CORRESPONDING STATE OF PURE ORGANIC LIQUIDS WITH RESPECT TO "CONTACT VOLUME"

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A method of estimating molal volume of organic liquids at any temperature by means of the addition of "contact volume" is suggested. Different from previous methods in which critical density and pressure data are indispensable basic information, the present method needs orthobaric melting point and critical temperature. Many organic liquids have been proved to have the same fixed values with respect to "contact volume", provided that the energy level parameter, θ , of the liquid defined by $\theta = (t - t_o)/(t_c - t_o)$ is the same. Where t_c = critical temperature, t_o = melting point, t = the temperature of the liquid.

"contact volume" is the local free volumes denoted by a^2 , ab , b^2 , bc , ac , ... etc., where a , b , c , ... etc. represent the atomic groups CH_3 -, CH_2 -, $-\text{CH}-$, ... etc. Thus, the molal free volume of *n*-heptane, for instance, is shown to be

$$v_f = V_t - V_o = \sum \Delta v_f = (2a + 5b)^2 = 4a^2 + 20ab + 25b^2$$

where V_t and V_o are the molal volume at t and t_o respectively.

For some fifty organic liquids consisting of paraffins, aromatics and alcohols, v_f in $\theta = 0.05$ – 0.60 have been analyzed.

The result shows good agreement with experimental data in the literature and endorses the new liquid corresponding state concept.

Introduction

In dealing with the molal volume of pure organic liquids, the nature of the volume additionally increasing during the temperature interval from the melting point (m.p.) to the critical point (c.p.) must first be understood. The liquid molecule throughout the thermal expansion from its m.p. to c.p. is considered to be a rigid body. In other words, the expansion is accompanied by the creation of "free volume", v_f , among the molecules in contact, instead of breakage or enlargement of interatomic distance of a molecule. On the contrary, the good agreement of Lydersen's method⁽²³⁾ estimating liquid molal volume using group contribution with experimental data and those of Chow and Bright⁽⁴⁾, and of Johnson and Huang⁽¹²⁾, etc., on the heat capacity give rise to a question as to the validity of taking the molal free volume v_f as the whole. At least, their results explicitly make it sure that the molal free volume of liquid can be localized independent of the whole structure of the liquid molecule. The local molal free volume must be affected by the nature of the groups surrounding them. So, we may call it tentatively "contact volume".

In the next section, "Contact Volume", the proportion and nature of the contact of organic liquid molecules, which determine the quantity of the local

molal free volume, or contact volume, is discussed. In the estimation of the molal volume of the liquid most methods available now^(11,15,17,22,23,26) use corresponding state theory as their basis. The corresponding state theory originates from van der Waals' kinetic theory of gases, followed by the development of Pitzer, etc.⁽¹⁹⁾.

The theory has been extended to liquids and supported by ample empirical evidence including the molal volume correlation.^(11,12) The theory is largely empirical and takes the liquid state as something like the gaseous state. Furthermore, the reduced temperature used in the theory takes absolute temperature from zero to c.p. as the whole range. However, all liquids begin at their m.p. and end at c.p., which does not include the temperature range of the crystal state. Also, they all form polycrystalline bodies at m.p. and dense gases at c.p. During thermal expansion the polycrystalline bodies are supposed to disintegrate all the way in a pattern similar for all liquids, until they become individual discrete molecules at c.p.

The t vs. V_t curves of many homologous series show similar changes from m.p. to c.p. Then, it may be natural to imagine that there may also be a "corresponding state" at the same fraction between m.p. and c.p., inasmuch as the two terminal states are both "corresponding". Energy level parameter, θ , defined by $\theta = (t - t_o)/(t_c - t_o)$ was thus intro-

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$$y(\theta) = f(\theta) - \Delta y$$

$$4a^2: f(\theta) = 38.16\theta^3 - 11.583\theta^2 + 17.276\theta$$

$$4ab: f(\theta) = 8.80\theta - 0.249$$

$$10b^2: y(\theta) = \Delta y$$

Fig. 1 Contact volume, $y(\theta)$ of $4a^2$, $4ab$ and $10b^2$

$$y(\theta) = f(\theta) - \Delta y$$

$$2bc: f(\theta) = -2.416\theta^3 + 0.7916\theta^2 - 4.455\theta$$

$$2bd: f(\theta) = -0.416\theta^3 - 1.7083\theta^2 - 6.825\theta$$

$$d^2 + 8ad: f(\theta) = -101.416\theta^3 + 30.125\theta^2 - 29.283\theta$$

$$c^2: f(\theta) = -7.457\theta, 0 \leq \theta \leq 0.35$$

$$f(\theta) = 32.5\theta^2 - 33.5\theta + 4.96, 0.35 \leq \theta \leq 0.60$$

Fig. 2 Contact volume, $y(\theta)$, of $2bc$, $2bd$, $d^2 + 8ad$ and c^2

duced in place of the reduced temperature. The main object of this work is to know about the liquid structure in terms of the molal volume associated

with thermal expansion and to apply the conclusion reached for estimation of the excess volume of liquid mixtures as well as the molal volume of pure liquids. With the aid of contact volume and energy level parameter the above two objects have been attained for some hydrocarbon homologs.

Contact Volume

Consider 2,4-dimethyl pentane. For convenience, as shown in Figs. 1-5, groups CH_3- , $-\text{CH}_2-$, $-\text{CH}^*-\text{C}$, (see foot note[†]) ... etc. are denoted by

$a, b, c, \dots$ etc. and 2,4-dimethyl pentane is thus written as $(4a + b + 2c)$. So long as the homogeneous state of the liquids is assumed, the groups $a, b, c, \dots$ etc. would be in contact with, and surrounded by, the groups $(4a + b + 2c)$.

In other words, on one gram mole basis there are the contacts $4a(4a + b + 2c)$, $b(4a + b + 2c)$ and $2c(4a + b + 2c)$ in all. Their sum is equal to $v_f = (4a + b + 2c)^2 = 16a^2 + b^2 + 4c^2 + 8ab + 16ac + 4bc$, where contact volumes $a^2, ab, b^2, \dots$ etc. have the unit of cc/g-mole.

The numerical values of $a^2, b^2, c^2, ab, bc, \dots$ etc. are calculated from the experimental v_f data by algebraic means for many homologs in the literature^{2,7,8,14,17,23-25} between $\theta = 0-0.6$ at every 0.05 interval and are plotted on Figs. 1-5. When θ exceeds 0.6, the V_t vs. t curves change sharply and the error becomes so large that the contact volumes above $\theta = 0.6$ were not estimated. Contact volumes are estimated as follows.

n-alkanes

$a: \text{CH}_3-, b: -\text{CH}_2-$

[Compounds]	[Basic Formula]
1 n-propane	$(2a + b)^2 = 4a^2 + b^2 + 4ab =$
2 n-butane	$(2a + 2b)^2 = 4a^2 + 4b^2 + 8ab =$
3 n-pentane	$(2a + 3b)^2 = 4a^2 + 9b^2 + 12ab =$
4 n-hexane	$(2a + 4b)^2 = 4a^2 + 16b^2 + 16ab =$
5 n-heptane	$(2a + 5b)^2 = 4a^2 + 25b^2 + 20ab =$
6 n-octane	$(2a + 6b)^2 = 4a^2 + 36b^2 + 24ab =$
7 n-nonane	$(2a + 7b)^2 = 4a^2 + 49b^2 + 28ab =$
8 n-decane	$(2a + 8b)^2 = 4a^2 + 64b^2 + 32ab =$
9 n-undecane	$(2a + 9b)^2 = 4a^2 + 81b^2 + 36ab =$
10 n-dodecane	$(2a + 10b)^2 = 4a^2 + 100b^2 + 40ab =$
11 n-tetradecane	$(2a + 12b)^2 = 4a^2 + 144b^2 + 48ab =$
12 n-hexadecane	$(2a + 14b)^2 = 4a^2 + 196b^2 + 56ab =$
13 n-octadecane	$(2a + 16b)^2 = 4a^2 + 256b^2 + 64ab =$

$[v_f \text{ at } \theta = 0.30]$	[Difference]
7.7	
10.1	$(2-1) = 3b^2 + 4ab = 2.4$
12.4	$(3-2) = 5b^2 + 4ab = 2.3$
14.6	$(4-3) = 7b^2 + 4ab = 2.2$
16.7	$(5-4) = 9b^2 + 4ab = 2.3$
18.7	$(6-5) = 11b^2 + 4ab = 2.0$
21.1	$(7-6) = 13b^2 + 4ab = 2.4$
23.4	$(8-7) = 15b^2 + 4ab = 2.3$
25.8	$(9-8) = 17b^2 + 4ab = 2.4$
28.4	$(10-9) = 19b^2 + 4ab = 2.6$
33.7	$(11-10)/2 = 22b^2 + 4ab = 2.6$
38.7	$(12-11)/2 = 26b^2 + 4ab = 2.5$
43.9	$(13-12)/2 = 30b^2 + 4ab = 2.6$

Observing the difference, one may find that $4ab \doteq 2.30$ and $30b^2 \doteq 0.3$ approximately. However, in harmony with b^2 at other θ and for the higher homologs not listed here, more adequate $30b^2$ should be 0.2 or so. Substituting $4ab \doteq 2.3$ and $b^2 \doteq 0.006$ or $30b^2 \doteq 0.2$ into the basic formula, gives the average value of $4a^2 \doteq 5.24$.

[†] Star, * points at the group in question.

$-\text{CH}-$ of 2-type ($\text{C}-\text{C}^*-\text{C}-\text{C}-$) is denoted by "c", others ($\text{C}-\text{C}-\text{C}^*-\text{C}-\text{C}-$) by "c'".

iso-alkanes (2-type) $c: -\text{CH}-$

[Compounds]	[Basic Formula]	$[v_f(\theta=0.3)]$	[diff.]	$[2bc]$
1 2-methyl propane $\begin{array}{c} \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+c)^2$ $=9a^2+c^2+6ac=$ $(2-1)=b^2+6ab+2bc=$	10.40	2.2	-1.21
2 2-methyl butane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+b+c)^2$ $=9a^2+b^2+c^2+6ab+6ac+2bc=$ $(3-2)=3b^2+6ab+2bc=$	12.60	2.4	-1.04
3 2-methyl pentane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+2b+c)^2$ $=9a^2+4b^2+c^2+12ab+6ac+4bc=$ $(4-3)=5b^2+6ab+2bc=$	15.00	1.95	-1.50
4 2-methyl hexane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+3b+c)^2$ $=9a^2+9b^2+c^2+18ab+6ac+6bc=$ $(5-4)=7b^2+6ab+2bc=$	16.95	1.95	-1.51
5 2-methyl heptane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+4b+c)^2$ $=9a^2+16b^2+c^2+24ab+6ac+8bc=$	18.90		
6 2,3-dimethyl butane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	$(4a+2c)^2$ $=16a^2+16ac+4c^2=$ $(7-6)=b^2+8ab+4bc=$	14.20	2.20	-1.18
7 2,4-dimethyl pentane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	$(4a+b+2c)^2$ $=16a^2+b^2+4c^2+8ab+16ac+4bc=$ $(8-7)=3b^2+8ab+4bc=$	16.40	2.47	-1.05
8 2,5-dimethyl hexane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	$(4a+2b+2c)^2$ $=16a^2+4b^2+4c^2+16ab+16ac+8bc=$ $(9-8)=12b^2+16ab+8bc=$	18.87	3.13	-1.51
9 2,7-dimethyl octane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	$(4a+4b+2c)^2$ $=16a^2+16b^2+4c^2+32ab+16ac+16bc=$	22.00		

average $2bc \doteq -1.29$

Substituting $2bc$ obtained into the basic formula together with the known values of a^2 , b^2 and ab , gives c^2+6ac and c^2+4ac respectively.

A	B
$c^2+6ac=$ -1.41	$c^2+4ac=$ -1.70
-1.35	-1.65
-1.09	-1.53
-1.30	-1.76
-1.53	av. -1.66
av. -1.34	

$$2ac=(A-B)=0.32, c^2 \doteq -2.30$$

iso-alkanes (3-,4-, ... type)

Data are available for 3-methyl pentane, 3-methyl hexane, 3-methyl heptane and 4-(and 5-)methyl nonane only and they are insufficient as to the determination of ac' and c'^2 . Therefore, the following approximation technique was used.

[Compounds]	[Basic Formula]	$[v_f(\theta=0.30)]$	[diff.]	$[2bc']$
1 3-methyl pentane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+2b+c')^2$ $=9a^2+4b^2+c'^2+12ab+6ac'+4bc'=$ $(2-1)=3b^2+6ab+2bc'=$	14.4	3.1	-.35
2 3-methyl hexane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+3b+c')^2$ $=9a^2+9b^2+c'^2+18ab+6ac'+6bc'=$ $(3-2)=7b^2+6ab+2bc'=$	17.5	1.7	-1.76
3 3-methyl heptane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+4b+c')^2$ $=9a^2+16b^2+c'^2+24ab+6ac'+8bc'=$ $(4-3)/2=10b^2+6ab+2bc'=$	19.2	1.9	-1.58
4 4-methyl nonane $\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$(3a+6b+c')^2$ $=9a^2+36b^2+c'^2+36ab+6ac'+12bc'=$	22.9		

average $2bc' \doteq -1.23$

$$y(\theta) = f(\theta) - \Delta y$$

$$2bc': f(\theta) = -1.416\theta^3 - 2.0416\theta^2 - 3.3816\theta$$

$$6ac: f(\theta) = 3.1714\theta, 0 \leq \theta \leq 0.35$$

$$f(\theta) = -5.10 + 2.895, 0.35 \leq \theta \leq 0.45$$

$$f(\theta) = -336\theta^2 + 298.8\theta - 65.82, 0.45 \leq \theta \leq 0.55$$

$$f(\theta) = -75.6\theta + 38.46, 0.55 \leq \theta \leq 0.6$$

$$c'^2: f(\theta) = -23.5\theta - 0.125, 0 \leq \theta \leq 0.10$$

$$f(\theta) = -14.04\theta - 0.944, 0.15 \leq \theta \leq 0.40$$

$$f(\theta) = 332\theta^2 - 308\theta + 64.45, 0.45 \leq \theta \leq 0.60$$

$$g^2 + 10eg: f(\theta) = -9.5\theta^3 - 4.416\theta^2 - 5.463\theta$$

Fig. 3 Contact volume, $y(\theta)$, of $2bc'$, c'^2 , $6ac$ and $g^2 + 10eg$

$$y(\theta) = f(\theta) - \Delta y$$

$$2.5e^2: f(\theta) = 23.75\theta^3 - 1.4583\theta^2 + 20.9083$$

$$10be + 2bg: f(\theta) = -4.5\theta^3 + 5.583\theta^2 + 2.4867\theta$$

$$6ae + 6eg: f(\theta) = 21.6\theta^3 - 10.5\theta^2 + 12.53\theta$$

$$g^2 + 10ae + 2ag + 10eg: f(\theta) = 26.3\theta^3 - 10.83\theta^2 + 15.62\theta$$

Fig. 4 Contact volume, $y(\theta)$, of $2.5e^2$, $6ae + 6eg$, $10be + 2bg$ and $g^2 + 10ae + 2ag + 10eg$

$$y(\theta) = f(\theta) - \Delta y$$

$$h^2: f(\theta) = 9.16\theta^3 + 3.083\theta^2 + 2.9\theta$$

$$j^2: f(\theta) = 4.16\theta^3 + 3.75\theta^2 + 12.583\theta$$

$$2ah: f(\theta) = -19.16\theta^3 + 12.25\theta^2 + 7.5917\theta$$

$$2bh: f(\theta) = 5\theta^3 + 1.3\theta^2 + 0.316\theta$$

Fig. 5 Contact volume, $y(\theta)$, of h^2 , j^2 , $2ah$ and $2bh$

Average $c'^2 + 6ac'$ obtained by substituting the known values of a^2 , b^2 , ab , bc' , ... etc. into the above four basic formula were compared with $c'^2 + 6ac$ on all θ . Then, assume $6ac' \doteq 6ac$ and correlates c'^2 with c^2 . Similarly, assume $c'^2 \doteq c^2$ and correlates $6ac'$ with $6ac$. The result shows that $6ac' \doteq 6ac$ is more probable, and that the difference between $a-c'$ and $a-c$ contacts is small and $ac \doteq ac'$.

iso-alkanes (2,2-type) $\theta = 0.30$ $d: -\overset{|}{\underset{|}{\text{C}}}-$

[Compounds]	[Basic Formula]	$[v_r]$	[diff.]	[2bd]
1 2,2-dimethyl propane	$(4a+d)^2$			
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$= 16a^2 + d^2 + 8ad =$ $(2-1) = b^2 + 8ab + 2bd =$	11.9	2.70	-1.86
2 2,2-dimethyl butane	$(4a+b+d)^2$			
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$= 16a^2 + b^2 + d^2$ $+ 8ab + 8ad + 2bd =$ $(3-2) = 3b^2 + 8ab + 2bd =$	14.6	2.40	-2.18
3 2,2-dimethyl pentane	$(4a+2b+d)^2$			
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$= 16a^2 + 4b^2 + d^2$ $+ 16ab + 8ad + 4bd =$ $(4-3) = 5b^2 + 8ab + 2bd =$	17.0	2.00	-2.62
4 2,2-dimethyl hexane	$(4a+3b+d)^2$			
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	$= 16a^2 + 9b^2 + d^2$ $+ 24ab + 8ad + 6bd =$	19.0		

$$\text{average } 2bd \doteq -2.22$$

Substituting the known values of $16a^2$, b^2 , ab , bd , ... etc. into the above formula gives $d^2 + 8ad$.

$$d^2 + 8ad =$$

$$\begin{array}{r} -9.10 \\ -8.75 \\ -8.70 \\ -9.07 \\ \hline \text{av.} -8.91 \end{array}$$

aromatics

$$\theta = 0.30$$

(see opposite page.)

Substituting the above value into 10 gives $g^2 + 10eg$ of diphenyl methane as -2.44 and the average value of $g^2 + 10eg$ of 9 and 10 is -2.39 . Further substituting these values and all other known values of the contact volumes give the following values. $(g^2 + 10ae + 2ag + 10eg)_{\text{av.}} = 4.54$ (smoothed) and $10ae + 2ag = 6.93$ $(ae + eg)_{\text{av.}} = .56$

[Compounds]	[Basic Formula]	$[v_f]$	$[10be + 2bg]$
1 benzene	$(6e)^2 = 36e^2 =$	9.80	
2 toluene	$(5e + a + g)^2$ $= \frac{a^2 + 25e^2 + g^2 + 10ae + 2ag + 10eg}{g^2 + 10ae + 2ag + 10eg} =$	12.80	
3 ethyl benzene	$(3-2) = 10be + 2bg =$ $(a + b + 5e + g)^2$ $= \frac{a^2 + b^2 + 25e^2 + 2ab + g^2 + 10ae + 2ag + 2bg + 10be + 10eg}{g^2 + 10ae + 2ag + 10eg + 10be + 2bg} =$		.95
4 n-propyl benzene	$(4-3) = 10be + 2bg =$ $(a + 2b + 5e + g)^2$ $= \frac{a^2 + 4b^2 + 25e^2 + 4ab + g^2 + 10ae + 2ag + 4bg + 20be + 10eg}{g^2 + 10ae + 2ag + 10eg + 20be + 4bg} =$		1.15
5 n-butyl benzene	$(5-4) = 10be + 2bg =$ $(a + 3b + 5e + g)^2$ $= \frac{a^2 + 9b^2 + 25e^2 + 6ab + g^2 + 10ae + 2ag + 6bg + 30be + 10eg}{g^2 + 10ae + 2ag + 10eg + 30be + 6bg} =$		.93
6 n-hexyl benzene	$(6-5)/2 = 10be + 2bg =$ $(a + 5b + 5e + g)^2$ $= \frac{a^2 + 25b^2 + 25e^2 + 10ab + g^2 + 10ae + 2ag + 10bg + 50be + 10eg}{g^2 + 10ae + 2ag + 10eg + 50be + 10bg} =$		1.01
7 n-heptyl benzene	$(7-6) = 10be + 2bg =$ $(a + 6b + 5e + g)^2$ $= \frac{a^2 + 36b^2 + 25e^2 + 12ab + g^2 + 10ae + 2ag + 60be + 12bg + 10eg}{g^2 + 10ae + 2ag + 10eg + 60be + 12bg} =$		1.49
8 n-nonyl benzene	$(8-7)/2 = 10be + 2bg =$ $(a + 8b + 5e + g)^2$ $= \frac{a^2 + 64b^2 + 25e^2 + 16ab + g^2 + 10ae + 2ag + 80be + 16bg + 10eg}{g^2 + 10ae + 2ag + 10eg + 80be + 16bg} =$		1.08
9 biphenyl	$(10e + 2g)^2$ $= \frac{100e^2 + 4g^2 + 40eg}{g^2 + 10eg} = -2.30$	18.00	
10 diphenyl methane	$(10e + b + 2g)^2$ $= \frac{100e^2 + b^2 + 4g^2 + 20be + 40eg + 4bg}{g^2 + 10eg + 10be + 2bg} =$	21.80	
11 mesitylene	$10be + 2bg =$ $(3e + 3a + 3g)^2$ $= \frac{9e^2 + 9a^2 + 9g^2 + 18ae + 18ag + 18eg}{g^2 + 2ae + 2ag + 2eg} =$ $ae + eg = 0.54$		.95
12 o,m,p-xylene	$(4e + 2a + 2g)^2$ $= \frac{16e^2 + 4a^2 + 4g^2 + 16ae + 16eg + 8ag}{g^2 + 4ae + 4eg + 2ag} =$ $ae + eg = 0.58$	13.80	

average $(10be + 2bg) = 1.09$ (smoothed on the graph)

n-alcohols $\theta=0.30$, *j*: CH₃OH, *h*: -CH₂OH

[Compounds]	[Basic Formula]	[<i>v_f</i>]	[diff.]	[2 <i>bh</i>]
1 methanol	(<i>j</i>) ² = <i>j</i> ² =	4.30		
2 ethylene glycol	(2 <i>h</i>) ² =4 <i>h</i> ² =	5.30		
CH ₂ OH	<i>h</i> ² =	1.33		
3 ethanol	(<i>a</i> + <i>h</i>) ²			
CH ₃ CH ₂ OH	= <i>a</i> ² +2 <i>ah</i> + <i>h</i> ² =	5.60		
	(4-3)= <i>b</i> ² +2 <i>ab</i> +2 <i>bh</i> =		1.60	
	2 <i>bh</i> =			.46
4 <i>n</i> -propanol	(<i>a</i> + <i>b</i> + <i>h</i>) ²			
CH ₃ CH ₂ CH ₂ OH	= <i>a</i> ² + <i>b</i> ² + <i>h</i> ² +2 <i>ab</i> +2 <i>ah</i> +2 <i>bh</i> =	7.20		
	(5-4)=3 <i>b</i> ² +2 <i>ab</i> +2 <i>bh</i> =		1.50	
	2 <i>bh</i> =			.34
5 <i>n</i> -butanol	(<i>a</i> +2 <i>b</i> + <i>h</i>) ²			
CH ₃ CH ₂ CH ₂ CH ₂ OH	= <i>a</i> ² +4 <i>b</i> ² + <i>h</i> ² +4 <i>ab</i> +2 <i>ah</i> +4 <i>bh</i> =	8.70		
	(6-5)=5 <i>b</i> ² +2 <i>ab</i> +2 <i>bh</i> =		1.50	
	2 <i>bh</i> =			.33
6 <i>n</i> -amyl alcohol	(<i>a</i> +3 <i>b</i> + <i>h</i>) ²			
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	= <i>a</i> ² +9 <i>b</i> ² + <i>h</i> ² +6 <i>ab</i> +2 <i>ah</i> +6 <i>bh</i> =	10.20		
	(7-6)=7 <i>b</i> ² +2 <i>ab</i> +2 <i>bh</i> =		1.50	
	2 <i>bh</i> =			.32
7 <i>n</i> -hexyl alcohol	(<i>a</i> +4 <i>b</i> + <i>h</i>) ²			
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH	= <i>a</i> ² +16 <i>b</i> ² + <i>h</i> ² +8 <i>ab</i> +2 <i>ah</i> +8 <i>bh</i> =	11.70		
average 2 <i>bh</i> = .37				

Substituting the known values of 2*bh*, *a*², *b*², *ab*, ... etc. into the above basic formula gives the average value of *h*²+2*ah* and 2*ah* as follows.

$$\begin{aligned}
 h^2 + 2ah &= 4.29 \\
 4.37 & \quad (h^2 + 2ah)_{\text{av.}} = 4.32 \\
 4.35 & \quad 2ah = 4.32 - 1.33 = 2.99 \\
 4.31 & \\
 4.25 &
 \end{aligned}$$

The contact volumes obtained in this way are plotted in Figs. 1-5 between $\theta=0-0.60$. The average error of the molal volumes estimated using the figures and *V_o* data for some fifty compounds is around 0.5%. (*V_o* data are available in Table 2¹⁹.)

Application

Example 1 M.p., c.p. and *V_o* of 3-ethyl pentane are -118.8°C, 267.4°C and 122.9 cc/g-mol, respectively. What is the molal volume of 3-ethyl pentane at -40°C and 80°C?

At -40°C

$$\theta = \frac{118.8 - 40.0}{267.4 + 118.8} = .204$$

v_f: Using Figs. 1-3,

[At $\theta = .204$]

9 <i>a</i> ²	3.48 × 9/4	=	7.83
9 <i>b</i> ²	0.00 × .9	=	0.00
<i>c'</i> ²		=	-1.98
18 <i>ab</i>	1.51 × 18/4	=	6.80
6 <i>ac'</i>	.45 × 3	=	1.35
6 <i>bc'</i>	-.775 × 3	=	-2.33
			11.67
			<i>V_o</i> = 122.90
			<i>V_t</i> = 134.57
			(<i>V_t</i>) _{exp} = 133.6, error = .74%

At 80°C

$$\theta = \frac{118.8 + 80.0}{267.4 + 118.8} = .515$$

[At $\theta = .515$]

9 <i>a</i> ²	11.0 × 9/4	=	24.75
9 <i>b</i> ²	.113 × .9	=	.10
<i>c'</i> ²		=	-3.15
18 <i>ab</i>	4.32 × 18/4	=	19.44
6 <i>ac'</i>	-1.0 × 3	=	-3.00
6 <i>bc'</i>	-2.39 × 3	=	-7.17
			30.97

$$V_o = 122.90$$

$$V_t = 153.87$$

$$(V_t)_{\text{exp}} = 155.56, \text{ error} = 1.09\%$$

Example 2 M.p., c.p. and V_t at 20°C of 2,7-dimethyl octane are -52.5°C, 323.6°C and 196.48 cc/g-mole respectively.

What is the V_t at 86°C?

$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ | \qquad \qquad | \\ \text{C} \qquad \qquad \text{C} \end{array}$
 At 20°C, $\theta = .193$. At 86°C, $\theta = .368$. 2,7-dimethyl octane has 4a, 4b and 2c, and the basic formula should be written as

$$(4a + 4b + 2c)^2 = 16a^2 + 16b^2 + 4c^2 + 32ab + 16ac + 16bc$$

[At $\theta = .193$]

$$\begin{array}{rcl} 16a^2 & 3.28 \times 4 & = 13.12 \\ 16b^2 & & = 0 \\ 4c^2 & -1.25 \times 4 & = 5.00 \\ 32ab & 1.42 \times 32/4 & = 11.36 \\ 16ac & .42 \times 16/6 & = 1.12 \\ 16bc & -.83 \times 16/2 & = -6.64 \\ \hline & & 13.96 \end{array}$$

$$(V_t)_{20} = 196.48$$

$$V_o = 182.52$$

[At $\theta = .368$]

$$\begin{array}{rcl} 16a^2 & 6.715 \times 4 & = 26.86 \\ 16b^2 & .80 \times 1.6 & = 1.28 \\ 4c^2 & -2.975 \times 4 & = -11.90 \\ 32ab & 2.91 \times 8 & = 23.28 \\ 16ac & 1.10 \times 16/6 & = 2.93 \\ 16bc & -1.64 \times 16/2 & = -13.12 \\ \hline & & 29.33 \end{array}$$

$$V_o = 182.52$$

$$(V_t)_{86} = 211.85$$

$$(V_t)_{\text{exp}} = 211.11$$

$$\text{error} = 0.34\%$$

Example 3 1-Methyl-4-ethyl benzene have m.p., c.p., V_o and V_t at 20°C as follows: m.p. = -62.4°C, c.p. = 370.0°C, $V_o = 128.3$ cc/g-mole and $(V_t)_{20} = 139.32$ cc/g-mole.

What is $(V_t)_{162} = ?$

$$\begin{array}{c} \text{C} \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}-\text{C} \\ \qquad \qquad \qquad | \\ \qquad \qquad \qquad \text{C} \end{array}$$

$$v_f = (2a + b + 2g + 4e)^2$$

$$= 4a^2 + b^2 + 4g^2 + 16e^2 + 4ab$$

$$+ 8ag + 16ae + 8be + 4bg + 16eg$$

$$\theta_{20} = .191 \text{ and } \theta_{162} = .519$$

In the above equation, $4g^2 + 16ae + 8ag + 16eg$ and $8be + 4bg$ are not available in Fig. 4. But the former can be divided by 4 and then the difference obtained between the divided and $g^2 + 10ae + 2ag + 10eg$ in Fig. 4, which is $6ae + 6eg$. Therefore, subtract $6ae + 6eg$ in Fig. 4 from the difference and get the answer.

For $8be + 4bg$, however, sophisticated treatment is necessary. First, get $10be + 2bg$ on Fig. 4 and multiply

it by 2. Then, subtract $8be + 4bg$ from $2(10be + 2bg)$, which is $2(6be)$. Looking over the curve $10be + 2bg$ between $\theta = .191 - .519$ on Fig. 4, one may imagine that the components $10be$ and $2bg$ both must also be monotonous upward curves, which means that $2(6be)/2(10be + 2bg)$ can be taken approximately as constant.

[At $\theta = .191$]

$$\begin{array}{rcl} 4a^2 & & = 3.24 \\ b^2 & & = 0 \\ 16e^2 & .40 \times 16/2.5 & = 2.56 \\ 4ab & & = 1.40 \\ 4(g^2 + 10ae + 2ag + 10eg) & & = 11.48 \\ -4(6ae + 6eg) & -2.18 \times 4 & = -8.72 \\ 2(10be + 2bg) & .625 \times 2 & = 1.25 \\ \hline & & 11.21 \\ -((V_t)_{20} - V_o) & & = -11.00 \\ 2(6be) & & = .21 \end{array}$$

$$\frac{2(6be)}{2(10be + 2bg)} = .168$$

[At $\theta = .519$]

$$\begin{array}{rcl} 4a^2 & & = 11.16 \\ b^2 & & = .01 \\ 16e^2 & 1.37 \times 16/2.5 & = 8.77 \\ 4ab & & = 4.36 \\ 4(g^2 + 10ae + 2ag + 10eg) & & = 35.12 \\ -4(6ae + 6eg) & -6.85 \times 4 & = -27.40 \\ 2(10be + 2bg) & 2.19 \times 2 & = 4.38 \\ -2(6be) & -4.38 \times .168 & = -.74 \\ \hline & & 35.66 \end{array}$$

$$V_o = 128.30$$

$$163.96$$

$$(V_t)_{162} = 162.56$$

$$\text{error} = .86\%$$

Result and Discussion

The work is essentially the continuation of the previous work of the author¹⁸. In the calculation of contact volumes, it has been found that

- In accordance with the degree of the freedom of the atomic groups $a > b > c > d$, the values of the the contact volumes are arranged as $a^2 > ab > b^2$ $ac \dots > d^2$ for chain compounds.
- No difference was found among *o*-, *m*-, and *p*- of aromatics. In *n*-alcohols, -OH cannot be looked upon as a group and CH_3OH , $-\text{CH}_2\text{OH}$, $-\text{CHOH} \dots$ must be taken as groups.
- In chain compounds 2-type isomer differs from other isomers.
- Many compounds are in lack of molal volume data in the region below 0°C and many V_o were estimated by extrapolation. The larger errors are common in the region of larger θ , because of

the sharp change of the curves in the region, especially in $\theta > 0.60$.

- e) Physical meaning of the negative values of some contact volumes may be explained as 1) the reduction of free space at the contact from that in the crystal state and 2) reduction of the activity of the group "a" branching from "c" or "d".

Nomenclature

$a, b, c, d, e, f, g, h, j, \dots$ etc. = atomic group (see Figs.)

$a^2, b^2, 4ab, 2bd, \dots$ etc. = contact volume (local molal free volume)

t_c	= critical temperature	[°C]
t_o	= melting point	[°C]
v_f	= liquid molal free volume	[cc/g-mol]
V_t	= liquid molal volume at temperature t	[cc/g-mol]
V_o	= liquid molal volume at melting point	[cc/g-mol]
θ	= energy level parameter defined by $(t-t_o)/(t_c-t_o)$	[—]

<Subscripts>

av.	= average
diff.	= difference
exp.	= experimental

Literature Cited

- 1) Annual Review of Physical Chemistry, **16**, 147 (1965).
- 2) "Bussei Teisu", Vol. I~X, Maruzen (1967~1972).
- 3) Buerger, M. J.: "X-ray Crystallography" (1953).
- 4) Chow, W. H. and J. A. Bright, Jr.: *Chem. Eng. Prog.*, **49**, 175 (1953).
- 5) Compton, A. H. and S. K. Allison: "X-rays in Theory and Experiment", John Wiley & Sons Inc. (1936).
- 6) Debye, P. and H. Mencke: *Phys. Zeits.*, **31**, 797 (1930).
- 7) Driesbach, R. R.: "Phys. Properties of Chem. Compds", American Chemical Society (1955).
- 8) Egloff, G.: "Physical Constants of Hydrocarbons", Vol. I~V, Reinhold (1953).
- 9) Eyring, H.: *J. Chem. Phys.*, **4**, 283 (1936).
- 10) Eyring, H. *et al.*: *Trans. Faraday Society*, **33**, 73 (1937).
- 11) Gold, P. I. and G. J. Ogle: *Chem. Eng.*, Nov. **18**, 170 (1968).
- 12) Johnson, A. I. and C. J. Huang: *Can. J. Tech.*, **33** (1-6), 421 (1955).
- 13) Kirkwood, J. G.: *J. Chem. Phys.*, **7**, 919 (1939), **18**, 380 (1950).
- 14) Kudchadker, A. P. *et al.*: *Chem. Review*, **68**, 659 (1968).
- 15) Lu, B. C. Y. *et al.*: *J. Chem. Eng. Data*, **18**, 241 (1973).
- 16) Menke, H.: *Phys. Zeits.*, **33**, 593 (1932).
- 17) Orwell, R. A. and P. J. Flory: *J. Am. Chem. Soc.*, **89**, 6822 (1967).
- 18) Ouyang, R.: *J. Chem. Eng. Japan*, **7**, 237 (1974).
- 19) Ouyang, R.: *ibid.*, **9**, 179 (1976).
- 20) Pitzer, K. S.: *J. Chem. Phys.*, **7**, 583 (1939).
- 21) Prins, J. A.: *Z. F. Physik*, **56**, 617 (1929).
- 22) Rackett, H. G.: *J. Chem. Eng. Data*, **15**, 514 (1970).
- 23) Reid, R. C. and T. K. Sherwood: "The Properties of Gases and Liquids" 2nd Ed., McGraw-Hill (1968).
- 24) "Selected Values of Properties of Hydrocarbons": U.S. Dept. of Commerce, Nat'l Bureau of Standard (1947).
- 25) Timmerman, J.: "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, 1st Ed. (1950), 2nd Ed. (1966).
- 26) Tamada, T. and R. D. Gunn: *J. Chem. Eng. Data*, **18**, 234 (1973).