermore, the non-planarity of cyclopentane has been clearly demonstrated on the basis of thermal data (12).

Other structural details of a more specific character will also be considered in the following section.

#### CALCULATIONS FOR THE CYCLOHEXANES.

An excellent illustration of the use of the general topics just described is provided by the analysis of the thermodynamics of cyclohexane and the alkylcyclohexanes. All of the above methods must be utilized in the theoretical calculations involved for these compounds.

Chair-Boat Tautomerism: From electron diffraction (7) and spectral (28) information, it has been determined that cyclohexane exists predominantly in the chair form. In the latter form of cyclohexane all the hydrogen atoms are in staggered

positions and for this reason each carbon-carbon bond is assumed to lie in the position of minimum energy for the restricted rotation barrier. Upon transforming to the boat configuration, two of the carbon-carbon linkages are twisted to the maximum position for the potential barrier. As a result, the boat form should be the tautomer of highest energy.

Fortunately, sufficient spectral data were available so that reasonable assignments were made, with the aid of a normal coordinate analysis, for all but one of the lower frequencies (2). The value of the latter mode was chosen to fit the experimental data for the entropy and heat capacity after other corrections described below had been made (2,4).

In order to calculate the entropy and heat capacity of cyclohexane the equations and methods already given were used to evaluate those contributions due to translation, rotation and vibration, with the exception of that of the undetermined frequency. Then the effect of the chair to boat tautomerism was calculated. This transformation involves the twisting of two carbon-carbon bonds from the minimum in the potential of rotation to the maximum. While it



was found that at low temperatures only a small amount of the compound exists in the boat form, the fraction increases with temperature, and the energy absorbed in the transition contributes appreciably to the heat capacity. In addition, the entropy is increased due both to the mixing of the tautomers and to the fact that the symmetry number of the chair variety is six and that of the boat two. These contributions are readily determined for the reaction involved:



For this transition the difference in the entropies of the two is only  $R \ln 3$ , since all other contributions are assumed to be the same for both. The equilibrium constant for the reaction becomes,

$$\text{XXVI. } K = \exp(-\Delta H/RT) = \exp(\Delta S/R) \exp(-\Delta H/RT) = \frac{N_2}{1-N_2}$$

where  $\Delta H$  is the energy required for the change and  $N_2$  is the mol fraction of boat form. Assuming that the potential barrier to internal rotation is 2.8 kilocalories per mol for each bond (estimated from determinations for other hydrocarbons (18)),  $\Delta H$  was taken as 5.6 kilocalories. Equation XXVI and



the values of  $\Delta S$  and  $\Delta H$  chosen thus permit evaluation of the concentration of each tautomer. Since

$$\text{XXVII} \quad \Delta S_{\text{mixing}} = \sum_i N_i \ln N_i$$

the entropy of mixing may be computed.

In calculating the heat capacity contribution due to chair-boat tautomerism, the rate of formation of the boat tautomer with change in temperature is found by solving XXVI for  $N_2$  and differentiating with respect to  $T$ .

XXVIII.

$$\frac{\partial N_2}{\partial T} = \frac{\frac{\Delta H}{RT^2} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)}{1 + \exp\left(-\frac{\Delta H}{RT}\right)} \left[ 1 - \frac{\exp\left(-\frac{\Delta H}{RT}\right)}{1 + \exp\left(-\frac{\Delta H}{RT}\right)} \right]$$

The last equation permits calculation of the amount of boat tautomer formed for a rise in temperature of one degree. Multiplying this figure by  $\Delta H$ , the energy per mol required for the reaction, gives the contribution to the heat capacity of the chair-boat tautomerism.

When these additions were made to the values of the thermodynamic functions derived in the usual way, the calculated values of the heat capacity and entropy agreed with the experimental values of Spitzer

and Pitzer (32) within experimental limits of error, (2).

Thermodynamic Calculations for Alkylcyclohexanes: Beckett, Pitzer and Spitzer also give theoretical calculations of the thermodynamic properties of some of the alkylcyclohexanes (2). Experimental data were available for the heat capacity and entropy of methylcyclohexane (4, 32), but spectral information was more limited than in the case of the unsubstituted compound. Nevertheless, the authors made an assignment, adjusted to fit the experimental heat capacity and entropy, which they considered to be reasonable. The method used for the calculation for methylcyclohexane was the same as that just described, except for the complications due to the substituted methyl group. These consist of an added tautomerism and the restricted rotation of the methyl group. The latter was calculated using the concepts discussed above (page 14).

Polar Equatorial Tautomerism: A study of models of the cyclohexane molecule reveals that the hydrogen atoms may be classified as either polar,



i.e., above or below the carbon ring, or equatorial, i.e., in a belt around the carbon ring(2) (see plate 3). Of the hydrogen atoms on one carbon, one is polar and the other equatorial. In the chair to boat tautomerism those six hydrogens which were polar become equatorial and vice versa. While this situation has no effect on the thermodynamic properties of cyclohexane, the same is not true when a methyl group replaces one of the hydrogens. Study of a model of methylcyclohexane indicates that when the methyl group is in the polar position there are considerably more steric interactions than occur in the equatorial position. It was suggested by Beckett, Pitzer and Spitzer that these interactions are similar to those arising in n-paraffins, for which the value of the strain energy, "a", had been given by Pitzer as about 0.8 kilocalories per mol in n-butane (19). Since there are two such interactions for methylcyclohexane, the value of the strain energy should be approximately 1.6 kilocalories. It was found that a value of 1.8 kilocalories gave the best agreement with the experimental data (2).

By using the last value for the difference in energy between the tautomers, the entropy and heat



capacity contributions can again be calculated by employing equations XXVII and XXVIII. Here the symmetry number of both tautomers is unity. For that reason  $\Delta S$  was assumed to be zero. It will be shown below that  $\Delta S$  is probably greater than zero, but the treatment of Beckett, Pitzer and Spitzer will be followed in the present discussion.

The theoretical calculation of the thermodynamic properties of methylcyclohexane also agreed with the experimental values (2,32).

The Dimethylcyclohexanes: When Beckett, Pitzer and Spitzer carried out their treatment for the two compounds just discussed, sufficient experimental thermal data did not exist for the application of a similar treatment to the seven dimethylcyclohexanes. A method was described, however, by which an estimation of the properties of these and other alkylcyclohexanes can be made (2).

With two methyl groups attached to the ring the possibility of tautomerism is further increased. In addition to cis and trans positions for the two groups, the variety of polar-equatorial tautomers is greater. For example, in cis 1,2-dimethylcyclohexane

one methyl is polar and the other equatorial, while in trans 1,2-dimethylcyclohexane there are two possibilities, either with both groups polar or both equatorial. In the former case there is no contribution to the thermodynamic functions as a result of polar-equatorial tautomerism, for the tautomers are of equal energy except for the strains accounted for in chair to boat tautomerism. The latter compound must be treated differently. With both methyl groups equatorial there is a strain similar to one n-butane-like interaction, and a strain energy of "a" was assigned to this form. There are four such interactions when both methyl groups are in polar positions, and a strain energy of 4 "a" was taken for the latter configuration (plate 3). The difference in energy of the two forms may then be used in equations XXVII and XXVIII to calculate the contribution to the entropy and heat capacity from this source. Again, the assumption was made that there is no change in entropy accompanying the polar-equatorial tautomerism.

In a similar manner the strain energies for the other dimethylcyclohexanes were estimated, and the contributions of polar-equatorial tautomerism to



the thermodynamic functions evaluated.

The validity of these assumptions as to strain energy was verified by Beckett, Pitzer and Spitzer by using the assigned values to calculate the heats of isomerization. Excellent agreement was obtained with the experimental values of Prosen, Johnson and Rossini (26).

In order to calculate the complete thermodynamic functions of the dimethylcyclohexanes, Beckett, Pitzer and Spitzer assumed that each methyl group contributes the same amount to the total function. The methyl increment was derived from the experimental values of Spitzer and Pitzer for cyclohexane and methylcyclohexane (32): the difference between the values for these two compounds without the contribution of polar-equatorial tautomerism was used. This methyl increment was then added to the value for methyl-cyclohexane and the corrections due to the tautomers of the particular isomer in question applied. In the cases of 1, 1-dimethylcyclohexane and cis 1,2-dimethylcyclohexane the potential barrier for internal rotation was increased to 6.6 and 4.3 kilocalories per mol, respectively, to account for



the interference of the two methyl groups with one another. It was also necessary to account for the fact that certain dimethylcyclohexanes exist as optical isomers. Since the energies of such isomers are identical, this double probability adds the term  $R \ln 2$  to the entropy.

When the value of 0.9 kilocalories per mol was used for "a", this method of increments gave excellent agreement with experimental values of the entropy of the perfect gas at 298.16°K (2,8). Since the last data were the only experimental values available, the accuracy of the method for calculating the vapor heat capacities could not be estimated. It was pointed out that a similar method had been fairly satisfactory for the methyl derivatives of benzene (25). It should be noted that the benzene compounds are not subject to the steric effects so pronounced in the alkylcyclohexanes.

Revision of the procedure outlined in this section became necessary in order to account for the experimental data obtained in the present work. A discussion of the changes made will be presented in a later section (DISCUSSION OF RESULTS).

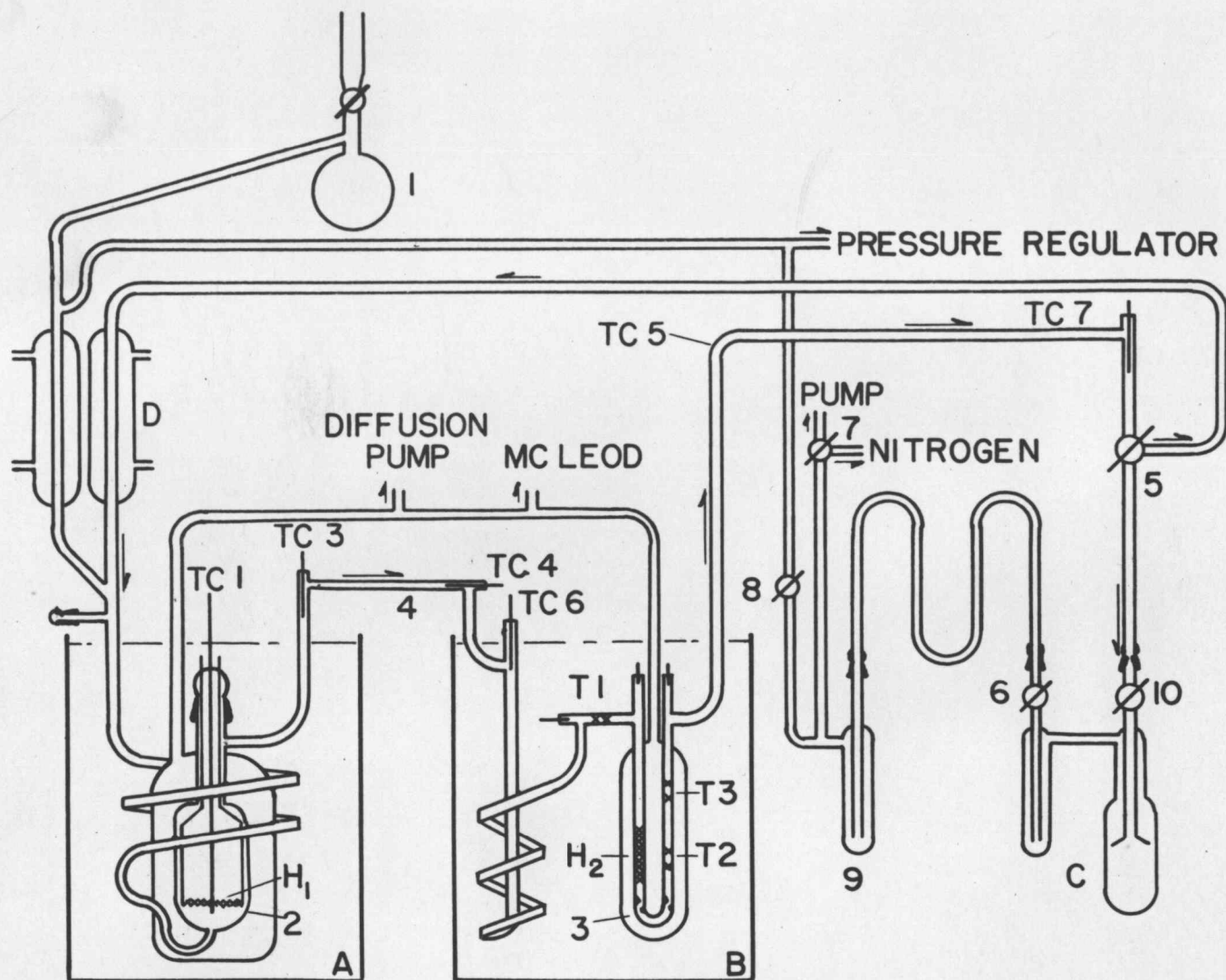
## EXPERIMENTAL

### Brief Description of Apparatus and Method:

The principle of the cycling calorimeter has been used in building several apparatus for the purpose of measuring the vapor heat capacity of liquid compounds (21,38). That of Waddington, Todd, and Huffman (38) represents an improved design which enables measurements to be made with a precision of approximately 0.1%. The main features of their machine were incorporated into that used in the present work.

Before describing the construction and operation of the calorimeter in detail, it will be well to outline briefly the technique used with reference to figure 1, page 30, and plates 1 and 2, pages 31 and 32. The compounds studied were distilled from vessel 1 into vaporizer 2 situated in thermostated bath A. Once a sample was in place, the liquid was boiled by heater  $H_1$  and the vapor passed to calorimeter 3, also in a thermostated bath E, through heated flow lines 4. In the calorimeter a measured quantity of energy was imparted to the vapor by heater  $H_2$ ; vapor stream temperatures before and after passing over the heater were measured by

FIGURE 1: FLOW DIAGRAM





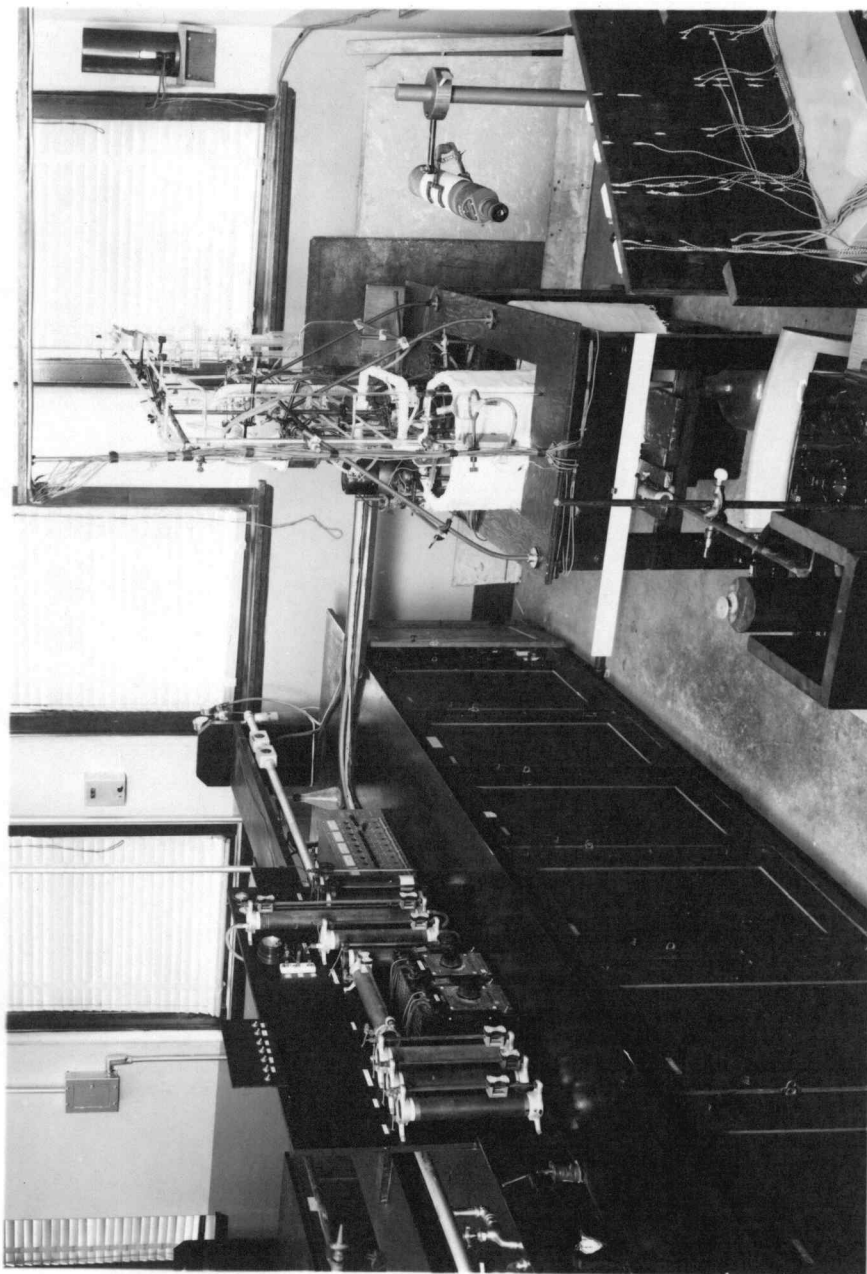


Plate 1: Experimental Apparatus



Plate 2: Experimental Apparatus

platinum resistance thermometers T1, T2 and T3. After leaving the calorimeter the substance was condensed, D, and returned to the vaporizer, thus completing the cycle.

In order to calculate the vapor heat capacity it was necessary to know the rate of flow of vapor through the calorimeter in addition to the energy required to produce a certain elevation in temperature. This information was obtained in separate experiments in which, after steady cycling had been secured, the vapor was diverted into double trap C by stopcock 5. The quantity collected over a period of time was determined. By measuring the power input to the vaporizer heater  $H_1$ , it was then possible to compute the heat of vaporization of the substance in question. The data obtained in this manner then permitted calculation of the rates of flow used in subsequent heat capacity measurements.

#### CONSTRUCTION DETAILS.

Vaporizer: The vaporizer, as depicted in figure 1, was surrounded by an outer jacket for thermal insulation. The inner walls of the jacket and outer walls of the vaporizer



were both silvered by Brashear's process (35, page 152) so that when a vacuum of  $10^{-5}$  millimeters of mercury or better was maintained within the separating space, heat leaks were found to be negligible (16). Removal and replacement of the heater was facilitated by suspending the vaporizer heater from 16-gage tungsten leads passed through a standard taper joint at the top of the vaporizer.

The vaporizer heater was constructed of 36-gage glass insulated advance resistance wire, braided and soldered in parallel so as to give a total resistance of approximately 21.5 ohms. The resulting element was wound into a flexible helix 1 centimeter in diameter, looped into a circle about 4 centimeters in diameter and soldered to the tungsten leads. This arrangement allowed the assembly to fold and bend enough to pass through the narrow neck at the top of the vaporizer. From observations made prior to installation it was found that the heater produced excellent ebullition with minute bubbles even at high rates of vaporization. Both potential and current leads were taken from the tungsten leads outside of the vessel.

Calorimeter: Another principal part of the

equipment was the calorimeter. Here, also, thermal insulation was provided by use of a vacuum jacket whose inner walls were silvered. The calorimeter itself consisted of a U-tube of 11 millimeter pyrex. In one leg was placed the heater and in the other the two resistance thermometers, T2 and T3. The calorimeter heater was comprised of two concentric helices of 28-gage chromel resistance wire; a jig of small glass rods supported and separated the two coils. The total heater resistance was 35 ohms. Both potential and current leads of 22-gage copper wire were taken from the heater and out of the vessel through tungsten seals. In order to insure adequate mixing of the heated vapors baffles were made into both legs of the U-tube. This arrangement also served to eliminate the effect upon T2 and T3 of radiant energy from the heater.

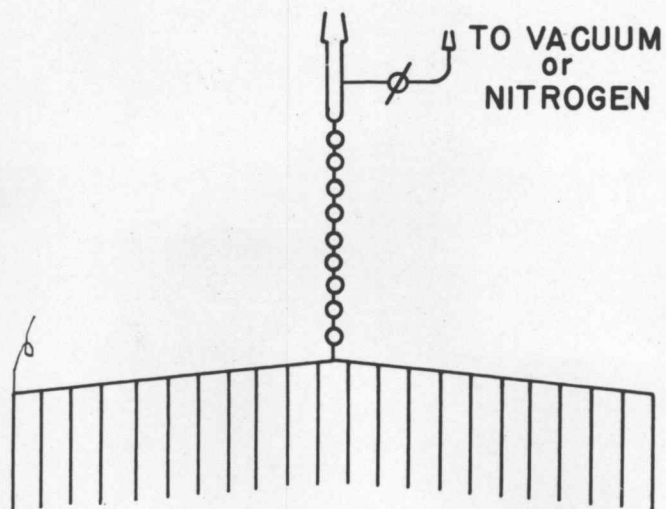
Since the apparatus was designed for use with materials whose boiling points are considerably above room temperature, it was necessary to provide means for maintaining the vapor above the condensation temperature in its course from the vaporizer to a point beyond stopcock 5. The flow lines between these points were of 11 millimeter pyrex tubing, as were all

other lines through which vapor passed. Around those tubes which had to be heated were wrapped first asbestos paper, then 28-gage chromel wire at one-half inch spacing and finally one-half inch asbestos rope.

Pressure Regulator: One of the most difficult problems encountered in precise thermochemistry is adequate control of conditions of temperature and pressure. The problem was accentuated in this case by the necessity for operating over a wide range of these variables.

Pressures in the system were to be varied from atmospheric to about 200 millimeters of mercury. Because the boiling temperature in the vaporizer, the heat of vaporization and the heat capacity all changed significantly with small pressure fluctuations, control to  $\pm 0.1$  millimeters of mercury was desirable. The pressure regulator designed for the apparatus being described resembled a mercury manometer with one short leg ending in capillary tubing and one long leg attached to the system (figure 2B). Mercury could be admitted or removed at the bottom of the regulator from a leveling bulb. Sufficient mercury was drawn into the manometer by evacuating the system

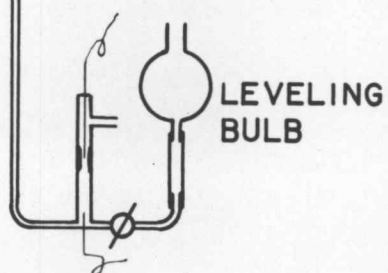




2A, THERMOREGULATOR

---

TO SYSTEM



2B, PRESSURE REGULATOR

FIGURE 2: SPECIAL APPARATUS

until the desired pressure was attained and the supply cut off by a stopcock. Then a small leak of nitrogen was introduced causing an increase of pressure and a rise of mercury in the capillary. When the mercury made contact with a fixed tungsten needle in the capillary, a relay circuit was closed which opened a solenoid valve in the vacuum line. Evacuation continued until the contact was broken and the valve closed. This process then repeated itself continuously. A surge tank and throttle on the vacuum line smoothed out the fluctuations so that none could be detected visually. From boiling fluctuations, however, it was estimated that the pressure could be controlled to  $\pm 0.3$  millimeters of mercury at best and at lower pressures only to  $\pm 0.5$  millimeters.

Temperature Regulators: Variations in temperature of  $\pm 0.01^{\circ}\text{C}$  could be tolerated in the vaporizer thermostat A, for the fluctuations in boiling temperature were of the same order of magnitude and did not cause significant errors. However, this thermostat could be controlled to  $\pm 0.005^{\circ}\text{C}$  by operating a control heater through a

sensitive mercury thermoregulator. The bath contained ten gallons of SAE 10 oil which was agitated by a stirrer placed in a column at the edge of the container. Both the control heater and main heater were within the stirring column. The control heater was a 125 watt knife heater which could be varied by a series resistor. The main heater was specially constructed of resistance wire and had a maximum output of 500 watts. It was operated through a variac. Auxiliary heaters were used in heating the bath to temperature more rapidly.

More precise temperature control was desirable in the calorimeter thermostat. This vessel contained nearly twenty-five gallons of SAE 60 oil which was agitated by a powerful stirrer in a column at one side. A 1400 watt finned heater comprised part of the wall of the stirring column, an arrangement which provided rapid circulation past the main source of heat. The 250 watt variable control heater was also inside the column, and auxiliary knife heaters were placed about the container to shorten the heating period.

The thermoregulator used in the calorimeter



bath was similar in appearance to large toluene regulators, but it contained approximately 11 pounds of mercury as the sensitive fluid (figure 2A). Since it was desired to operate this thermostat at temperatures up to  $300^{\circ}\text{C}$ , conventional means for removing excess mercury could not be utilized, and provisions for preventing oxidation and evaporation of mercury had to be made. For these reasons the usual capillary was replaced by a vertical column consisting of ten small bulbs separated by capillary tubing. Each bulb held a volume of mercury sufficient to take up the expansion due to a  $30^{\circ}\text{C}$  change in temperature. At the top of the column and above the oil level was a standard taper joint. The female part of the joint was detachable and ended in a water-jacketed capillary tube. Through a wax seal at the top of this piece a long tungsten rod could be inserted until the lower end was within the capillary separating any two of the expansion bulbs. By means of the movable contact, the temperature could be regulated at one of ten temperatures up to  $300^{\circ}\text{C}$ . The column head was also connected to vacuum and nitrogen lines so that an inert atmosphere could be maintained over the mercury. While the thermoregulator was

unwieldy, it was very sensitive, its principal disadvantage having been its higher time lag.

Upon first attempting to regulate the calorimeter bath, it was discovered that fluctuations in the line voltage caused sufficient variation in heat input to the bath to make temperature control impossible. Consequently, a type of current regulator was constructed. The line voltage was first rectified by a full wave, voltage doubling rectifier of 200 volt D.C. output. The rectified potential was applied to a 2000 ohm resistor in series with a 2 ohm potentiometer. In this manner was obtained a direct current potential of from 0 to 200 millivolts whose fluctuation was proportional to that of the line voltage. When the potential was applied to a Brown recording potentiometer, the mechanical motion of that instrument was also related to line voltage variations. A slight modification of the recording potentiometer enabled its mechanical motion to be transmitted proportionately to a variable inductance in series with the main calorimeter heater. By calculations and experiment the proper relationship between potential applied to the potentiometer, gear ratio in the mechanical

system and size of inductance was derived which would cause enough impedance to be added or removed from the heater circuit to maintain a constant current in the main heater. Small fluctuations of about  $\pm 0.05$  amperes occurred due to the time lag in the potentiometer, but larger variations (up to 10%) over the period of a run were adequately eliminated.

It was possible to regulate the temperature of the calorimeter bath to  $\pm 0.002-0.003^{\circ}\text{C}$  by the use of this equipment. Over a period of four to five hours the mean bath temperature ordinarily drifted about  $0.02^{\circ}\text{C}$ . Such a drift was easily corrected for by continual observations of T1. At the higher temperatures the regulation and drift increased to  $\pm 0.004-0.005^{\circ}\text{C}$  and  $0.04-0.05^{\circ}\text{C}$  respectively.

Auxiliary Equipment: In addition to the major elements of the cycling calorimeter just described, specific reference to some of the auxiliary pieces of equipment must be made at this time.

The vacuum pump used in maintaining thermal insulation for the vaporizer and calorimeter units



was an Eck and Krebs silicone oil diffusion pump. Since the Hyvac pump backing this diffusion pump was to be used in other operations, a large flask was connected to the low vacuum side in order to serve as a fore-pump when the occasion demanded it. A McLeod gage was constructed after the conventional design (35, page 138) and was used to measure the vacuum attained. Diffusion of mercury to the silvered surfaces was minimized by keeping the gage shut off from the system when not actually in use.

Temperature measuring devices used in this work were of two kinds: platinum resistance thermometers and copper-advance thermocouples. The former were constructed in so far as possible according to the procedure developed at the Bureau of Standards (13). Mica crosses were made on a specially designed jig to fit snugly in 11 millimeter pyrex tubing. The edges of the cross were notched on a different jig and 40-gage platinum wire wound in the notches of the assembled piece. Sufficient wire was used to result in a thermometer with a resistance of approximately 25 ohms at 0°C. Since T2 and T3 were to be in one leg of the calorimeter, they were wound on a single mica cross

and had two leads in common. All soldering was done with 30-gage gold wire, and the same material served as leads from the thermometer to the tungsten seals leading out of the system. Copper wire was used externally. Other details of construction were the same as used in the reference cited above, the principal modification having been in the use of a single rather than double helix of platinum wire.

All resistance thermometers were measured on a Mueller bridge calibrated to  $\pm 0.00003$  ohms. Thermometer calibrations were made by measuring the resistance of each at  $0^{\circ}\text{C}$  in a stirred bath of distilled water and ice. After the thermometers were installed in the apparatus, the calorimeter thermostat was used as a constant temperature bath and all thermometers compared with a Leeds and Northrup thermometer (number 546222) certified by the Bureau of Standards. A slow stream of air was passed through the equipment during the process. Comparative readings at two different temperatures and the zero resistance provided sufficient data to calculate the constants for the Callendar equation for each thermometer. A deviation from customary values in the constant  $\delta$ , which is characteristic

of the platinum wire used, indicated that the material used in these thermometers was not of the best grade.

While the absolute accuracy of the temperature calibrations was not great, i.e., temperatures as read from the three thermometers varied as much as  $0.01^{\circ}\text{C}$  at intermediate temperatures and  $0.05^{\circ}\text{C}$  at  $225^{\circ}\text{C}$ , at no time was it necessary to compare one thermometer to another. The calibration was sufficiently precise to obtain the desired temperature rise more accurately than the bath temperature could be controlled.

The copper-advance thermocouples used were calibrated by measuring their electromotive force at the temperature of boiling water and at the freezing points of tin and lead. A Leeds and Northrup type K-2 potentiometer was used both in measurement of the thermocouple potentials and in the power measurements described below. Thermocouples TC1 and TC2 (in the bath A, not shown in figure 1) could be connected as a difference thermocouple. Since the differences in temperature measured were less than  $0.3^{\circ}\text{C}$ , the temperature coefficient as determined from the above data was taken without further calibration.



Use was made of standard procedures in measuring the electrical energy input of the vaporizer and calorimeter heaters. A bank of sixteen Edison batteries provided power for these heaters under the conditions of operation the voltage of the batteries fell about 0.01-0.1% over a thirty minute period. The potential across each heater was reduced by a voltage divider to a magnitude which could be read with the potentiometer. In series with each heater was a standard resistance,  $0.2986_4$  ohms in the vaporizer circuit and  $0.9997_0$  ohms in that of the calorimeter. The first resistor was constructed of 14-gage manganin wire and the second was Leeds and Northrup resistor number 8080 certified by the Bureau of Standards. Both resistors were calibrated with the Mueller bridge and are accurate within the limits of calibration of that instrument ( $\pm 0.00003$  ohms). Measurement of the potential across each resistor allowed the current flowing in each circuit to be calculated. From these data it was possible to determine the energy input of both heaters.

In experiments to determine heats of vaporization, it was necessary to know precisely the

time during which a sample of the compound was collected in the double trap. A Meylan stopwatch was mounted on a panel so that it could be started and stopped by means of a solenoid operated lever arm. In order to eliminate the human element as much as possible, a tilting mercury switch was attached to the stem of stopcock 5. On turning the stopcock  $90^{\circ}$  to divert the vapor into the trap, the switch momentarily closed a relay circuit which energized the solenoid just long enough to start the watch. Since the contact was broken immediately, the lever arm was pulled back into position by a spring, ready to stop the watch in the same manner when the vapor was turned back into the system. As the same lags were incurred both in starting and stopping the watch, it is believed that the error in time measurement was less than  $\pm 0.05$  seconds.

Further description of auxiliary items of equipment may be best presented in the discussion of the operational procedure given below.

#### OPERATIONAL PROCEDURE.

A better understanding of the experimental procedure may be obtained if the overall objective is

known. It was the purpose of the experiments described here to obtain values of  $C_p^0$  at a number of temperatures, consequently, for each temperature the heat capacity was measured at two or more pressures and  $C_p^0$  obtained by extrapolation to zero pressure. The heats of vaporization for each pressure were the first data sought, for from this information the rate of flow of vapor was calculated in subsequent heat capacity measurements. As the apparent heat capacity at any particular pressure was shown to be a linear function of the rate of flow, determinations were made at four rates. By plotting the data against the reciprocal of the flow rate and extrapolating to infinite velocity, the effect of heat losses in the calorimeter was virtually eliminated (figure 3). To summarize, the following data were collected in order:

- i. heats of vaporization at two or more pressures;
- ii. at each pressure and temperature, heat capacities for four rates of flow, the extrapolated value at infinite flow rate being taken as correct for the conditions in question;
- iii. for every temperature, values of the heat



capacity at two or more pressures, regarding the extrapolated value at zero pressure as  $C_p^0$ .

Operation of the cycling calorimeter was an involved and tedious undertaking. Its complexity makes the unified description of procedural details to be presented here desirable in order that persons unfamiliar with the apparatus may be able to utilize it in the future.

Readying Procedure: The presence of either air or water within the flow system was undesirable for obvious reasons. After thoroughly drying the interior by evacuation with the Hyvac pump, nitrogen dried over magnesium perchlorate and phosphorus pentoxide was admitted to the system. During the period in which experimental data were collected, care was taken that the calorimeter was never opened to the air at any point. Similarly, a nitrogen atmosphere was maintained over the mercury in the calorimeter regulator at all times of operation.

Between the experiments on each compound the Edison batteries were completely discharged and then given a double charge to increase their stability.

A rectifier was used to charge the entire bank at one time. "Booster" charges were given to the batteries about once a week when in operation, or whenever their potential began to fall too rapidly.

With the apparatus properly cleaned and dried, all equipment tested, repaired and placed in working order, the compound whose heat capacity was to be determined was distilled into the system from vessel 1. The design of the flask permitted the operation to be accomplished without admitting air to the calorimeter. Once a sample was in the vaporizer, heating of both thermostats was begun with all available heaters at full capacity. The vaporizer bath could be heated from room temperature to  $100^{\circ}\text{C}$  in about one and one-half hours. Approximately an equal length of time was required for heating the calorimeter bath to the same temperature, but nearly five hours were needed to attain a temperature of  $200^{\circ}\text{C}$ .

After some practice it was not difficult to stop the heating of the baths at the proper temperature and to adjust the amount of energy supplied by both the main and control heaters so as to obtain the desired temperature regulation.



Adjustments were made to the heaters by series resistors or variacs. These devices, as well as controls for all other alternating current equipment, were installed on the panel shown in the left hand side of plate 1.

Shortly before the vaporizer bath reached operating temperature the four line heaters were turned on and adjusted so that the temperatures recorded by TC 3,4,5,6 and 7 were all well above the condensation point of the substance under study. With this accomplished, the vaporizer bath regulating properly, and the calorimeter bath either regulating or at a sufficiently elevated temperature so as to prevent condensation, the system was next evacuated to approximately the correct operating pressure (as determined from vapor pressure data). At this point the vaporizer heater was turned on with a current of about 1.0 amperes until boiling commenced. Because of the danger of "bumping", higher currents were not used until cycling actually began. The heater current then was adjusted to give the rate of flow desired. Since the pressure at the regulator differed from that in the vaporizer by the pressure drop through the system, it was necessary to adjust



the regulator for each rate of flow in order to obtain the proper boiling temperature. It has been found most efficient to maintain the boiling temperature about  $0.2^{\circ}\text{C}$  below that of the thermostat (16,38).

Once the compound was cycling smoothly, the line temperatures were readjusted. The vapor was kept at approximately the same temperature as the calorimeter when it entered that bath, for otherwise changes in rate of flow could upset the temperature regulation there. In addition, the vapor had to be maintained at a sufficiently high temperature to prevent condensation in stopcock 5.

All of the above operations were carried out regardless of whether heat capacity or heat of vaporization data were to be determined.

Heats of Vaporization: When the heat of vaporization was the object of a run, it was unnecessary to control the calorimeter bath temperature accurately. The main bath heater could be adjusted so that with the maximum amount of control heat adequate regulation was easily obtained.

At this stage preliminary readings were

made of the energy input to the vaporizer and of the several temperatures involved. After it had been ascertained that these variables were sufficiently constant, and thus, that the system was smoothly operating, a timed run was made. The double trap, C, was immersed in a suitable refrigerating agent, evacuated and filled with nitrogen by means of stopcocks 6 and 7. Then, with trap 9 also refrigerated in order to prevent the vapor from reaching trap C by diffusion, stopcock 8 was carefully turned to connect trap C to the pressure regulation system. Because of pressure differences between the collecting and the cycling systems, the last sequence of operations would upset conditions slightly if not executed cautiously. For this reason at least one more series of preliminary readings was observed. If all remained in order, the cycling vapor was diverted to trap C by stopcock 5, while at the same instant the timer was automatically actuated.

The following readings were then made as rapidly as possible consistent with the accuracy required for each:

- i. difference thermocouple (TC1 and TC2),  
measuring the difference between the



temperature of the thermostat and that  
at the heater level in the vaporizer;

- ii. potential across the vaporizer heater;
- iii. potential across the standard resistor in series with the vaporizer heater.

At least two series of observations were carried out and usually three or four were obtained. When sufficient vapor had been trapped, about 25 to 30 grams, stopcock 5 was turned to its original position, ending the timed run. A final observation of the difference thermocouple was then made and the barometric pressure, pressure regulator reading and other pertinent data as to the condition of the apparatus during the interval were recorded.

After making certain that the material collected in trap C had solidified, the nitrogen was pumped from the trap as before and stopcocks 6 and 10 closed. The trap then was removed and weighed, the quantity collected being determined by difference from the weight of the evacuated empty trap.

Data obtained in this manner were sufficient for the calculation of the heat of vaporization sought. It has been shown that the value obtained



for the heat of vaporization with this instrument was not a function of the rate of vaporization (16). Consequently, in this experimental work, three or more determinations were made at the same rate of vaporization. As a matter of convenience a slow rate was always chosen. At high rates of flow the increased pressure drop and danger of plugging in trap C made operation more difficult. If a plug developed in the trap, the pressure on the regulated side remained constant while the pressure in the vaporizer changed. It was impossible to make corrections for an appreciable variation of this sort.

The method of calculating the heat of vaporization from the data thus acquired and a discussion of the accuracy of the method are included in a later section.

Heat Capacity Experiments: As was stated above the procedure when operating for the purpose of obtaining heat capacity data differed very little from that just discussed until actual observations were to be made. In heat capacity runs the heat of vaporization was known and rates of vapor flow were

calculated from power measurements alone. It was necessary, of course, to adjust the calorimeter bath controls for accurate temperature regulation.

After it had been ascertained that the calorimeter bath temperature was constant to  $\pm 0.002-0.004^{\circ}\text{C}$  by observing T1, and that vapor was cycling smoothly, two or three preliminary readings of T1, T2 and T3 were made. The calorimeter heater was then energized and the temperature rise of the vapor adjusted to about  $8^{\circ}\text{C}$  by variable resistors in the heater circuit. Approximately twenty to thirty minutes were required before the temperature of the heated vapor became steady. As rapidly as possible readings were then made of the difference thermocouple, vaporizer and calorimeter heater potentials, standard resistor potentials and, finally, T1, T2 and T3. At least two such series of observations were made, more being required in case the fluctuations in T2 and T3 were large ( $\pm 0.005^{\circ}\text{C}$  or greater). A small variation in pressure was sufficient to cause large oscillations in T2 and T3. T2 was always somewhat erratic, for complete mixing of the heated vapors did not occur

immediately after passing over the heater.

In most of the runs temperature fluctuations were large enough so that averaged readings were necessary. At the 225°C temperature T2 fluctuated almost  $\pm 0.02^\circ\text{C}$ . The procedure adopted for taking such averages was to observe galvanometer oscillations for both the normal and reverse bridge positions of each thermometer for a period of five minutes each (twenty minutes in all were required to read both T2 and T3). From a knowledge of the galvanometer sensitivity the visually averaged readings were recorded. One or more rounds of rapid observations were made after the first round, and if these checked the averaged values (usually better than the maximum observed fluctuations), the latter were taken to be correct. The reproducibility of the averaged temperature was usually better than 0.1% of the temperature rise. At the highest temperature the reproduction was about 0.1%. Further evidence of the accuracy of this method may be seen in the precision of the calculated heat capacities (figure 3).

The procedure just outlined was carried out at four rates of flow--from about 0.07 to 0.2 mols



per minute. After the data had been obtained at one rate of flow, it was not necessary to cool the calorimeter before changing the velocity. Some time was saved by adjusting both the rate of flow and calorimeter heater input simultaneously. By the time smooth cycling had been attained once more, the temperature rise was usually at the proper value. It was necessary to so adjust the temperature rise as to insure that the average temperatures of the vapor at the various flow rates were within  $0.01-0.02^{\circ}\text{C}$  of each other. At the end of the day's run the calorimeter heater was cut off and several readings of T1, T2 and T3 were made after the calorimeter had returned to bath temperature. Over the period of operation (three to five hours), the calorimeter bath temperature was found to drop  $0.01-0.05^{\circ}\text{C}$ . This change was constantly observed by T1 in order to obtain the proper base temperatures for T2 and T3. The temperature rise at each of the last thermometers was then determined by the difference between the observed temperature and the adjusted base temperature. By this procedure the temperature rise was obtained without comparison of one thermometer against the other.

## MATERIALS.

The hydrocarbons used in this research were synthesized by the American Petroleum Institute Research Project 45 and purified by Project 6 (34). The purity of the cis 1,2-dimethylcyclohexane was  $99.95 \pm 0.02$  mol percent and that of trans 1,2-dimethylcyclohexane  $99.82 \pm 0.08$  mol percent, as determined by the supplier from freezing point measurements.

Proper selection of the stopcock lubricants to be used at each point in the equipment must be made for the particular compound being studied. For the work described in the present paper, the following greases were used:

- i. at points in contact with liquid only---tetraethyleneglycol citrate (30), or silicone;
- ii. at points in contact with vapor only---lithium stearate and oil (27), or silicone;
- iii. for high vacuum system---a special grease for mass spectrometers (rubber base) or Apiezon.
- iv. all other places---Lubraseal.



### CALCULATIONS.

More detailed consideration of the calculation of experimental values are given by Person (16).

Heats of Vaporization: The calculation of the heat of vaporization consists primarily of correcting the power measurements to obtain the actual amount of energy imparted to the substance collected during a timed run. It was necessary to make four corrections, the sum of which varied from zero to 0.3% of the molar heat of vaporization. As a result of pressure fluctuations the boiling temperature was observed to increase or decrease by as much as  $0.05^{\circ}\text{C}$  during a timed run. Hence, a correction was made for the corresponding changes in enthalpy of the liquid remaining in the vaporizer and of the glass vessel. A further correction was required by the temperature gradient between the heater level (TC1) and the boiling surface of the liquid. As an approximation of sufficient accuracy, the last correction can be made by considering the heat effect due to the transfer of  $m_1$  grams of liquid at the mean heater level temperature to  $m_1$  grams of vapor at the



surface temperature, where  $m_1$  is the mass of the sample collected. The boiling temperature can be calculated from the observed heater level temperature and the change in pressure due to the static head of liquid.

Although there will be an added change in the heat content of the glass vessel as a result of the changing liquid level, the effect was estimated to be negligible.

The first two corrections are thus given by the expression

$$m_1 C_{p1} \Delta T_1 + m_2 C_{p2} \Delta T_2 + m_t C_{p1} \Delta T_2 ,$$

where  $m_1$ ,  $m_2$  and  $m_t$  refer to the masses of vapor, glass and remaining liquid, respectively,  $C_{p1}$  and  $C_{p2}$  to the heat capacity of the liquid and the glass,  $\Delta T_1$  and  $\Delta T_2$  to the difference in temperatures at TC1 and the surface and to the change in boiling temperature during the timed run.

A small correction was necessary for the energy generated in those portions of the tungsten heater leads which were not immersed in liquid.

After these corrections had been applied to the energy input, the heat of vaporization was

calculated from the formula

$$\text{XXVIX} \quad H_v = Q (1 - v/V) \frac{m_1}{M}$$

where  $Q$  is the corrected energy and  $M$  the molecular weight, The term  $1 - v/V$  allows for the fact that the vapor occupying the space evacuated by the liquid could not be collected. The molar volume of the liquid,  $v$ , was estimated from density data and the molar volume of vapor,  $V$ , from the perfect gas equation (since equation of state data were not available for the compounds studied). The error introduced in this approximation is negligible.

Heat Capacities: Three corrections were applied in the calculation of the heat capacity. Two were used in determining the rate of flow of vapor. The energy input to the vaporizer was corrected for the leads loss as described above. Since the liquid returned to the vaporizer superheated  $0.1-0.2^{\circ}\text{C}$ , it was necessary to account for the corresponding unmeasured energy. These corrections seldom amounted to more than  $0.1-0.3\%$  of the measured power. From a knowledge of the length of copper leads in contact with vapor in the calorimeter and the current flowing in them, a correction was also made for the unmeasured energy generated in these leads. This correction



amounted to about 0.1% of the total heat input in the calorimeter.

It is possible that a Joule-Thompson effect could occur in the calorimeter due to the pressure drop across the heater. Since the drifts in T1, T2 and T3 over the period of a run (at varying flow rates) were the same within the limits of error of the temperature measurements, this effect was too small to be taken into consideration.

#### ACCURACY OF MEASUREMENTS.

The heat of vaporization and heat capacity of benzene were measured in order to estimate the accuracy which could be obtained with the present apparatus. A more detailed consideration of these calibration measurements is given by Person (16), but a summary of the pertinent conclusions to be drawn will be presented here. Heat of vaporization measurements were made at one temperature and at a variety of rates of flow. These data indicate that the precision attained was approximately  $\pm 0.3\%$  for properly executed runs. The average of nine determinations was  $7605 \pm 24$  calories per mol. Waddington and Douslin, using the apparatus to which reference was



made previously (37), obtained  $7606 \pm 2$  as the mean of four determinations at the same temperature. Their values are probably accurate to about  $\pm 0.1\%$ , and certainly as good as  $\pm 0.3\%$  (38).

As experience was gained in operating the apparatus and some modifications in design and procedure made, more precise values of the heats of vaporization of the compounds studied here were determined. Although the precision of the measurements recorded in table 1 is about  $\pm 0.1\%$ , systematic errors appear to have reduced the accuracy to about  $\pm 0.2-0.3\%$ . When the data were compared graphically with the accurate ( $0.1\%$ )  $25^{\circ}\text{C}$  value of Osborne and Ginnings (1,15), it was found that a straight line could be drawn through the latter point and those presented here with a maximum deviation of points of  $\pm 0.2\%$ . While the heat of vaporization does not vary linearly with temperature, the deviation from linearity is probably very slight over the range of temperatures used. In fact, the three values presented by Person (16) for trans 1,4-dimethylcyclohexane show only normal scattering and the two values for cis 1,2-dimethylcyclohexane given here lie within  $0.05\%$  of a straight line through the Osborne and Ginnings datum.

From these considerations the accuracy of the heat of vaporization data recorded here is estimated to be  $\pm 0.3\%$  or better.

In calculating the rates of flow of vapor used in heat capacity runs, smoothed values of the heats of vaporization were obtained from plotted data. This procedure was decided upon in order to reduce both systematic and cumulative errors. The latter errors arise from the fact that in plotting heat capacities at two or more pressures in order to obtain  $C_p^0$  by extrapolation, opposite errors in the points are considerably magnified (figure 4). Not only are the smoothed values of the heat of vaporization probably more accurate, but since their errors are in the same direction, a magnification does not occur in the extrapolation for  $C_p^0$ .

The excellent linearity of the plot of experimental heat capacities against reciprocal flow rates justifies this means of eliminating the effects of heat leaks. In all the measurements presented here the points deviated from a straight line by 0.05 to 0.1%, and the intersection of the lines at the ordinate was as good or better. It can be said that the precision of the heat capacity measurements



was about  $\pm 0.1\%$ .

As has been mentioned, cumulative errors in the extrapolation to zero pressure arising from errors in heats of vaporization are thought to be small. Systematic errors in the heat capacity measurements can not be reduced in a similar manner. Nevertheless, the linearity of the points of figure 4 is  $\pm 0.05\%$ . From this diagram it is estimated that those values of  $C_p^0$  obtained from measurements at only two pressures are precise to about  $0.2\%$ . At higher temperatures, for which  $C_p^1 - C_p^0$  is smaller, the accuracy of the extrapolation should be greater.

It is shown by Person (16) that the results for the heat capacity of benzene are about  $0.1-0.3\%$  lower than the values given by Scott, Waddington, Smith and Huffman (31). The data of the latter are accurate to about  $\pm 0.1\%$ . In view of these facts, it is estimated that the heat capacity data presented here are accurate to about  $\pm 0.3\%$ . It is possible that some of the data are more accurate, but on the other hand, a somewhat improbable accumulation of errors could lead to less accurate results.



### SUGGESTIONS FOR IMPROVING APPARATUS.

It is believed that the principal cause for the temperature fluctuations observed on T2 and T3 during heat capacity measurements was the fluctuation in the system pressure. Slight changes in pressure undoubtedly cause momentary fluctuations in the flow of vapor. A better means for pressure regulation, such as a sulfuric acid manostat, would serve to decrease the temperature oscillations. Since the variation in temperature cannot be eliminated entirely, more precise averages could be taken in less time if a White double potentiometer were substituted for the Mueller bridge.

The large size of the calorimeter thermostat makes its temperature control more difficult. A resistance thermometer type thermoregulator instead of the large mercury regulator would permit the bath size to be reduced. With this change better temperature regulation with less effort should be possible.

Perhaps the most serious problem to be solved is in improving the accuracy of heat of vaporization measurements. While a number of minor

effects---insufficiently accurate balance for weighing traps, pressure fluctuations--- enter here, it is thought that the strain thrown on the system by diverting the vapor into trap C is the most important. A number of alternative methods for collecting samples appears feasible but have not been investigated. For example, a device similar to that used to control reflux ratios in automatic distilling columns could be inserted just below the condenser D of figure 1. Such mechanisms consist of small pivoted glass funnels, with attached iron arm, by which the liquid could be returned to vaporizer or diverted to a suitable collecting system by means of an external solenoid magnet. It will require experimentation to decide whether errors due to possible losses of liquid exceed those caused by disturbing the system as in the present method.



## EXPERIMENTAL RESULTS

HEATS OF VAPORIZATION.

The experimentally determined heats of vaporization for cis 1,2-dimethylcyclohexane and trans 1,2-dimethylcyclohexane are presented in table 1. Included in the same table are the smoothed values which were used in calculating the vapor flow rate for heat capacity measurements. Each of the experimental values is the mean of the number of experiments given in parenthesis. The data of Osborne and Ginnings at 25°C are also recorded for comparison.

In determining the heat of vaporization of cis 1,2-dimethylcyclohexane at 113.7°C operational difficulties were encountered. The high temperature at which it was necessary to maintain stopcock 5 apparently affected the stopcock lubricant (lithium stearate-oil) so that the stopcock stuck after the first run had been completed. Since the quantity of this compound available was small (200 cc.), the added losses attending the process of removing the material from the apparatus in order to replace the stopcock were prohibitive. The stopcock plug



Table 1

HEATS OF VAPORIZATION

<sup>a</sup> Compound	Temperature °C	H <sub>v</sub> (cal/mol) (Experimental)	H <sub>v</sub> (cal/mol) (Smoothed)
Cis 1,2	25	-	9492 <sup>b</sup>
Cis 1,2	96.7	8484±3 (3 exp.)	8484
Cis 1,2	113.7	8251±11(2 exp.)	8250
Trans 1,2	25	-	9167 <sup>b</sup>
Trans 1,2	88.1	-	8355 <sup>c</sup>
Trans 1,2	100.1	8213±5 (3 exp.)	8198
Trans 1,2	114.1	8001±6 (3 exp.)	8016

(a) All compounds are dimethylcyclohexanes

(b) Data from table 7m of reference (1).

(c) Interpolated values

was freed in place and regreased. Then a second run was made, but after it had been completed, the stopcock "froze" once more and could not be loosened in place. Because of this it was impossible to proceed further with heat of vaporization measurements. Nevertheless, the values obtained for this compound agree more closely with that of Osborne and Ginnings than do those of trans 1,2-dimethylcyclohexane. In fact the "smoothed" values which were used for computations do not deviate significantly from the means of the observed data.

The experimental values for trans 1,2-dimethylcyclohexane at  $114.1^{\circ}\text{C}$  and  $100.1^{\circ}\text{C}$  were used together with the  $25^{\circ}\text{C}$  datum of Osborne and Ginnings for the graphical interpolation of the heat of vaporization at  $88.1^{\circ}\text{C}$ . It will be noted that although the precision of the experimental data is better than  $\pm 0.1\%$ , the smoothed values used agreed with the measured to about  $\pm 0.2\%$ .

Since the freezing point of trans 1,2-dimethylcyclohexane is  $-88.2^{\circ}\text{C}$  (1, table 7a), it was thought advisable to use liquid air as a refrigerating agent for the double trap C. The rapid condensation and freezing of the sample collected

during a run appeared to cause the equipment to function more smoothly than when a dry ice-acetone bath was utilized for refrigeration. It might have been worthwhile to have used liquid air for all compounds regardless of freezing point and vapor pressure.

For both compounds the heat of vaporization at the boiling point is presented in table 7m of "Selected Values of Properties of Hydrocarbons", Volume II (1). The source of the latter values is not known, but presumable they were estimated from vapor pressure data by use of the Clapeyron equation. These data are about 1-2% higher than the values obtained by extrapolating the experimental data of table 1. As there are no adequate equation of state data for use in calculating the estimated heats of vaporization referred to, and since the stated limits of accuracy for these data are  $\pm 2.0\%$  such disagreement is not surprising. The linearity when compared to the accurate  $25^{\circ}\text{C}$  value is a more important criterion of accuracy.

#### HEAT CAPACITIES.

The observed heat capacities of cis 1,2-dimethylcyclohexane and trans 1,2-dimethylcyclohexane



Table 2

EXPERIMENTAL HEAT CAPACITIES AT VARIOUS  
PRESSURES AND TEMPERATURES

Compound <sup>a</sup>	Temperature °C	Pressure (mm of Hg)	Observed Heat Capacity (cal/degree-mol)
Cis 1,2	133.8	485	50.99
Cis 1,2	133.8	285	50.80
Cis 1,2	163.8	485	54.89
Cis 1,2	163.8	285	54.84
Cis 1,2	226.4	285	62.55
Trans 1,2	134.0	585	52.76
Trans 1,2	134.0	390	52.50
Trans 1,2	134.0	260	52.20
Trans 1,2	164.1	585	56.50
Trans 1,2	164.1	390	56.40
Trans 1,2	228.7	390	64.30

(a) All compounds are dimethylcyclohexanes

Table 3

HEAT CAPACITIES FOR THE PERFECT GASES

Compound <sup>a</sup>	Temperature °C	(C <sub>p</sub> <sup>o</sup> ) <sub>obs</sub> (cal/degree-mol)	C <sub>p</sub> <sup>1</sup> -C <sub>p</sub> <sup>o</sup> (cal/degree-mol)	(C <sub>p</sub> <sup>o</sup> ) <sub>calc</sub> <sup>b</sup> (cal/degree-mol)	Deviation <sup>c</sup> (%)
Cis 1,2	133.8	50.55±0.15	0.68	53.0	2.8
Cis 1,2	163.8	54.76±0.15	0.21	55.9	2.0
Cis 1,2	226.4	62.54±0.2	(0.03) <sup>d</sup>	63.5	1.6
Trans 1,2	134.0	51.82±0.15	1.24	52.8	1.8
Trans 1,2	164.1	56.20±0.15	0.44	56.8	1.1
Trans 1,2	228.7	64.26±0.2	(0.08) <sup>d</sup>	64.5	0.4
Trans 1,4 <sup>e</sup>	133.4	51.52±0.15	0.98	52.4	1.8
Trans 1,4 <sup>e</sup>	194.7	59.16±0.2	0.54	59.9	1.4

(a) All compounds are dimethylcyclohexanes.

(b) Interpolated from table X, reference (2).

(c) Deviation of calculated and observed heat capacities

(d) Estimated

(e) Taken from data presented by Person (16).

are recorded in table 2 for a number of temperatures and pressures. Each value of  $(C_p)_{obs}$  was obtained from a plot of data at four vapor flow rates as shown in figure 3 for trans 1,2-dimethylcyclohexane. On all graphs, the size of the circle for experimental points represents 0.1% of the ordinate value. Both sets of plotted data were measured at 134.0°C, but the pressures used were 260 and 390 millimeters of mercury. It is evident that the variation of heat capacity with the reciprocal of flow rate is essentially linear over the range covered. The extrapolation to infinite flow rate seems justified as a procedure for reducing the effects of heat losses as the vapor passes through the calorimeter. The heat capacities calculated from observations on T3 were always larger than those obtained from T2, for the vapor cooled slightly in its passage from T2 to T3. The excellent coincidence at the ordinate axis of the curves for T2 and T3 provides further evidence of the accuracy of the extrapolation made.

In table 3 are presented observed values of  $C_p^0$ , and  $C_p^1 - C_p^0$  as well as those values calculated by Beckett, Pitzer and Spitzer (2). The latter were obtained for the exact temperatures needed



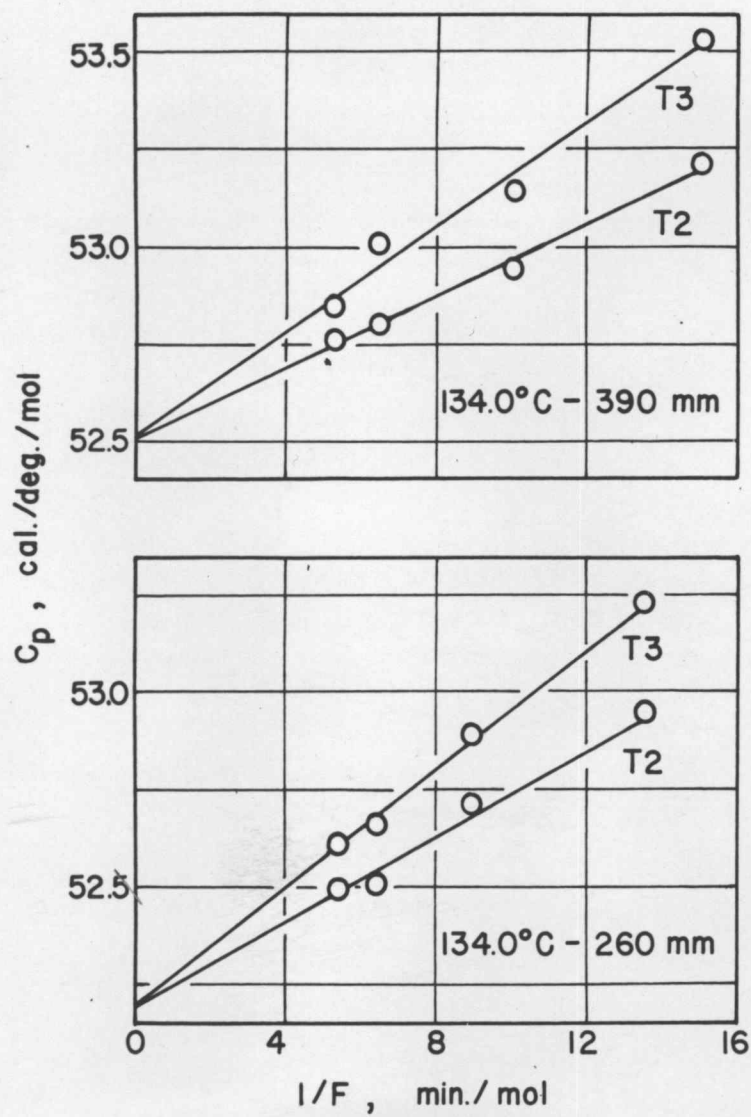


FIGURE 3: APPARENT HEAT CAPACITY OF TRANS 1,2-DIMETHYLCYCLOHEXANE AS A FUNCTION OF FLOW RATE

by graphical interpolation from the data tabulated in the reference cited. For completeness, the data observed with the present apparatus for trans 1,4-dimethylcyclohexane are also included (16).

The values for  $C_p^0$  and  $C_p^1 - C_p^0$  were derived from the data of table 2 by plotting the latter against pressure and extrapolating to zero pressure (figure 4). Since gases at zero pressure are assumed to be perfect, the value thus determined was taken to be  $C_p^0$  for the temperature in question. By extrapolation to 760 millimeters of mercury pressure,  $C_p^1 - C_p^0$ , a measure of the gas imperfection, may be evaluated. It is probable that the error of extrapolation is nearly doubled for this quantity. The deviations from linearity of the experimental points in figure 4 are about  $\pm 0.05\%$ .

At the higher temperatures  $C_p^1 - C_p^0$  is very small and can be estimated. For this reason measurements at only one pressure were made for the runs at 225°C. In the absence of equation of state data the following procedure was used in this estimation. Using the virial equation,  $PV = RT + BP$ , it can be shown that,

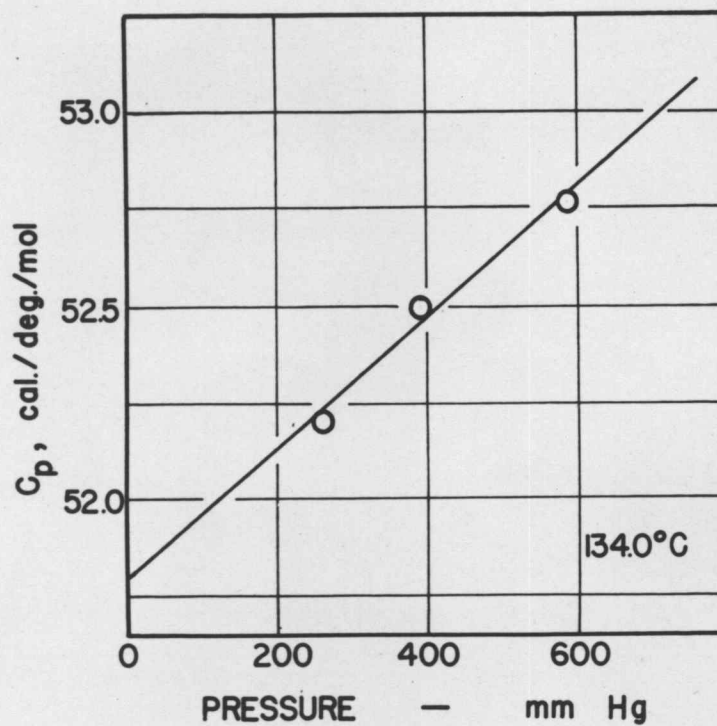


FIGURE 4: HEAT CAPACITY OF TRANS 1,2-DIMETHYLCYCLOHEXANE AS A FUNCTION OF PRESSURE



$$\text{XXX} \quad \left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 B}{\partial T^2} \right)_P.$$

The following empirical equation has been found to serve for the second virial coefficient for a number of hydrocarbons (31):

$$\text{XXXI} \quad B = b - c \exp (a/T).$$

From these two expressions, it is easily shown that

$$\text{XXXII} \quad \left( \frac{\partial C_p}{\partial P} \right)_T = C_p^1 - C_p^0 = c \left( \frac{a^2}{T^3} + \frac{2a}{T^2} \right) \exp (a/T).$$

The constants  $a$  and  $c$  were determined from the experimental values of  $C_p^1 - C_p^0$ . Since this correction for gas imperfection is quite small at 225°C (table 3), the error in such an estimation is not great.

Effect of Water in Compounds: A very sensitive test for water in those hydrocarbons which freeze much below 0°C may be readily carried out by freezing them. Upon first melting, small "floaters" of ice may be seen if water is present. Although the compounds used in this work were dried over magnesium perchlorate until this test was negative, and precautions were taken to prevent water from entering the system when in operation, a small amount did get into both compounds. A few "floaters"

were observed upon melting the solid collected in double trap C during heat of vaporization runs. The error in the measured heats of vaporization due to such small quantities of water is practically insignificant. Even if saturated (about 0.1 mol% water) the differences in the heats of vaporization of the hydrocarbons and water are small enough so that the errors in experimental values would be about 0.01%. A similar amount of water would cause about 0.1% error in measured heat capacities. However, since the amount of water observed was so small, the error from this source in the heat capacity data of table 3 is not appreciable.

## DISCUSSION OF RESULTS

AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL VALUES.

A comparison of the experimental heat capacities presented here with the calculated values of Beckett, Pitzer and Spitzer shows the latter to be appreciably high (table 3). Before considering possible causes for such discrepancies, the method by which the calculated data were obtained must be examined further.

The procedure used to calculate the heat capacities of the dimethylcyclohexanes has been described above (page 23). It was pointed out in Part B that a number of generalizations regarding the structure of hydrocarbons have been developed in recent years and that these concepts have been fruitful in providing explanations of the properties of such compounds.

To summarize what has been said above:

(i) rotation about the carbon-carbon bond is assumed to be restricted by a symmetrical, three maxima potential barrier such as in ethane; (ii) the same potential barrier is assumed to stabilize certain of the possible structural configurations of a



molecule with respect to more strained tautomers; (iii) steric interactions among the component parts of a molecule are accounted for by empirically determined strain energies, e.g., polar-equatorial tautomerism; (iv) the concepts developed in simple molecules, together with the parameters determined from such molecules, are applied with full use of analogies and with suitable adjustments to more complex cases; (v) substituted groups are assumed to contribute additively to the total thermodynamic function without affecting the contribution of the nucleus molecule if allowance is made for the possible occurrence of tautomerism.

All of these ideas were employed by Beckett, Pitzer and Spitzer in their calculation of the thermodynamic properties of the alkylcyclohexanes. In an attempt to reproduce their calculated values, it was discovered that the method outlined in their paper (2) omitted some important factors. The appropriate value of the methyl increment for these calculations must include that contribution which is due to the vibration and rotation of the methyl group alone. It will be shown that the method used in the article cited does not produce

the "true" value of the methyl increment.

#### REVISED CALCULATION PROCEDURE.

The effects of chair to boat tautomerism are computed by assuming the boat form to be strained by 5.6 kilocalories per mol as compared to the chair (page 19). Then, the difference in entropy of the two forms is ascribed to change in symmetry number, if any. From these two quantities the fraction of each tautomer at any temperature and the amount of conversion for 1°C rise in temperature may be determined as described above (page 22). The heats (relative strain energies) and entropies of the reaction, chair → boat, for the compounds of interest here are presented in table 4.

As a result of the fact that chair and boat forms of cyclohexane have different symmetry numbers while those of methylcyclohexane are equal, from equation XXVIII (page 22) it may be seen that the ratio of symmetry numbers ( $\exp(\Delta S/R) = \frac{\sigma_2}{\sigma_1}$ ) enters the expression for heat capacity as a multiplier. Hence, the contribution of chair to boat tautomerism for cyclohexane is just three times that for methylcyclohexane. For the same reason the chair-boat

Table 4

ESTIMATED PARAMETERS FOR CHAIR TO BOAT TAUTOMERISM

<u>Compound</u>	<u>Symmetry</u> <u>Chair</u>	<u>numbers</u> <u>Boat</u>	<u>Heat of</u> <u>Transformation</u> <u>(kcal/mol)</u>	<u>Entropy of</u> <u>Transformation</u> <u>(entropy units)</u>
Cyclohexane	6	2	5.6	R Ln 3
Methyl- cyclohexane	1	1	5.6	0
Cis 1,2 <sup>a</sup>	1	1	5.6 -	0
Trans 1,2 <sup>a</sup>	2	1	5.6 +	R Ln 2
Trans 1,4 <sup>a</sup>	2	1	6.6	R Ln 2

(a) Dimethylcyclohexanes



contribution for the dimethylcyclohexanes is not the same as that for cyclohexane when allowance is made for the actual change in symmetry number for each compound.

A further consideration has been made by the author for the sake of improving the consistency of the treatment. Upon studying Fischer-Hirschfelder models of the several molecules, it was observed that there was a type of steric interaction which apparently had not been considered--or which at least was thought to be unimportant--in the calculations of Beckett, Pitzer and Spitzer. When trans 1,4-dimethylcyclohexane is in the chair form, either both methyl groups will be equatorial or both will be polar. The difference in energy between the two tautomers is so large that the effect of the polar form on the chair-boat tautomerism is entirely negligible. For this tautomerism only the lowest energy polar-equatorial tautomer need be considered. In the best form of trans 1,4-dimethylcyclohexane both methyl groups cannot be entirely equatorial. Even in the best possible configuration one of the methyl groups interferes with the ring atoms at two points. These interactions are not of the type

occurring in n-butane (page 24) but are similar to those in a propane molecule twisted  $180^\circ$  from the most stable position about one of the carbon-carbon bonds.

An evaluation of the magnitude of this effect has not been made for propane. It is undoubtedly less than the more severe butane-like interaction. Since there are two points at which this interference occurs, it is believed to be important enough to warrant allowance for its effect on the heat capacity. A value of 1.0 kilocalories per mol was assigned arbitrarily as the magnitude of those interactions involved in trans 1,4-dimethylcyclohexane in the boat form. The total difference in energy of the chair and boat forms of this compound was increased to 6.6 kilocalories per mol.

Effects similar to that mentioned in the preceeding paragraph are encountered in the other dimethylcyclohexanes. For example, the chair form of cis 1,2-dimethylcyclohexane exists with one methyl group always equatorial while the other is polar. Three n-butane-like steric interactions are thus present. In the boat tautomer, on the other hand, one of those interactions between the methyl



group and the ring appears to be slightly relieved. The interaction which is involved for this tautomer is similar to the smaller propane effect just discussed. Such a possibility would be expected to stabilize the boat form by the difference between the two types of strain. However, since this difference has not been evaluated and is probably small, no allowance was made for the effect.

The situation encountered for trans 1,2-dimethylcyclohexane is analogous to that for trans 1,4-dimethylcyclohexane except that in this case only one added propane-like interaction occurs in the boat configuration. The energy difference between chair and boat tautomers should be increased slightly, but, again, the effect was neglected in calculation. As will be brought out below, these last considerations do not seem important in view of the disparity between experimental and recalculated values of the heat capacity.

From such observations as these it is apparent that the method of Beckett, Pitzer and Spitzer did not consistently account for all the possible tautomeric effects upon the vapor heat capacity. According to their procedure (as outlined



on page 25 of this thesis) the methyl increment to a thermodynamic property is found by "subtracting values for cyclohexane from those for methylcyclohexane without the polar-equatorial tautomerism" (2). In table 5, however, the contributions of chair-boat tautomerism to the heat capacities of these two compounds are seen to differ significantly. The contributions of chair-boat and polar-equatorial tautomerism tabulated in table 5 were calculated as described on page 22 of this paper, using the magnitudes of the heats and entropies of transformation assigned in table 4.

It is apparent that the methyl increment obtained in the manner of Beckett, Pitzer and Spitzer neglects the unequal tautomeric contributions involved. While the presence of one methyl group on the cyclohexane ring does reduce the effect of the chair-boat tautomerism on the heat capacity, the actual methyl increment should be larger than that found by the above authors by  $(0.257 - 0.086)$  calories per degree-mol. This error will then appear in the calculated values for the dimethylcyclohexanes, lowering their theoretically determined heat capacities by varying amounts. The magnitude of the error depends upon the

size of the chair-boat tautomeric effect for the individual compounds. These last contributions, in turn, are different as a result of the heat and entropy assignments given in table 4.

The following procedure was decided upon by the present author in order to eliminate the inconsistencies discussed in the foregoing paragraphs. The methyl increment was obtained by first subtracting the contributions of both the chair-boat and polar-equatorial tautomerism from the values for cyclohexane and methylcyclohexane. Then the difference between the two figures derived in this fashion was considered to be the increment due to the motions of the methyl group alone. A "base" value for the heat capacities of the dimethylcyclohexanes was found by adding twice the new methyl increment to the value for cyclohexane without chair-boat tautomerism. After this figure had been evaluated, the calculated heat capacity for each of the dimethylcyclohexanes was determined by adding the two tautomeric contributions for the particular compound to the "base" value.

Table 5 summarizes the results of the last calculation. The contributions due to polar-equatorial tautomerism were calculated in the manner described on

Table 5

REVISED CALCULATIONS WITHOUT ENTROPY PARAMETER FOR  
POLAR-EQUATORIAL TAUTOMERISM

Compound	Temper- ature (°K)	Tautomeric Heat Capacity Contributions (Cal/degree-mol)		Heat Capacity, C <sub>p</sub> <sup>o</sup> (Cal/degree-mol)			Deviation <sup>d</sup> (%)
		Chair-Boat	Polar- Equatorial	Calculated		Experimental <sup>c</sup>	
				BPS <sup>a</sup>	Revised <sup>b</sup>		
Cyclo- hexane	400	0.257	0	35.82	--	--	--
Methyl- cyclo- hexane	400	0.086	0.864	44.35	--	--	--
Cis 1,2 <sup>e</sup>	400	0.086	0	51.1	51.31	49.6	3.4
Trans 1,2 <sup>e</sup>	400	0.171	0.663	51.9	52.05	50.9	2.2
Trans 1,4 <sup>e</sup>	400	0.069	0.353	51.6	51.65	50.4	2.4
Cyclo- hexane	500	0.688	0	45.47	--	--	--
Methyl- cyclohexane	500	0.229	0.828	55.21	--	--	--



Table 5 (Continued)

REVISED CALCULATIONS WITHOUT ENTROPY PARAMETER FOR  
POLAR-EQUATORIAL TAUTOMERISM

Compound	Temper- ature (°K)	Tautomeric Heat Capacity Contributions (Cal/degree-mol)		Heat Capacity, $C_p^0$ (Cal/degree-mol) <sup>p</sup>			Deviation <sup>d</sup> (%)
		Chair-Boat	Polar- Equatorial	BPS <sup>a</sup>	Revised <sup>b</sup>	Experimental <sup>c</sup>	
Cis 1,2 <sup>e</sup>	500	0.229	0	63.5	63.8	62.5	2.1
Trans 1,2 <sup>e</sup>	500	0.461	0.823	64.2	64.8	64.0	1.2
Trans 1,4 <sup>e</sup>	467.9	0.173	0.515	59.9	60.2	59.2	1.7

(a) Calculations of Beckett, Pitzer and Spitzer (2)

(b) Calculations with zero entropy change for polar-equatorial tautomerism

(c) Interpolated

(d) Deviation between revised calculated values and experimental data

(e) Dimethylcyclohexanes

page 24, using for the differences in strain energies 2 "a", 3 "a" and 4 "a" for methylcyclohexane, trans 1,2-dimethylcyclohexane and trans 1,4-dimethylcyclohexane, respectively. There is no contribution from this source for cis 1,2-dimethylcyclohexane. The value for "a", the n-butane-like interaction, of 0.97 kilocalories per mol was used in the new calculations as recommended by Beckett, Pitzer and Spitzer.

Unfortunately, the revised calculated heat capacities compare less favorably with experimental values than do the original figures.

In order to demonstrate more clearly the manner in which the difference between the two treatments arises, the latter are expressed below in terms of observed and calculated quantities:

- i. according to Beckett, Pitzer and Spitzer (2),

$$\text{Methyl increment} = \Delta M = (C_7)_{\text{obs}} - (C_6)_{\text{obs}} - (PE)_7.$$

- ii. By the present method,

$$\begin{aligned} \text{Methyl increment} = \Delta M' = (C_7)_{\text{obs}} - (PE)_7 \\ - (CB)_7 - (C_6)_{\text{obs}} + (CB)_6. \end{aligned}$$

Here, and subsequently,  $(C_6)$ ,  $(C_7)$  and  $(C_8)$  refer to the heat capacities of cyclohexane, methylcyclohexane and a dimethylcyclohexane, respectively, while (PE) and (CB) are the polar-equatorial and chair-boat

contributions for the particular compound denoted by the subscript.

The methyl increments thus obtained are applied in calculating the heat capacity of a dimethylcyclohexane as follows:

iii. Beckett, Pitzer and Spitzer

$$(C_8)_{\text{calc}}^{\text{BPS}} = (C_7)_{\text{obs}} + \Delta M + (PE)_8 - (PE)_7.$$

iv. Present method

$$(C_8)_{\text{calc}} = (C_6)_{\text{obs}} + 2\Delta M' + (PE)_8 + (CB)_8 - (CB)_6.$$

Upon inserting the expressions i and ii for the methyl increments into equations iii and iv and subtracting iii from iv, it may be seen that

$$v. (C_8)_{\text{calc}} = (C_8)_{\text{calc}}^{\text{BPS}} + (CB)_6 + (CB)_8 - 2(CB)_7.$$

That the last equation is valid may be easily verified: first, the methyl increment of Beckett, Pitzer and Spitzer is too low by the term  $(CB)_6 - (CB)_7$  (page 88); second, equation iii neglects the difference between the chair-boat contributions for methylcyclohexane and the dimethylcyclohexane,  $(CB)_8 - (CB)_7$  see table 5).



Before discussing possible reasons for the discrepancy between the newly calculated heat capacities and those experimentally determined, the excellent agreement between the calculated entropies at 298<sup>0</sup>K and the data of Prosen, Johnson and Rossini (26) will be explained. At the temperature in question the contribution of chair-boat tautomerism to the entropy of cyclohexane gas amounts to only 0.01% of the total entropy (2). For the substituted cyclohexanes this tautomerism is even less important and the effect of the above revisions upon the entropies is negligible.

#### CAUSES FOR DISCREPANCIES.

In order to be useful in practice such a method as that under discussion must be of easy and general applicability. For this reason a number of approximations have been made in the above treatment. First, it has been assumed that certain parameters, such as the steric interaction for polar-equatorial tautomerism, are approximately equal. This has been shown to be close to the truth for several compounds (19). The thermodynamic properties are not seriously affected by fairly large changes in these parameters, and it is probable that the error from this source

is comparatively minor.

Previously the changes in entropy for the various types of tautomerism have been taken to be due to changes in symmetry number alone. For the chair-boat tautomerism the entropy change so computed is more likely to be a minimum value. The greater flexibility of the carbon ring in the boat form presumably would tend to increase the entropy of that tautomer. There does not appear to be any way in which this effect can be considered other than by empirical fitting of data. Actually, if the entropy for chair to boat tautomerism were to be increased, the calculated results of table 5 would compare even less favorably with experimental data.

It will be shown in the next section that the assumption of zero entropy change for polar-equatorial tautomerism is probably incorrect.

Perhaps the most fundamental supposition made in these approximate treatments is that each group in a molecule contributes its normal share to the vibration-rotation thermodynamic function. Involved in this assumption is the consideration that the vibrational frequencies of the cyclohexane ring



remain unaffected by the addition of a methyl group. Unless adequate spectral data are available, no other assumption can be made, but undoubtedly a part of the inaccuracy of calculated results must be attributed to this source.

Any of the above considerations may be invalid. For one particular compound the several parameters may be so adjusted as to result in agreement with experimental data for at least one temperature. The acid test is whether the same parameters produce adequate results for more than one compound over a sufficiently wide range of temperatures. The fact that the methods discussed produce calculated values which agree reasonably well with experimental for a number of compounds indicates that, within the limits of the approximations pointed out above, the fundamental concepts developed are probably correct. Since the deviations shown in table 5 are all of the same order of magnitude it seems possible that some effect common to all the dimethylcyclohexanes has been neglected.

#### THE ENTROPY CHANGE FOR POLAR-EQUATORIAL TAUTOMERISM.

As has already been mentioned, the assumption



of zero entropy change for polar-equatorial transformation is open to serious question. The relatively large effect of an entropy change upon the polar-equatorial contribution to the heat capacity makes it important to consider whether or not such a change could occur.

It has been pointed out that it was necessary to increase the potential barrier restricting rotation of the methyl groups from 2.8 to 4.3 kilocalories per mol for cis 1,2-dimethylcyclohexane in order to obtain agreement with the experimental entropy (page 27). This adjustment was necessary because one of the methyl groups always occupies the more restricted polar position. Similarly, the polar tautomer of any of the other dimethylcyclohexanes should be assigned a greater restricting potential than the corresponding equatorial form. It is evident that there must be an entropy change in polar-equatorial tautomerism due to the differing contributions from restricted rotation in the two tautomeric forms.

In order to evaluate the change in entropy arising in such a fashion, the difference between  $S_{fr} - S_{rr}$  for the tautomers was calculated as described

on page 14 . For a particular compound the restricting potential for each methyl group was estimated by adding to the customary ethane barrier the magnitude of the strain energies arising from n-butane-like interactions. The figure thus obtained is only an approximation, for barriers in such complex cases are not well established. As a matter of fact, the procedure yields about the same height of barrier as that empirically assigned to cis 1,2-dimethylcyclohexane.

The contribution of restricted rotation (or better  $S_{fr}-S_{rr}$ ) was next calculated for each tautomeric form (page 14 ). The difference in the two figures was considered to be the difference in entropy between the polar and equatorial forms of the compound in question. It was necessary to take into account two methyl group contributions for the dimethylcyclohexanes.

After these entropy changes had been calculated, the contributions of polar-equatorial tautomerism to the heat capacity of each compound was recomputed. This was accomplished readily by multiplying the polar-equatorial contributions listed in table 5 by the factor,  $\exp( S/R)$ , using the appropriate value



for the entropy change. Then the methyl increment and, finally, the heat capacities of each compound were recalculated just as described previously.

The results of the last calculation are recorded in column three of table 6. It may be seen that these figures more closely approximate the experimental values. There remains as much as 2% deviation.

#### THE EMPIRICAL ENTROPY PARAMETER.

While it may be that such calculations cannot be expected to be more accurate than those referred to in the last paragraph, a better empirical fit for a series of related materials is feasible. The entropy change in polar-equatorial tautomerism has been assumed to arise only from differences in the potentials restricting the rotation of the methyl groups. It is possible that the actual entropy change in such transformations is greater, but no way is yet apparent to evaluate this function other than that already discussed.

In attempting to obtain better agreement with experimental data, any of the various parameters used in the calculation might be adjusted. Except for



Table 6

EFFECT OF ENTROPY PARAMETER: FINAL CALCULATION

Compound <sup>a</sup>	Temperature (°K)	Heat Capacity, $C_p^0$ (cal/degree-mol)			Deviations <sup>e</sup> (%)
		Calculated <sup>b</sup>	Calculated <sup>c</sup>	Experimental <sup>d</sup>	
Cis 1,2	400	50.6	49.6	49.6	0
Trans 1,2	400	51.6	51.0	50.9	+0.2
Trans 1,4	400	51.3	50.3	50.4	-0.2
Cis 1,2	500	63.2	62.1	62.5	-0.6
Trans 1,2	500	64.5	64.0	64.0	0
Trans 1,4	467.9	60.0	59.0	59.2	-0.3

(a) Dimethyleyclohexanes

(b) Calculated using theoretically determined entropy change for polar-equatorial tautomerism.

(c) Calculated using empirically assigned entropy change of  $R \ln 2$  for polar-equatorial tautomerism

(d) Interpolated

(e) Deviation of values of column 4 from those of column 5.

the aforementioned entropy change, all of these parameters have been shown to be nearly constant for a number of compounds (2, 18). It seemed best to adjust the entropy parameter alone. It would not be possible to obtain the results desired with reasonable changes of the other quantities.

Since the effect of polar-equatorial tautomerism does not appear in the calculation of the heat capacity of cis 1,2-dimethylcyclohexane, that compound was decided upon as reference substance. Twice the methyl increment which would be required to bring the calculated heat capacity into agreement with the experimental was determined by subtracting the cyclohexane figure without chair-boat tautomerism and the chair-boat contribution of the substituted compound from the experimental value for cis 1,2-dimethylcyclohexane (equation iv, page 92). By the use of equation ii (page 91) the contribution of polar-equatorial tautomerism to the heat capacity of methylcyclohexane was obtained. As the last figure is just the contribution already found (table 5) multiplied by  $\exp(\Delta S/R)$  (equation XXVIII, page 22), the adjusted entropy can be evaluated.

This procedure gave a value of approximately



R Ln 2 for the entropy parameter. It is not likely that this quantity should have the same value for all the dimethylcyclohexanes. The entropies calculated as described in the last section amounted to about one-half to three-fourths the value just found but were not constant. Nevertheless, it was decided to regard the entropy parameter as the same for all the compounds studied.

New polar-equatorial contributions were calculated for the three compounds in which that tautomerism occurs by multiplying those figures in table 5 by two. Using the new values so acquired, the heat capacities of the dimethylcyclohexanes were again computed. The results of this final computation appear in column four of table 6. It is apparent that the new parameter brought the calculated values of the heat capacity of all compounds close to the experimental data. In addition, the proper temperature coefficient was attained.

Some justification for the introduction of the entropy parameter has been given above, and the closer approximation to experimental values offers better proof of its validity. At the present time, however, further explanation of the size of this



entropy change cannot be made. It would be necessary to increase the restricting potential for a polar methyl rotation to about 8.0 kilocalories per mol in order to account for the entire amount of the change, It does not seem correct to do so.

Actually, the tables and formulas used for calculating  $S_{fr}-S_{rr}$  assume a symmetrical potential barrier. This is definitely not true for a polar methyl group. For this reason the calculated values of the entropy parameter are probably not too accurate. In view of these facts, the empirical evaluation of the entropy parameter is not an unreasonable solution to the problem until a better method is discovered.

There is a possibility that some of the discrepancy between experimental values and those calculated on the basis of the theoretical entropy parameter is due to inaccuracies in the data for cyclohexane and methylcyclohexane. The latter are accurate to only  $\pm 1.0\%$  (32), and this error might have affected the computed heat capacities for the dimethylcyclohexanes by as much as 2%. In that event, the assumption of the empirical entropy parameter would not be required. The magnitude of the entropy parameter cannot be established with much

certainity until better values are available for the heat capacities of cyclohexane and methylcyclohexane.

It might be supposed that the introduction of the entropy parameter would affect the calculated value of the entropy at 298°K. However, the small size of the polar-equatorial tautomerism contribution at 298°K makes the effect of the new considerations negligible.

## SUMMARY

Experimental: The heats of vaporization (table 1) and heat capacities (tables 2 and 3) for cis 1,2-dimethylcyclohexane and trans 1,2-dimethylcyclohexane have been measured with a cycling calorimeter built according to the design used by Waddington, Todd and Huffman (38). A description of the construction details for the apparatus and the operational procedure followed in making experimental determinations have been presented.

Both types of data acquired are believed to be accurate to approximately  $\pm 0.3\%$ . Although there are no experimental values for the heat capacities of the compounds studied other than those presented in this paper, the heats of vaporization obtained compared favorably with the 25°C data of Osborne and Ginnings (15).

Comparison With Calculated Heat Capacities:

It has been demonstrated that the simple method for the calculation of the thermodynamic properties of alkylcyclohexanes proposed by Beckett, Pitzer and Spitzer (2) gives results which deviate from experimental



data by as much as 3%. A more detailed treatment of the problem using only those parameters discussed by the above authors resulted in even greater disparity between theoretically and experimentally determined heat capacities. While the agreement which was found by either treatment was sufficient for many practical purposes, means for improving the calculated results were sought.

Both the calculations mentioned in the last paragraph neglected the difference in entropy between polar and equatorial tautomers. This entropy change was calculated, assuming it to arise from an increased potential barrier for rotation of a polar methyl group. Upon repeating the more detailed calculations already developed in this paper, but using the newly determined entropy changes for the polar-equatorial contributions, the best correspondence to experimental values yet attained was found.

Finally, the entropy change was considered to be an adjustable parameter, the magnitude of which was taken to be that required to reproduce the experimental heat capacity for *cis* 1,2-dimethylcyclohexane at 400°K. When the figure evaluated in this manner was used to calculate the heat capacities of

cis 1,2-dimethylcyclohexane, trans 1,2-dimethylcyclohexane and trans 1,4-dimethylcyclohexane at two temperatures differing by  $100^{\circ}\text{C}$ , the computed values differed in no case by more than 0.6% from the experimental.

Conclusion: Several empirical parameters are involved in the theoretical treatments summarized in the foregoing section. These are:

- i. the potential barrier for rotation about the carbon-carbon bond;
- ii. the n-butane-like steric interaction important in consideration of polar-equatorial tautomerism;
- iii. the entropy parameter assumed for polar-equatorial tautomerism;
- iv. the propane-like interaction postulated for the chair-boat equilibrium.

No conclusions can be drawn concerning the last factor since its effect in the cases studied is not pronounced. However, further evidence has been presented to confirm the values previously assigned to the first two quantities. It may be concluded that the introduction of the entropy parameter for polar-equatorial tautomerism, as well as the assignment of

its magnitude, is probably valid, since heat capacities computed by taking it into account agree well with the experimental.

The agreement between calculated and experimental heat capacities ultimately attained is regarded as providing important substantiation for the overall concept of the structure of hydrocarbons which has gained prominence in recent years.



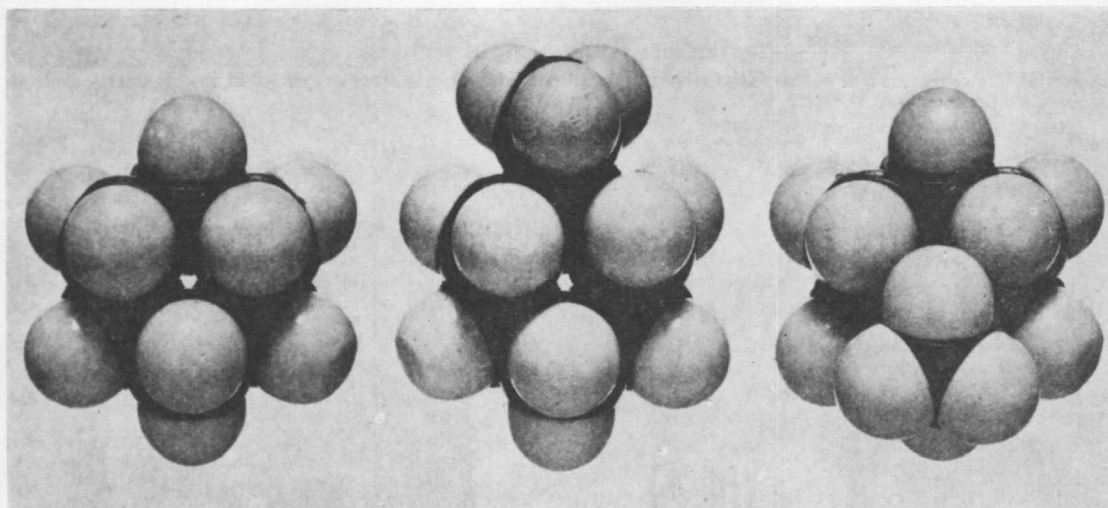


Plate 3: Polar-Equatorial Tautomerism

Cyclohexane (left), methylcyclohexane,  
equatorial (middle) and polar (right).

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