Second and Third Virial Coefficients for *n*-Hexane and Its Isomers

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Second and third virial coefficients for 2,2-dimethylbutane, 2,3-dimethylbutane, 3-methylpentane, 2-methylpentane, and *n*-hexane were determined from experimental compressibility data. Plots of the reduced coefficients compared favorably with published correlations.

DAVID AND HAMANN (*2*) summarized the second and third virial coefficients for a number of hydrocarbons. The only hexane isomer data included were two third virial coefficients for 2,3-dimethylbutane. McGlasahan and Potter (*9*) calculated second virial coefficients for normal paraffins at temperatures below 137° C. Additionally, Connolly and Kandalic (*1*) calculated second virial coefficients for *n*-hexane from 240 to 300° C. using the compressibility data of Griskey and Canjar (*5*).

The present work was undertaken to determine the second and third virial coefficients of the isomeric hexanes as well as the third virial coefficients for *n*-hexane. These coefficients were calculated from experimental data from the following sources:

Compound	Investigators	Ref.
n-Hexane	Griskey and Canjar	(*5*)
2-Methylpentane	Griskey and Canjar	(*6*)
	Kelso and Felsing	(*8*)
3-Methylpentane	Day and Felsing	(*3*)
2,2-Dimethylbutane	Griskey and Canjar	(*6*)
	Felsing and Watson	(*4*)
2,3-Dimethylbutane	Kelso and Felsing	(*7*)

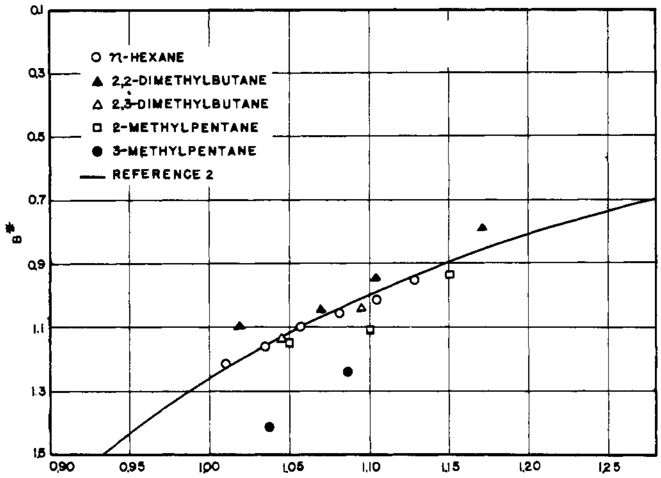
The method used was to fit the experimental data to the relation:

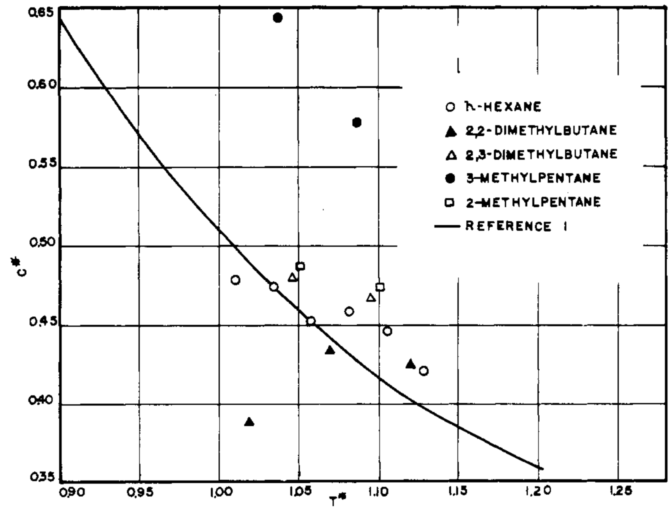
$$V(Z-1) = B + C/V \qquad (1)$$

using the least squares technique. Ranges of average deviations (in ml./gram mole) obtained in fitting the experimental data to Equation 1 for the various compounds were: *n*-hexane (3.5 to 7.8), 2-methylpentane (7.5 to 15.1), 2,2-dimethylbutane (5.2 to 6.8), 2,3-dimethylbutane (7.9 to 8.4), and 3-methylpentane (11.0 to 14.5).

Results are plotted as reduced coefficients *vs.* reduced temperature in Figures 1 and 2. The behavior of the reduced second virial coefficients (except those of 3-methylpentane) with respect to reduced temperature (Figure 1) compared favorably with the correlation (solid line) of McGlasahan and Potter (*9*). The second virial coefficients calculated for *n*-hexane by Connolly and Kandalic (*1*) also checked well with this correlation.

The greater uncertainty of the 3-methylpentane points can be explained thus: The second virial coefficient represents the intercept of the least squares line of $(Z - 1)V$ *vs.* $1/V$ at $1/V = 0$. Hence, considerable experimental com-





("Second and Third Virial Coefficient for *n*-Hexane and Its Isomers")

Figure 1. B^* vs. T^*

Figure 2. C^* vs. T^*

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pressibility data in the region of low $1/V$ must be available to determine the intercept precisely. This was not the case for 3-methylpentane, since the lowest density ($1/V$) measured was 3.2 gram moles/liter at pressures of 41 and 55 atm., respectively.

A certain amount of scatter was found when the reduced third virial coefficients for the isomeric hexanes were plotted against reduced temperature (Figure 2). This result was not surprising, since David and Hamann (*2*) had found about the same degree of scatter (except the deviation of the 3-methylpentane points) for varied data in determining the solid line of Figure 2.

Here again the greater deviation of the 3-methylpentane data is probably due to lack of low density compressibility data.

NOMENCLATURE

B = second virial coefficient, liter/gram mole
C = third virial coefficient, liter/gram mole
R = gas constant, liter atmosphere/gram mole ° K.
T = temperature, ° K.
V = molal volume, liter/gram mole
Z = compressibility factor
B^* = B/V_c reduced second virial coefficient
C^* = C/V_c^2 = reduced third virial coefficient
T^* = T/T_c = reduced temperature
T_c = critical temperature, ° K.
V_c = critical molal volume, liter/gram mole

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Heats and Free Energies of Formation of the Alkali Aluminum Hydrides and of Cesium Hydride

Heat of Formation of Aluminum Chloride in Hydrochloric Acid

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Standard heats of formation of five metal hydrides were determined by measuring their heats of reaction with HCl. The following values are reported for ΔH_f^0 (25° C.) in kcal./mole: $LiAlH_4$(c), −28.4; $NaAlH_4$(c), −27.0; $KAlH_4$(c), −39.8; $CsAlH_4$(c), −39.4; CsH(c), −11.92. Free energies of formation were calculated. Thermodynamic stabilities of the alkali aluminum hydrides are discussed. Heat of formation of aluminum chloride in HCl was determined for the HCl molality range 0 to 4.6 and for $H_2O/AlCl_3$ mole ratios ranging from 200 to 500.

WITH THE EXCEPTION of lithium aluminum hydride (*2*), the heats of formation of the alkali aluminum hydrides have not been reported. Published values for cesium hydride, −19.9 (*7*) and −13.48 (*6*), agree poorly. These hydrides react rapidly and completely with HCl to form products having known heats of formation. Measurement of the heats of these reactions therefore provided an excellent method of obtaining the heats of formation. To facilitate the calculation of the heats of formation, the heat of formation of aluminum chloride in HCl was determined over suitable ranges of HCl molality and $H_2O/AlCl_3$ ratio.

EXPERIMENTAL

Materials. The five crystalline hydrides were synthesized in this laboratory. Analyses and estimated purities are summarized in Table I. The potassium aluminum hydride was assumed to contain 2.3% KH, and the heats of hydrolysis were corrected accordingly.

All other chemicals used were reagent-grade materials.

APPARATUS AND PROCEDURE

The calorimeter consisted of a 300-ml. silvered borosilicate glass Dewar fitted with a rubber stopper. Temperatures were read to the nearest 0.01° C. with an accurately cali-