

TABLE IV. Tait equation parameters.

PSU No.	Temperature											
	37.8°C		60.0°		79.4°		98.9°		115.0°		135.0°	
	C cc/gm	B bars	C	B	C	B	C	B	C	B	C	B
174			0.2316	1378	0.2350	1264	0.2384	1160	0.2416	1061	0.2455	976.4
87	0.2438	1315	0.2481	1170	0.2520	1048	0.2560	941.3	0.2598	857.9	0.2645	756.6
88	0.2505	1275	0.2551	1140	0.2590	1019	0.2632	907.6	0.2670	831.7	0.2717	736.0
532	0.2721	983.3	0.2778	876.5	0.2830	762.8	0.2884	676.7	0.2935	607.8	0.3000	532.0

of other observers. In a separate PVT study Bradbury<sup>17</sup> examined samples of PSU 25, 111, and 19 at 37.8° and 98.9°C. The average percent difference, without regard to sign, between Bradbury's data and the data of this study is 0.6%.

Table III presents data for the two mixtures studied. For these mixtures the equivalence of average molecular structure and molecular weight for the physical mixture with that for a certain pure chemical compound, termed "chemical" mixture, has been shown by previous work of Schiessler and co-workers<sup>10</sup> to produce also an equivalence in such atmospheric pressure physical properties as density, viscosity, and refractive index. Griest<sup>18</sup> has shown that the viscosity for three physical mixtures was identical (within 3%) to that for the corresponding "chemical" mixture for pressures to 3450 bars. In Table III relative volumes (relative volume = volume at a given pressure/volume at atmospheric pressure) for the physical and "chemical" mixtures studied by the present authors are compared. This comparison is made by listing the magnitude of the quantity  $c/p$ , which was the ratio of the value of the relative volume for the "chemical" mixture to the value of the relative volume for the physical mixture. The agreement over the full pressure range indicates that compression is determined by the coexistence in proper ratio of units smaller in size than the molecule itself.

## DISCUSSION AND ANALYSIS OF RESULTS

### Tait Equation

Although no attempt was made in this study to develop a three-dimensional equation of state for the liquid hydrocarbons, considerable effort was devoted to attempts to express the pressure-volume isotherms analytically. Of chief interest in this connection was the Tait equation.<sup>19</sup>

The form of the Tait equation used in this study was

$$v_0 - v = C \log(1 + P/B),$$

<sup>17</sup> D. Bradbury, D.Sc. dissertation, Harvard University (1950).

<sup>18</sup> Griest, Webb, and Schiessler, *J. Chem. Phys.* **29**, 711 (1958), this issue.

<sup>19</sup> P. G. Tait, *Physics and Chemistry of the Voyage of H. M. S. Challenger*, Vol. II, Part IV, S. P. LXI (1888).

where  $v_0$  is the specific volume at atmospheric pressure,  $v$  is the specific volume at pressure  $P$ , and  $C$  and  $B$  are constants. The data used to determine  $C$  and  $B$  were obtained from the smoothed volume-pressure isotherms. The initial values of  $C$  and  $B$  were determined by a method suggested by Wohl.<sup>20</sup>

A number of investigators<sup>20-27</sup> have observed that  $C/v_0$  was a constant independent of temperature. The value of  $C/v_0$  was evaluated for 20 hydrocarbons from this study and a study by Spencer,<sup>28</sup> using data from 103 isotherms. The average value obtained for  $C/v_0$  was 0.2058, the standard deviation being 0.0045. The 20 hydrocarbons used in this evaluation cover a molecular weight range of 170 to 535 and included paraffinic, isoparaffinic, cycloparaffinic, aromatic, and fused ring compounds. It is believed that this is the widest range, both in respect to molecular weight and hydrocarbon structure, over which the constancy of  $C/v_0$  has been ascertained.

Using the expression  $C = 0.2058 v_0$ , a value of  $C$  was calculated for each isotherm and a corresponding value of  $B$  was computed by a least-squares procedure. Representative values of  $C$  and  $B$  appear in Table IV.

A comparison between observed values of the specific volume change and the specific volume change computed from the Tait equation was made. The average percent of difference, without regard to sign, was 0.45%. The largest differences were at low pressures, this being particularly true for the normal paraffins.

An examination of the data showed that the temperature dependence of  $B$  was adequately described by a quadratic about 79.4°C. Representative values

<sup>20</sup> A. Wohl, *Z. physik. Chem.* **99**, 234 (1921).

<sup>21</sup> H. Carl, *Z. physik. Chem.* **101**, 238 (1922).

<sup>22</sup> R. E. Gibson, and J. F. Kincaid, *J. Am. Chem. Soc.* **60**, 511 (1938).

<sup>23</sup> R. E. Gibson, and O. H. Loeffler, *J. Am. Chem. Soc.* **61**, 2877 (1939), **61**, 2515 (1939).

<sup>24</sup> R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.* **43**, 207 (1939).

<sup>25</sup> R. E. Gibson and O. H. Loeffler, *J. Am. Chem. Soc.* **63**, 898 (1941).

<sup>26</sup> Eduljee, Newitt, and Weale, *J. Chem. Soc. (London)*, Part IV, 3086 (1951).

<sup>27</sup> D. M. Newitt, and K. E. Weale, *J. Chem. Soc. (London)*, Part IV, 3092 (1951).

<sup>28</sup> J. W. Spencer, Ph.D. dissertation, The Pennsylvania State University (1952).