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Examination of the Expression, $T(dP/dT)_v+B$ $=f(v)$, for a Number of High Purity Liquid Hydrocarbons

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THE failure of the pressure coefficient, $(dP/dT)_v$, of liquids to be a function of volume alone invalidates the use of an equation of state of the Van der Waals type for liquids. A number of investigators have attempted to find a quantity that is a function of volume only. Gibson and Loeffler[1,2] have proposed the quantity $T(dP/dT)_v+B$, where B is the Tait equation[3] parameter B, and their examination of this quantity for benzene and benzene derivatives has shown it to be a function of volume alone. Eduljee, Newitt, and Weale[4] have verified that the above quantity is a function of volume only for a number of normal paraffins of low molecular weight.

Volume-pressure data to 10 kilobars for a series of structurally related hydrocarbons of high purity have been determined by the High Pressure Laboratory[5] of The Pennsylvania State University. These high purity hydrocarbons are synthetically produced by the Hydrocarbon Laboratory[5] of the Pennsylvania State University. The experimental data have been smoothed graphically and the Tait equation has been fitted to the resulting smooth curve. The values of $(dP/dT)_v$ were obtained by measuring the slopes of isochores drawn from the smooth curve volume-pressure data.

TABLE VI. Values of $T(dP/dT)_v+B$ (expressed in kilobars).

n-Pentadecane

Temp. (°F)	Volumes (cc/mole) 288.9	280.4	271.9	267.6	263.4
140°		4.33	4.82		
175		4.23	4.70	4.98	5.26
210	3.80	4.33	4.75	5.00	5.25
239	3.78	4.21	4.77	4.86	5.33
Average	3.79	4.28	4.76	4.95	5.28

n-Octadecane

Temp. (°F)	Volumes (cc/mole) 333.4	323.2	318.1	307.9
175	4.13	4.77	5.20	
210	4.11	4.69	5.02	5.94
239	4.13	4.60	4.19	5.78
Average	4.12	4.69	5.04	5.86

1-α-Naphthylpentadecane

Temp. (°F)	Volumes (cc/mole) 386.1	379.3	372.6	365.8
175		5.28	5.88	6.15
210	5.10	5.35	5.82	6.24
239	5.05	5.35	5.83	6.31
Average	5.08	5.33	5.84	6.24

9(2-Phenylethyl)heptadecane

Temp. (°F)	Volumes (cc/mole) 410.0	396.3	382.5	368.7	354.9
140		5.42	6.44	7.17	7.79
175	4.75	5.46	6.34	6.99	7.90
210	4.76	5.47	6.36	6.95	8.13
239	4.76	5.50	6.06	6.86	8.27
Average	4.76	5.46	6.31	6.99	8.02

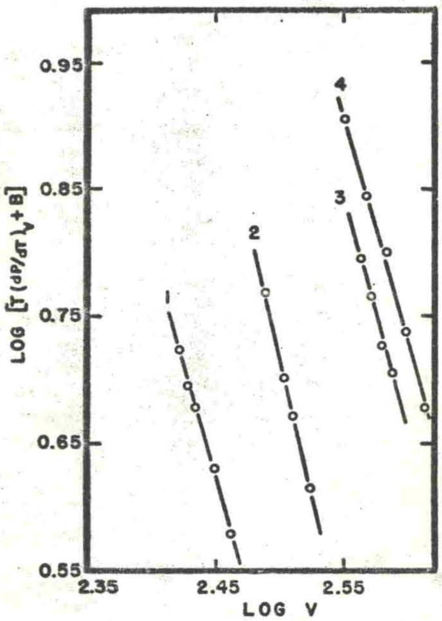

FIG. 1. Log$[T(dP/dT)_v+B]$ *versus* log$v$. Line 1: *n*-Pentadecane, Line 2: *n*-Octadecane, Line 3: 1-α-Naphthylpentadecane, Line 4: 9(2-Phenylethyl) heptadecane.

Resulting values of $T(dP/dT)_v+B$ for representative compounds and volumes are shown in Table I. Although the quantity in question is not exactly constant for a given volume the deviations are believed to be within the experimental error and the data therefore support the proposal that $T(dP/dT)_v+B$ is a function of volume only.

If one plots log$[T(dP/dT)_v+B]$ *versus* log$v$, straight lines are obtained. Figure 1 shows such a plot for four hydrocarbons. For the compounds examined, including normal paraffins, cycloparaffins, aromatics, and fused-ring compounds, and encompassing a molecular weight range of 170 to 351, the average value obtained for the slope was -3.89.

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1 R. E. Gibson, and O. H. Loeffler, J. Am. Chem. Soc. 61, 2515 (1939).

2 R. E. Gibson, and O. H. Loeffler, Ann. N. Y. Acad. Sci. 51, 727 (1948).

3 An empirical equation for liquids proposed by P. G. Tait in 1888. This equation states: $v_0-v=C\log(1+P/B)$, where v_0 is the specific volume at atmospheric pressure, v is the volume at pressure P, and C and B are constants for a given liquid and temperature.

4 Eduljee, Newitt, and Weale, J. Chem. Soc. (London) Part IV, 3086 (1951).

5 Partly supported by the American Petroleum Institute and jointly known as American Petroleum Institute Research Project 42.