

from lot I indicates that the average aromatic ring is tetra-substituted. Because of band overlap no attempt was made to interpret the nonaromatic portion quantitatively.

DISCUSSION

Hood, Clerc, and O'Neal (4), from a study of mass spectral patterns, came to the conclusion that the typical alkylbenzene from lubricating oil contains one long chain substituent and that the other substituents are methyl— and possibly ethyl—groups. The results of the present investigation, in which both mass and nuclear magnetic resonance spectrometry were used to examine an alkylbenzene concentrate which was substantially free from cyclanobenzenes, has shown that the greater part, about 75%, of the alkylbenzenes, that is, those from the lower adsorbed portion, contain one long straight chain substituent and that the other substituents are methyl and ethyl groups. This confirms the conclusions of Hood, Clerc, and O'Neal. A small part of the alkylbenzenes, principally those from the unadsorbed portion, about 10%, appear to be very different in structure and contain branched chains or multiple chains of intermediate length. The monocyclanobenzenes from the lower adsorbed portion contain a single long chain substituent as well as methyl and possibly ethyl substituents.

In a previous investigation, the API Research Project 6 (10) showed that the optical activity of the lubricant fraction of its reference petroleum could be concentrated in two sets of fractions, one set consisting of polycycloparaffins, the other of polycyclanobenzenes. Because of an overlap of distillation ranges, the optically active polycyclanobenzene fractions from the lubricant fraction and those obtained in the present investigation have approximately the same carbon number range, and the optical activity in both cases is due to the same component or components. The present investigation has shown that the optical activity is not attributable to the tricyclanobenzenes, as previously was thought probable, but is due instead to tetra- or pentacyclanobenzenes with 25 or 26 carbon atoms per molecule. Apparently, these optically active compounds are not derived from steroids which have four rings per molecule but are more probably derived from higher cyclic terpenoids; for example, the tetracyclano-benzenes could be generated from pentacyclic terpenoids of the

β -amyryn group; these are widely distributed in plant materials.

Oakwood *et al.* (11) isolated crystalline materials with specific optical rotations in the range +32.7° to 36.8°. Hood (3) examined two of these materials by mass spectrometry and found that they were essentially mixtures of C₂₉ and C₃₀ pentacycloparaffins.

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Enthalpy, Heat Capacity, and Heat of Fusion of Magnesium from 404° to 1300° K.

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The enthalpy, $H_T - H_{298.15^\circ \text{K.}}$, of magnesium has been redetermined, confirming a suspected error in earlier measurements. The heat of fusion was 2026 ± 50 cal. per mole. The heat capacity of the liquid appears to be essentially constant at 8.20 cal. per (mole deg.) from 922° to 1300° K. Smoothed values of enthalpy and heat capacity from 298° to 1300° K. are given.

AN EARLIER determination of the heat of fusion of magnesium (10) was questionable because of a possible container correction error related to the magnetic transformation in the stainless steel container. Ginnings has published an analysis of the effects of such a transformation (3). The present work, using a tantalum-lined platinum-10% rhodium container, was undertaken to check on the magnitude of this error and to obtain the enthalpy of liquid magnesium at higher temperatures.

EXPERIMENTAL

A cylindrical sample of doubly sublimed magnesium—commonly referred to as 99.95-99.98% magnesium—was provided by the Metallurgical Laboratory of the Dow Chemical Co. Surface oxidation was removed by washing with dilute nitric acid and rinsing with water and acetone. Spectrographic analysis indicated the presence of 0.002% Al, < 0.01% Ca, < 0.0005% Cu, < 0.0005% Fe, 0.0006%

Mn, < 0.0005% Ni, < 0.008% Pb, < 0.001% Si, < 0.001% Sn, and 0.001% Zn.

The magnesium—4.772 grams—was sealed in a tantalum container—11.512 grams—which was then sealed in a platinum-10% rhodium capsule—14.363 grams. Both closures were made by arc welding under helium at a pressure of about 15 cm. of mercury.

The enthalpy, $H_T - H_{298.15^\circ \text{K}}$, was measured in a copper block drop calorimeter previously described (6). Corrections for the container were made from previous measurements on the tantalum and from platinum-10% rhodium "empty can" determinations.

A few determinations of the enthalpy of alpha aluminum oxide contained in platinum-10% rhodium were made, also.

RESULTS AND DISCUSSION

The observed enthalpies of $\alpha\text{-Al}_2\text{O}_3$ are compared with values calculated from the work of Furukawa *et al.* (2) in Table I.

The observed enthalpies of magnesium are presented in Table II. The enthalpies for the solid state were smoothed as described by Shomate (9), using the low temperature heat capacities determined by Craig *et al.* (1), after correction (7), to aid in the smoothing operation. The observed enthalpy data for liquid magnesium were smoothed using a least squares straight line fit:

$$H_T - H_{298.15} = 8.199T - 1,293 \text{ cal./mole (922}^\circ \text{ to } 1300^\circ \text{ K.)}$$

from which

$$C_p = 8.20 \text{ cal./mole deg. (922}^\circ \text{ to } 1300^\circ \text{ K.)}$$

Table I. Enthalpy of $\alpha\text{-Al}_2\text{O}_3$ ^a

T, °K. ^b	$H_T - H_{298.15}$, Cal./Mole		Deviation, Obsd. - Calcd.	Deviation from NBS, %
	Obsd. ^b	NBS equation ^c		
396.13	2,056.7	2,055.0	+1.7	+0.08
601.06	7,237.5	7,228.4	+9.1	+0.12
603.27	7,333.2	7,284.2	+49.0	+0.67
744.66	11,429.3	11,199.8	+229.5	+2.05
766.40	11,952.3	11,818.0	+134.3	+1.14
920.30	16,403.6	16,284.1	+119.5	+0.73
1114.73	22,200.3	22,091.4	+108.9	+0.49
1314.53	28,324.2	28,183.5	+140.7	+0.50

^a Gram molecular weight, 101.96. ^b More significant figures are given than are experimentally justified to minimize rounding error. ^c Furukawa *et al.* (2).

Table II. Observed Enthalpy of Magnesium^a

T, °K.	$H_T - H_{298.15}$, Cal./Mole	Deviation from Smooth Curve	
		Cal./mole	%
403.6	640.0	-6	-0.93
589.3	1850	-1	-0.05
683.0	2489	0	0.00
777.2	3157	-3	-0.09
874.1	3876	+4	+0.10
914.0	4176	-2	-0.05
954.1	6513	-17	-0.26
990.5	6835	+7	+0.10
1030.6	7161	+4	+0.06
1139.4	8067	+19	+0.24
1262.9	9049	-13	-0.14

^a Gram atomic weight, 24.312.

Table III. Smoothed Enthalpy and Heat Capacity of Magnesium^a

T, °K.	$H_T - H_{298.15}$, Cal./Mole	C_p , Cal./Mole °K.
298.15	0	5.95
300	11	5.95
350	313	6.12
400	622	6.26
450	938	6.39
500	1261	6.51
550	1589	6.63
600	1923	6.74
650	2264	6.87
700	2610	7.00
750	2963	7.14
800	3324	7.29
850	3693	7.46
900	4070	7.65
922(crystal)	4240	7.75
922(liquid)	6266	8.20
950	6496	8.20
1000	6906	8.20
1050	7316	8.20
1100	7726	8.20
1150	8136	8.20
1200	8546	8.20
1250	8956	8.20
1300	9366	8.20

^a Gram atomic weight, 24.312.

Deviations of the observed from the smoothed enthalpy values are shown in Table II. Smoothed enthalpies and heat capacities are listed in Table III.

The melting point, 922°K., was taken from the JANAF Thermochemical Tables (5) and is based on the work of Haughton and Payne (4). The present investigation indicates a heat of fusion at 922°K. of 2026 ± 50 cal. per mole.

The values for the enthalpy of solid magnesium, presented here, are essentially in agreement with the earlier values (10) although the new heat capacities are lower by 1.3 to 2.2% from 700° to 900°K.

The new liquid state enthalpies—and hence the heat of fusion—are definitely lower than those which were obtained using the stainless steel container, supporting Ginnings' hypothesis (3).

The present smoothed heat capacity follows closely the data of Craig *et al.* (1), and Saba *et al.* (8).

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