addition, the values of $W_u$ would have then have been too low, and an improperly high value for the volume change on fusion would have resulted. Since the unfed ingots were sound, however, there is no reason to suspect the results.

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# Thermal Stability Studies of Pure Hydrocarbons in a High Pressure Isoteniscope

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Monsanto Research Coporation

**Decomposition temperatures were determined in a high pressure isoteniscope for 80 naphthenic and 9 paraffinic saturated hydrocarbons. The effect of the number of rings, length of side chains, and number of side chains on the thermal stability was studied. The naphthenic compounds investigated were 14 cyclohexanes, 7 hydrindans, 17 decalins, 26 nonfused dicyclohexanes, and 16 nonfused polycyclic hydrocarbons. The paraffinic hydrocarbons ranged from $C_{12}$ to $C_{19}$. The decomposition temperature can be estimated with a precision of ±12.5° F. as a function of the critical pressure by the equation: $T_d = C + 8.31\ P_c$, where C is a characteristic constant for each homologous series of hydrocarbons.**

THERMAL stability of a number of saturated hydrocarbons was investigated in the course of this study. The stability was determined by measuring the pressure of the decomposition products in an isoteniscope (*1*, *2*, *4*, and *6*). This method gives quantitative information about the decomposition of hydrocarbons into gaseous products.

A semi-automatic isoteniscope was used in the present investigation. This high pressure isoteniscope was recently described in detail (*3*). By this instrument the vapor pressure of the sample is measured at incrasing temperatures until the sample begins to decompose. Then isothermal rates of pressure increase due to decomposition are measured, usually at three temperatures. To express the thermal stability by a single value the decomposition temperature is defined as that temperature at which the rate of decomposition is 1 mole %. The isoteniscope required only very small samples (3 ml.) and results were reproducible within ± 6° F.

The thermal decomposition temperatures of 89 paraffinic and naphthenic hydrocarbons were determined, and the results are given in Table I. The purity data given in the table are estimated values from vapor phase chromatographic data. Isomers were not separated in this investigation. The sources of the samples are given in Table I. The samples did not contain detectable quantities of peroxides. To prove this further, a number of hydrocarbons were deperoxidized with ferrous sulfate, and their decomposition temperature was determined. The results were within the experimental precision of the method.

## EXPERIMENTAL

At temperatures below decomposition levels, the vapor pressure of the hydrocarbon under investigation was measured at a series of temperatures. If the pressure was constant for 15 minutes at a given temperature, the pressure was recorded, and the temperature was adjusted to the next higher value. At temperatures where decomposition occurred, the pressure increase was recorded for 20 to 60 minutes, usually at three temperature levels. Since only 1 to 2% of the material decomposed in each experiment, the rate of pressure increase was constant at a given temperature, and no correction was applied for any previous decomposition.

## EVALUATION OF RESULTS

To correlate the results, the rate was assumed to be first order for the hydrocarbon—i.e.,

$$\frac{dn}{dt} = kn \qquad (1)$$

and it was assumed further that there was a 1 to 1 correspondence between moles of hydrocarbon decomposed and moles of gas produced:

$$dn = -d(n_{\text{gas}}) = -d\left(\frac{PV}{RT}\right) = -\frac{V}{RT}\,dP \qquad (2)$$

Table I. Experimentally-Determined and Calculated Decomposition Temperatures

| No. | Name | $P_c$, atm. | $T_d$, ° F. | | Purity, % | Source[a] |
|---|---|---|---|---|---|---|
| | | | Exptl. | Calcd. | | |
| 1 | Cyclohexane, *n*-propyl- | 28.0 | 730 | 748 | 99.5 | M |
| 2 | isopropyl- | 28.4 | 750 | 751 | 98.4 | M |
| 3 | 1,3,5-trimethyl- | 27.6 | 788 | 744 | 99.8 | M |
| 4 | 1-ethyl–4-methyl- | 27.8 | 774 | 746 | 99.8 | M |
| 5 | *n*-butyl- | 25.4 | 710 | 721 | 99.9 | U |
| 6 | *tert*-butyl | 25.5 | 730 | 722 | 99.9 | M |
| 7 | 1,1-diethyl- | 26.0 | 716 | 731 | 99.9 | U |
| 8 | diethyl-(mixed isomer) | 25.0 | 744 | 723 | 99.8 | M |
| 9 | 1,2,4,5-tetramethyl- | 24.9 | 705 | 722 | 99.8 | M |
| 10 | triethyl- | 26.4 | 732 | 734 | 98.0 | U |
| 11 | diisopropyl- | 21.8 | 703 | 696 | 99.9 | U |
| 13 | 1,3-dimethyl–5-*tert*-butyl- | 21.4 | 723 | 693 | 99.0 | M |
| 13 | 3-*tert*-butyl–5-ethyl–1-methyl | 20.6 | 721 | 686 | 99[b] | M |
| 14 | 1,2,3,4,5,6-hexaethyl- | 14.0 | 650 | 631 | 99[b] | M |
| 15 | Bicyclohexyl, | 25.5 | 745 | 747 | 99.2 | M |
| 16 | 2-methyl- | 23.0 | 732 | 736 | 99.2 | NN |
| 17 | 2-ethyl- | 21.4 | 709 | 713 | 99.9 | NN |
| 18 | 4-ethyl- | 21.4 | 735 | 713 | 100.0 | M |
| 19 | isopropyl- | 19.9 | 715 | 700 | 99.6 | M |
| 20 | isopropyl- | 19.9 | 710–735 | 700 | 99.4 | U |
| 21 | *tert*-butyl- | 18.6 | 707 | 690 | 99[b] | M |
| 22 | 2,2′, 4,4′, 6,6′-hexamethyl- | 15.9 | 664 | 667 | 98.0 | M |
| 23 | 4-heptyl- | 15.4 | 715 | . . . | 98.0 | DR |
| 24 | 4-nonyl- | 13.8 | 729 | . . . | 98.0 | DR |
| 25 | Methane, dicyclohexyl- | 23.1 | 750 | 760 | 99.9[b] | NN |
| 26 | Ethane, 1,2-dicyclohexyl- | 21.3 | 745 | 745 | 99.7 | M |
| 27 | Methane, cyclohexyl–2-methylcyclohexyl- | 16.8 | 706 | 708 | 99.6 | NN |
| 28 | cyclohexylethylcyclohexyl- | 19.7 | 705 | 732 | 100.0 | M |
| 29 | bis(ethylcyclohexyl)- | 17.1 | 701 | 710 | 99.9 | M |
| 30 | bis(2,4,6-trimethylcyclohexyl)- | 15.0 | 695 | 703 | 99.9 | M |
| 31 | Ethane, 1,1-dicyclohexyl- | 21.6 | 690 | 694 | 100.0 | M |
| 32 | Propane, 1,2-dicyclohexyl- | 20.0 | 681 | 680 | 100.0 | M |
| 33 | Butane, 2,3-dicyclohexyl- | 18.9 | 689 | 672 | 95.7 | M |
| 34 | Ethane, 1,1-bis(4-methylcyclohexyl)- | 19.7 | 680 | 679 | 100.0 | |
| 35 | Propane, 1,1-dicyclohexyl–2-methyl- | 18.9 | 650 | 672 | 99.0 | M |
| 36 | Ethane, 1-cyclohexyl–1-isopropylcyclohexyl- | 17.4 | 685 | 660 | 99.5 | M |
| 37 | Propane, 2,2-bis(methylcyclohexyl)- | 17.0 | 655 | 656 | 99.0 | M |
| 38 | Ethane, 1,1-bis(dimethylcyclohexyl)- | 16.1 | 660 | 649 | 99[b] | M |
| 39 | Ethane, 1,1-bis(ethylcyclohexyl)- | 16.3 | 705 | 650 | 97.9 | M |
| 40 | Heptane, 1,1-dicyclohexyl- | 15.5 | 665 | 644 | 95.7 | U |
| 41 | Indan, hexahydro- | 30.7 | 774 | 775 | 99.8 | |
| 42 | hexahydromethyl- | 27.6 | 743 | 749 | 95.9 | AS |
| 43 | ethylhexahydro- | 25.1 | 729 | 729 | 99.4 | AS |
| 44 | hexahydroisopropyl- | 23.1 | 688 | 712 | 93.5 | U |
| 45 | diisopropylhexahydro- | 18.6 | 701 | 675 | 88.2 | U |
| 46 | triisopropylhexahydro- | 18.4 | 692 | 673 | 98.0 | U |
| 47 | 1-cyclohexylhexahydro-1,3,3-trimethyl- | 17.7 | 665 | 667 | 97.3 | M |
| 48 | Naphthalene, decahydro- | 28.7 | 782 | 783 | 94.9 | DP |
| 49 | *cis*-decahydro- | . . . | 788 | . . . | 99.4 | NN |
| 50 | *trans*-decahydro- | . . . | 798 | . . . | 99.8 | NN |
| 51 | decahydro–1-methyl- | 26.0 | 751 | 761 | 98.5 | M |
| 52 | decahydro–2-methyl- | . . . | 772 | . . . | 99.5 | M |
| 53 | decahydrodimethyl- | 23.4 | 750 | 739 | 99.9 | M |
| 54 | decahydro–2,3-dimethyl- | . . . | 760 | . . . | 100.0 | M |
| 55 | decahydro, ethyl- | 23.7 | 735 | 742 | 98.7 | M |
| 56 | decahydro–1-ethyl- | . . . | 742 | . . . | 99.2 | M |
| 57 | decahydro–2-ethyl- | . . . | 749 | . . . | 99.8 | M |
| 58 | decahydroisopropyl- | 22.3 | 730 | 730 | 99.9[b] | M |
| 59 | decahydro–1-isopropyl- | . . . | 726 | . . . | 99.9[b] | M |
| 60 | decahydro–1-propyl- | 21.8 | 720 | 726 | 98.9 | M |
| 61 | 1-butyldecahydro- | 20.2 | 710 | 713 | 99.5 | M |
| 62 | *tert*-butyldecahydro- | 20.3 | 720 | 714 | 99.4 | M |
| 63 | decahydro–1-(1′-methylpropyl)- | 20.4 | 697 | 715 | 98.3 | M |
| 64 | decahydro–1-(2′-methylpropyl)- | 20.4 | 704 | 715 | 98.7 | M |
| 65 | Dodecane | 18.0 | 700 | 700 | 99.5 | M |
| 66 | Undecane, 3-methyl- | 18.5 | 708 | 704 | 99.9 | M |
| 67 | Nonane, 5-*n*-propyl- | 18.8 | 683 | 706 | 99.9 | M |

(*Continued on page 66*)

Table I. Experimentally-Determined and Calculated Decomposition Temperatures (*Continued*)

| No. | Name | $P_c$, atm. | $T_d$, ° F. |  | Purity, % | Source[a] |
|---|---|---|---|---|---|---|
|  |  |  | Exptl. | Calcd. |  |  |
| 68 | Decane, 2,9-dimethyl- | 18.7 | 696 | 705 | 100.0 | M |
| 69 | Decane, 2,2-dimethyl- | 18.9 | 720 | 707 | 96.4 | M |
| 70 | Octane, 2,2-dimethyl-4-ethyl- | 18.7 | 694 | 705 | 98.4 | M |
| 71 | Nonane, 2,2,8,8-tetramethyl- | 17.5 | 714 | 695 | 99.9 | M |
| 72 | Hexadecane | 14.4 | 715 | 670 | 99.0 | AS |
| 73 | Nonadecane | 12.5 | 670 | 654 | 97.4 | M |
| 74 | Cyclooctane, cyclohexyl- |  | 699 |  | 99.4 | M |
| 75 | Propane, 1-cyclohexyl-3-cyclopentyl- |  | 719 |  | 100.0 | M |
| 76 | Tercyclopentyl |  | 735 |  | 99.6 | M |
| 77 | Methane, tercyclopentyl- |  | 650 |  | 98.1 | U |
| 78 | Methane, dicyclohexylcyclopentyl- |  | 649 |  | 100.0 | M |
| 79 | Bicyclohexyl, cyclopentyl- |  | 675 |  | 99.7 | M |
| 80 | *o*-Tercyclohexane |  | 728 |  | 97.8 | M |
| 81 | *m*-Tercyclohexane |  | 730 |  | 99.0 | M |
| 82 | *p*-Tercyclohexane |  | 735 |  | 99.3 | M |
| 83 | *o*-Tercyclohexane, 4-ethyl- |  | 712 |  | 100.0 | U |
| 84 | Tercyclohexane, *tert*-butyl- |  | 675 |  | 93-99 | U |
| 85 | *m*-Tercyclohexane, 4′-heptyl- |  | 696 |  | 99[b] | DR |
| 86 | *m*-Tercyclohexane, 4′-nonyl- |  | 691 |  | 99.7 | DR |
| 87 | Cyclohexane, bis(cyclohexylmethyl)- |  | 715 |  | 99.5 | M |
| 88 | Propane, 1,1,3-tricyclohexyl- |  | 660 |  | 99.1 | M |
| 89 | Cyclohexane, 1,3,5-tricyclopentyl- |  | 710 |  | 99.0[b] | M |

[a] Symbols used for source of samples: AS = Applied Science Laboratory, State College, Pa. DP = E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. DR = Denver Research Inst., Denver, Colo. M = Monsanto Research Corp., Boston Laboratories, Everett, Mass. NN = Natl. Aeron. Space Admin., Washington, D. C. U = Sample obtained from Materials Central, Wright-Patterson AFB, Ohio; no source given.

[b] These hydrocarbons systhesized under Contracts AF 33(616)-7190, AF 33(600)-38448, AF 33(600)-39634.

Inserting Equation 2 into Equation 1, and noting that *n* is nearly constant at its original value for small total decompositions,

$$-\frac{V}{RT}\int_{P_i}^{P} dP = (P_i - P)\ \frac{V}{RT} = kt \qquad (3)$$

Experimental data allowed $k$ to be determined at various temperatures using Equation 3, and $\ln k$ was found, as expected, to be linear with $1/T$. It is desirable to be able to label the relative stability of any particular compound. To accomplish this, as mentioned previously, a decomposition temperature ($T_d$) is defined as that temperature where 1 mole % of the material decomposes per hour, consistent with the assumption indicated in Equation 2—i.e., no further decomposition of the initial decomposition products into gases. The value of $k$ at $T_d$ is found from Equation 1,

$$k_{\mathrm{T}_d} = \frac{\ln(100/99)}{60} = 1.674 \times 10^{-4}\ \text{min.}^{-1} \qquad (4)$$

The interpolation of $\ln k$ *vs.* $1/T$ plots then yields a value of $T_d$ immediately so that the relative stability of various compounds may be compared by using this single parameter, $T_d$.

## SAMPLE CALCULATION

The decomposition temperature of *n*-propylcyclopentane was determined. The experimentally determined pressure increase curves are plotted in Figure 1 as a function of time at three temperatures. From these lines,

at $T_1 = 823°$ F. $(\Delta P/\Delta t)_1 = 3.52$ p.s.i./min.
at $T_2 = 798°$ F. $(\Delta P/\Delta t)_2 = 1.34$ p.s.i./min.
at $T_3 = 761°$ F. $(\Delta P/\Delta t)_3 = 0.364$ p.s.i./min.

Knowing the molecular weight and density of the compound, the sample weight, and the chamber volume, the rate constants were calculated by Equation 3. The results, $k_1 = 1.25 \cdot 10^{-3}$, $k_2 = 4.86 \cdot 10^{-4}$, and $k_3 = 1.40 \cdot 10^{-4}$, min.$^{-1}$, respectively, are plotted in Figure 2 as a function of reciprocal temperature; from the straight line of this plot, the temperature (corresponding to the $1.674 \cdot 10^{-4}$ min.$^{-1}$ value of the rate constant) was determined to be 765° F.

## CORRELATION AND ESTIMATION OF OF DECOMPOSITION TEMPERATURES

Six groups of saturated hydrocarbons were measured: paraffins, cyclohexanes, decahydronaphthalenes, hexahydroindanes, bicyclics, and polycyclics. The results (TableI) show that the thermal decomposition temperature for a pure saturated hydrocarbon is a function of the structure of the molecule. For Cyclic saturated hydrocarbons the thermal decomposition temperature decreases as the number of rings in the molecule increases (Table II). Side chains affect the thermal decomposition temperature as follows (Table III): (a) By increasing the number of carbon atoms in a linear side chain the thermal decomposition temperature is decreased. (b) Chain branching had a completely different effect. A branched chain compound usually had a decomposition temperature corresponding to a straight chain compound containing one carbon atom fewer in the chain. (c) An increase in the number of substituent groups in the rings

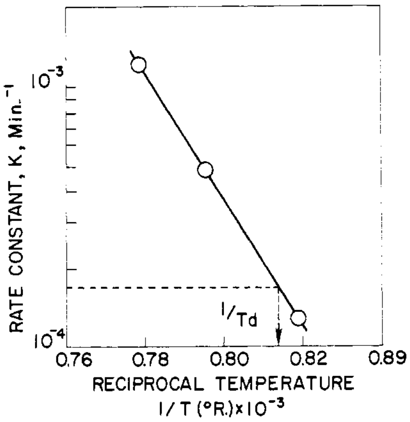


Figure 1. Rate of pressure increase for *n*-propylcyclopentane

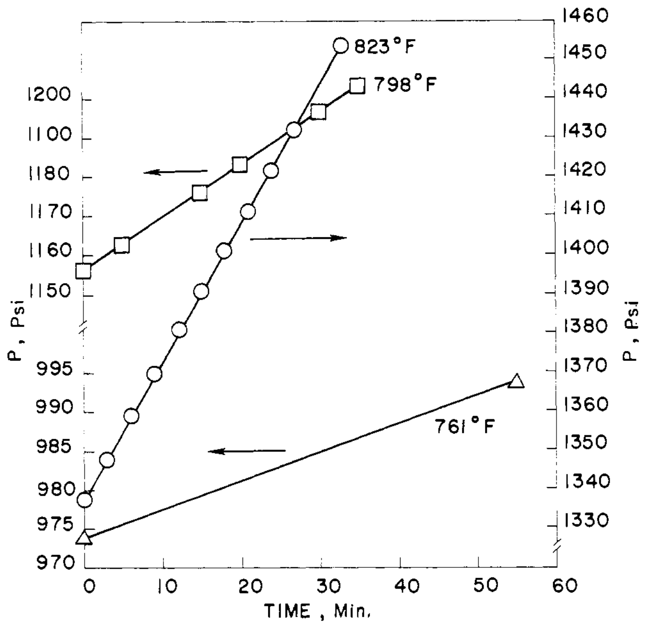
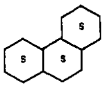
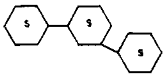
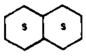
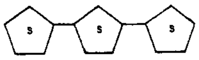
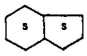
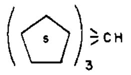
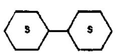
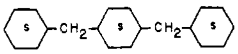
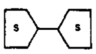
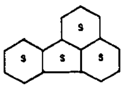
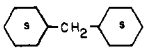
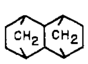
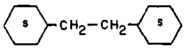
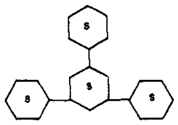


Figure 2. Rate constants of *n*-propylcyclopentane decomposition

Table II. The Effect of the Number of Rings in the Molecule on the Decomposition Temperature

| No. of Rings | Example | $T_d$, ° F. | No. of Rings | Example | $T_d$, ° F. |
|---|---|---|---|---|---|
| 0 | $n$-$C_{16}H_{34}$ | 730 | 3 |  | 750 |
| 1 |  | 852$^a$ | |  | 730-735 |
| 2 |  | 780 | |  | 735 |
| |  | 775 | |  | 650 |
| |  | 745 | |  | 715 |
| |  | 750 | 4 |  | 740 |
| |  | 750 | |  | 740 |
| |  | 745 | |  | 710 |

results in a gradual decrease in thermal decomposition temperature (Table IV). From these results it can be seen that the least stable molecules are those with the largest number of rings and side chains.

A correlation was developed between the decomposition temperatures and the critical pressure. The critical prssure was calculated by Lydersen's structural contribution method (5). For a given hydrocarbon family the decomposition temperature was found to be a linear function of the critical pressure, whereas the proportionality constant is the same for all hydrocarbon families. This can be expressed by the equation:

$$T_d = C + 8.31\,P_c \qquad (5)$$

where

$T_d$ = decomposition temperature, °F.
$P_c$ = critical pressure atm.
$C$ = constant for the hydrocarbon group

Values for $C$ are given in Table V.

The experimentally determined and calculated decomposition temperatures of 55 saturated hydrocarbons are compared in Table I. The average deviation between experimental and calculated data is 12.5°F. or 1.6%.

## NOMENCLATURE

$n$ = moles of sample
$n_{gas}$ = moles of gaseous products formed
$t$ = time, min.
$k$ = rate constant, min.$^{-1}$
$P$ = pressure, p.s.i.
$V$ = gas volume, ml.
$R$ = gas constant 669.7 $\frac{(\text{ml.})\ (\text{p.s.i.})}{(\text{gram mole})\ (^\circ\text{R.})}$
$T$ = temperature, ° R.
$T_d$ = decomposition temperature, ° F.
$P_c$ = critical pressure
$C$ = constant for the hydrocarbon group

Table III. The Effect of Side Chains on the Decomposition Temperature, ° F.

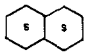
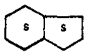
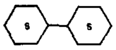
| Ring System | No. of Side Chains | $CH_3-$ | $CH_3CH_2-$ | $CH_3CH_2CH_2-$ | $CH_3$ $CH_3$<br>CH | $CH_3CH_2CH_2CH_2-$ | $CH_3CH_2CHCH_3$ | $CH_3$ $CH_3$<br>CH<br>$CH_2$ | $CH_3$ $CH_3$ $CH_3$<br>C |
|---|---|---|---|---|---|---|---|---|---|
|  | 780 | 750 | 740 | 720 | 725 | 710 | 695 | 705 | (720) |
|  | 770 | 740 | 730 | . . . | 690 | . . . | . . . | . . . | . . . |
|  | 852 | . . . | . . . | 730 | 750 | . . . | . . . | . . . | 730 |
|  | 745 | 730 | 710 | . . . | . . . | . . . | . . . | . . . | . . . |

Table IV. The Effect of the Number of Side Chains on the Decomposition Temperature

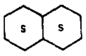
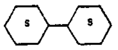
| Ring System | Group | $T_d$, ° F., No. of Side Chains | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
|  | $CH_3-$ | 770 | 760 | . . . | . . . | . . . | . . . |
| | $CH_3$<br>$>CH-$<br>$CH_3$ | 690 | 700 | . . . | . . . | . . . | . . . |
|  | $CH_3-$ | . . . | . . . | 790 | 705 | . . . | . . . |
| | $C_2H_5-$ | . . . | 745 | 730 | . . . | . . . | 650 |
| | $CH_3$<br>$>CH-$<br>$CH_3$ | 750 | 705 | . . . | . . . | . . . | . . . |
| | $CH_3-$<br>$C_2H_5-$ | | 775 | | | | |
|  | $CH_3-$ | . . . | 730 | . . . | . . . | . . . | 665 |

Table V. Value of C for Different Hydrocarbon Groups

| Hydrocarbon Group | Constant |
|---|---|
| Cyclohexane | 515 |
| Bicyclohexyl | 535 |
| Dicyclohexanes, separated by straight chains | 568 |
| Dicyclohexanes, separated by branched chains | 515 |
| Indan, hexahydro- | 520 |
| Naphthalene, decahydro- | 545 |
| Paraffin | 550 |

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# Vapor Pressure of Naphthalene

## Thermodynamic Consistency with Proposed Frequency Assignments

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**New vapor pressure measurements for solid naphthalene in the submicron region are presented. With present knowledge of the normal modes of vibration of the $C_{10}H_8$ molecule, a value $\Delta H_0^0 = 18.30 \pm 0.05$ kcal./mole may be deduced for the process of sublimation. From this and values of the vapor pressure of the liquid, the free energy function is derived up to 500° K. At 25° the free energy function is 63.21 ± 0.08 kcal./mole. The success of various vibrational frequency assignments in correlating vapor pressure and heat of vaporization data is discussed. Many previous vapor pressure data for the solid are shown to be grossly in error.**

THE FORMIDABLE task of assigning values to the 48 fundamental vibrational frequencies of the naphthalene molecule has been attempted by a number of spectroscopists in recent years. Although a good deal of progress has been made in this matter, as evidenced by recent normal coordinate calculations (*10*, *28*), it is not yet possible to calculate the thermodynamic functions of the ideal gas at elevated temperatures with even moderate accuracy by statistical methods. By combining each of seven recently reported frequency assignments with certain pertinent thermodynamic data, values of the free energy function may be derived with fair accuracy up to 500° K., and an improved value of the heat of sublimation at 25° may be obtained. In this connection previous values of the vapor pressure of the solid are critically evaluated and new measurements are presented in the range$^{-5}$ to $10^{-3}$ mm. of mercury. The derived values of the free energy functions allow a calculation of the vapor pressure of the solid up to the melting point with an estimated ±5% uncertainty. Naphthalene may therefore provide a convenient test substance for low pressure manometers such as the Knudsen effusion cell.

## EXPERIMENTAL

The vapor pressures of naphthalene, ice, benzene and carbon tetrachloride were measured between $10^{-5}$ and $10^{-3}$ mm. with a Knudsen gage. The construction of the gage and the method of correcting for nonlinearity of response have been described elsewhere (*22*). The latter three sub-