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# VAN DER WAALS' VOLUMES FROM DENSITIES AND VAPORIZATION ENTHALPIES

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## ABSTRACT

The authors propose a new criterion for the evaluation of the van der Waals' volumes $V_w$ for liquid substances. This criterion derives from simple hypotheses of interdependence between the van der Waals' volumes, the molar volumes, $V^0$, and the vaporization enthalpies, $\Delta H_v$. For all the cases examined the estimated values of $V_w$ are thus slightly dependent on temperature and agree with those derived from crystallographic data. It is remarkable that water presents a minimum in its $V_w$ value at 328 K in analogy with the behaviour of the electron polarizability. For some selected organic substances an exponential empirical correlation has been found between the vaporization entropy $(\Delta S_v)_T$ and the $[V_w/(V^0 - V_w)]_T$ ratio.

## INTRODUCTION

The so-called van der Waals' volume $V_w$ is the volume occupied by a molecule impenetrable to other molecules at the ordinary energy levels. It is a useful parameter in the study of the chemical and physical properties of condensed phases and, as proposed by some authors, in the evaluation of solute—solvent interaction [1—5].

Kitaigorodsky [6], Edward [7a,b] and Bondi [8] reported some methods of calculation of $V_w$ on the basis of crystallographic data. Single atoms in a non-bonded state are assumed to behave as spheres with radius $r_w$ equal to half the distance between their centres. These spheres intersect at distances from their centres equal to the so-called covalent radius when the atoms are bonded with the same or different atoms.

In this paper, we report a new criterion for the estimation of the van der Waals' volumes of liquid substances starting from the data of densities and vaporization enthalpies.

## BASIC REMARKS

Let us indicate the molar volume of a liquid substance at temperature $T$ as $(V^0)_T$ and the molar volume as calculated from the van der Waals dimensions evaluated by X-ray or neutron diffraction methods as $V_w = N_A v_w$, then the difference

$$(V_e)_T = (V^0 - V_w)_T \tag{1}$$

is called the "empty volume".

Now, we assume that, at all temperatures, the vaporization enthalpy $(\Delta H_v)_T$, which includes all energetic effects of the structural destruction of a liquid, is linearly dependent on the ratio $(V_w/V_e)_T$ that should be considered as an index of the entity of molecular interactions.

Hence, we assume that

$$(\Delta H_v)_T = K(V_w/V_e)_T \tag{2}$$

Now, from a review of the $(V^0)_T$ and $(V_w)$ data reported in the literature [1,3,7(b)], one observes that, at the boiling point $T_B$, the empty volume is frequently about 50% of molar volume and therefore the $(V_w/V_e)_{T_B}$ ratio is unity.

Let us generalize this observation and put the constant $K$ of eqn. (2) equal to $(\Delta H_v)_{T_B}$, consequently the expression

$$(V_w)_T = (V^0)_T/[1 + (\Delta H_v)_{T_B}/(\Delta H_v)_T] \tag{3}$$

is derived from eqns. (1) and (2). The validity of eqn. (3) is illustrated in the following sections.

## VAN DER WAALS' PARAMETERS OF SOME LIQUID SUBSTANCES

### *Mercury*

The van der Waals' volumes $(V_w)_T$ and diameters $(2r_w)_T$ of liquid Hg calculated by eqn. (3) from $(\Delta H_v)$ and $(V^0)_T$ data in a wide temperature range

TABLE 1

Hg — van der Waals' parameters [a]

| $T$ (K) | $V^0$ (cm$^3$ mol$^{-1}$) | $(\Delta H_v)_T$ (kcal mol$^{-1}$) | $V_w$ (cm$^3$ mol$^{-1}$) | $2r_w$ [b] (Å) |
|---|---|---|---|---|
| 293.16 | 14.80 | 14.615 | 7.53 | $2.88_0$ |
| 333.16 | 14.91 | 14.548 | 7.56 | $2.88_3$ |
| 373.16 | 15.02 | 14.484 | 7.60 | $2.88_8$ |
| 448.16 | 15.24 | 14.370 | 7.68 | $2.89_8$ |
| $630 = T_B$ | 15.75 | 14.131 | 7.87 | $2.92_2$ |

[a] Densities and enthalpies of vaporization from ref. 10, pp. 60, 74, 75.

TABLE 2

$H_2O$ — van der Waals' parameters [a]

| $T$ (K) | $V^0$ ($cm^3$ $mol^{-1}$) | $(\Delta H_v)_T$ (kcal $mol^{-1}$) | $V_w$ ($cm^3$ $mol^{-1}$) | $2r_w$ (Å) |
|---|---|---|---|---|
| 273.16 | 18.01823 | 10.7669 | 9.4710 | 3.106 |
| 278.16 | 18.01599 | 10.7165 | 9.4487 | 3.104 |
| 283.16 | 18.02075 | 10.6660 | 9.4300 | 3.102 |
| 293.16 | 18.04772 | 10.5647 | 9.4012 | 3.099 |
| 303.16 | 18.09404 | 10.4629 | 9.3816 | 3.097 |
| 313.16 | 18.15661 | 10.3604 | 9.3694 | 3.095 |
| 323.16 | 18.23344 | 10.2569 | 9.3633 | 3.095 |
| 328.16 | 18.27677 | 10.2048 | 9.3623 | 3.095 |
| 333.16 | 18.32321 | 10.1523 | 9.3624 | 3.095 |
| 346.16 | 18.42501 | 10.0463 | 9.3661 | 3.095 |
| 353.16 | 18.53829 | 9.9386 | 9.3738 | 3.096 |
| 363.16 | 18.66269 | 9.8289 | 9.3849 | 3.097 |
| 373.16 | 18.79815 | 9.7167 | 9.3991 | 3.099 |

[a] Densities and enthalpies of vaporization from ref. 14, pp. 67—69.

are summarized in Table 1.

The $(2r_w)_T$ values listed in the fifth column are in good agreement with the distances of closest approach reported for the Hg atom by many authors. Indeed, Lukesh et al. [9], reported values ranging between 2.87 and 3.00 Å.

### *Water*

Data concerning water in the temperature range 273—373 K are reported in Table 2. [The number of significant figures in the $(V_w)_T$ and $(2r_w)_T$ values are allowed by the accuracy in density and enthalpy data reported by literature [14].]

Two remarks must be emphasized

(a) The molar diameter for $H_2O$ (3.1 Å) calculated by eqn. (3) is in good agreement with the oxygen-to-oxygen first nearest neighbour distances experimentally found in liquid water (2.9—3.1 Å). (In ice this distance is shorter, namely 2.67 Å [11].)

(b) The van der Waals' volume is slightly temperature-dependent and a minimum occurs at 328 K even though $(V^0)_T$ and $(\Delta H_v)_{T_B}/(\Delta H_v)_T$ ratio increase with increasing temperature.

The electron polarizability—temperature curve also exhibits a minimum at the same temperature [12]. According to Bockris and Conway [13], this minimum is interpreted in terms of the entity of thermal destruction of structural cavities and the degree of occupation of the cavities by interstitial molecules.

$V_w$ and polarizability should be in some way correlated. Thus the validity of eqn. (3) is substantiated by the analogy of their temperature-dependence.

TABLE 3

Metallic elements — van der Waals' parameters at the melting point $T_M$ and boiling point $T_B$

| | Li | Na | K | Rb | Cs | Zn | Cd |
|---|---|---|---|---|---|---|---|
| $T_M/T_B$ (K) | 459/1640 | 371/1187 | 336.4/1052 | 312/952 | 301.9/963 | 692.7/1180 | 594.1/1040 |
| $(V^0)_T$ (cm$^3$ mol$^{-1}$)[a] | 13.40/17.47 | 24.79/31.03 | 47.73/59.85 | 58.40/72.75 | 72.36/91.08 | 9.92/10.68 | 14.02/- |
| $(\Delta H_v)_T$ (kcal mol$^{-1}$) | 34.88/32.48 | 25.11/23.40 | 20.51/18.88 | 19.95/18.11 | 18.32/16.32 | 27.43/28.66 | 24.81/23.86 |
| $(V_w)_T$ (cm$^3$ mol$^{-1}$) | 6.94/8.74 | 12.83/15.51 | 24.85/29.92 | 30.62/36.37 | 38.29/45.54 | 5.07/5.34 | 7.15/7.77 |
| $2r_w$ (Å) | 2.80/3.02 | 3.44/3.66 | 4.28/4.56 | 4.60/4.86 | 4.94/5.24 | 2.52/2.56 | 2.82/2.90 |
| $l_0$ (Å)[b] | 3.03 | 3.72 | 4.50 | 4.86 | 5.25 | 2.65[c] | 2.97[c] |
| $\Delta V_{wr} = \dfrac{(V_w)_{T_B} - (V_w)_{T_M}}{(V_w)_{T_M}}$ | 0.26 | 0.21 | 0.20 | 0.19 | 0.19 | 0.05 | 0.08 |
| $\alpha_W = \dfrac{\Delta V_{wr}}{T_B - T_M} \times 10^4$ | 2.19 | 2.56 | 2.85 | 2.93 | 2.86 | 1.1 | 1.87 |

[a] Densities and enthalpies of vaporization from ref. 15.

[b] Interatomic distances from ref. 16, p. 447.

[c] Shortest distance of hexagonal cell.

### *Selected metallic substances*

In Table 3 the van der Waals' parameters of some metallic elements are summarized. They have been calculated at only two temperatures: the melting point $T_M$, and the boiling point $T_B$.

In the temperature range reported above, experimental data of crystallographic radii are lacking, and hence a direct comparison with our results is not possible. However, it is remarkable that, at the temperature $T_B$ our $2r_w$ values are in good agreement with the interatomic distances, $l_0$, extrapolated at 0 K [16] (compare the fifth and sixth rows of Table 3). Furthermore, from the data reported in Table 3 alkali metals show $V_w$ values which are more temperature-dependent than Hg, $H_2O$, Zn and Cd.

This behaviour seems less fortuitous if one observes that the relative variations of $V_w$ and the average expansion coefficients in the $T_B$—$T_M$ range are constant along the series of alkali metals (compare data in seventh and eighth columns of Table 3).

### *Nonmetallic elements*

Table 4 refers to some non-metallic elements. The volumes $V_w$ are estimated only at the boiling point in the usual way by eqn. (3) which, at this temperature, reduces to

$$(V_w)_{T_B} = (V^0)_{T_B}/2$$

The radii $(r_w)_{TB}$ of biatomic molecules are obtained by simple geometrical considerations which are based on the correlation between volumes and half bond lengths. Also in this case there is a good agreement between calculated and observed average values for $r_w$ as reported by Bondi [8] (see the sixth row in Table 4).

The larger value for the hydrogen atom should be justified on the basis of Pauling's assumption that in directions other than that of the covalent bond, the electrons in an atom are in almost the same environment as those of the corresponding anion; therefore, the van der Waals' and anions radii are the same. Literature values for anion $H^-$ range between 1.5 and 1.7 Å, in good agreement with our value in Table 4.

### *Organic substances*

The parameters of the linear equations which correlate $(V^0)_{298}$ and $(V_w)_{298}$ volumes of some organic substances to the number ($n$) of —$CH_2$ groups in their molecules are reported in Table 5. The group contributions to $(V_w)_{298}$ values are derived from the appropriate parameters and are listed in Table 6. Bondi's values [8], also reported in Table 6, are in good agreement with all our data except —OH, =NH and I.

For —OH and =NH groups, Bondi's values indeed need correction because of the formation of hydrogen bonds which reduce the van der Waals' volume according to their number and length. Our values may be interpreted as

TABLE 4

Nonmetallic elements — van der Waals' parameters at the boiling point $T_B$

| | $H_2$ | Ne | Ar | Kr | Xe | $O_2$ | $N_2$ | $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_B$ (K) | 20.39 | 27.09 | 87.29 | 119.8 | 165.02 | 90.177 | 77.36 | 85.02 | 239.10 | 332.62 | 458.39 |
| $V^0$ [a] (cm$^3$ mol$^{-1}$) | 28.40 | 16.72 | 28.67 | 38.90 [e] | 56.15 | 28.07 | 34.65 | 25.12 | 45.45 | 54.58 | 68.30 |
| $V_w$ (cm$^3$ mol$^{-1}$) | 14.20 | 8.36 | 14.34 | 19.95 | 28.07 | 14.03 | 17.33 | 12.56 | 22.73 | 27.29 | 34.15 |
| $l$ [b] (Å) | 0.7461 | — | — | — | — | 1.208 | 1.098 | 1.42 | 1.98 | 2.27 | 2.715 |
| $r_w$ [c] (Å) | 1.61 | 1.49 | 1.78 | 1.99 | 2.23 | 1.52 | 1.67 | 1.43 | 1.72 | 1.81 | 1.93 |
| $r_w$ [d] (Å) | 1.20 | 1.54 | 1.88 | 2.02 | 2.18 | 1.52 | 1.6—1.7 | 1.47 | 1.75 | 1.85 | 1.96 |

[a] Densities from ref. 17, Vol. III, pp. 1021, 1105, 1173.

[b] Bond lengths from ref. 17, Vol. I, pp. 5, 20, 178; Vol. III, pp. 687, 708.

[c] Van der Waals' radii calculated from $V_w$ and bond lengths.

[d] Mean values of van der Waals radii from ref 8.

[e] Molar volumes from ref. 16, p. 408.

TABLE 5

Organic substances — parameters of linear equations [a]

| | | $(V^0)_{298} = a + b\,n(\mathrm{CH_2})$ | | $(V_w)_{298} = a_w + b_w n(\mathrm{CH_2})$ | |
|---|---|---|---|---|---|
| | | $a$ | $b$ | $a_w$ | $b_w$ |
| Alkanes | $(C_5-C_{10})$ | 67.82 | 15.98 | 27.43 | 10.36 |
| Alkenes | $(C_5-C_9)$ | 78.28 | 15.93 | 34.58 | 10.34 |
| Prim. alcohols | $(C_2-C_8)$ | 44.03 | 16.65 | 19.46 | 10.34 |
| Prim. monoamines | $(C_3-C_8)$ | 49.90 | 16.55 | 23.94 | 9.33 |
| Sec. monoamines | $(C_4-C_8)$ | 71.30 | 16.58 | 33.36 | 10.32 |
| Alkane ethers | $(C_4-C_{10})$ | 71.95 | 16.42 | 32.64 | 9.92 |
| Monochlorinated hydrocarbons | $(C_3-C_5)$ | 55.91 | 16.41 | 25.19 | 10.07 |

[a] Densities and enthalpies of vaporization from ref. 14.

including the mean effects of these bonds.

For the iodine atom our value differs by about 2% from the 1/2 $V_w$ value calculated as previously reported for inorganic iodine (Table 4), whereas Bondi's value differs more remarkably.

Two further observations may be derived from the $V_w$ vs. temperature dependence.

(a) Evaluating $(\Delta H_v)_T$ by a Watson [18] type equation

$$(\Delta H_v)_T = (\Delta H_v)_{T_B}[(T_c - T)/(T_c - T_B)]^m \tag{4}$$

where $T_c$ = critical temperature, and $m$ = 0.4073, 0.3970 and 0.4191 for alkanes, alkenes and alcohols, respectively, and evaluating $(V^0)_T$ by a

TABLE 6

Group contributions to the van der Waals' volumes at 298.16 K

| Group | Criteria for evaluation [a] | $V_w$ (cm$^3$ mol$^{-1}$) | |
|---|---|---|---|
| | | Our data | Bondi's data [b] |
| $-\mathrm{CH_3}$ | 1/2 $a_w$ (alkanes) | 13.72 | 13.67 |
| $=\mathrm{CH_2}$ | Averaged $b_w$ parameters | 10.30 | 10.23 |
| $-\mathrm{CH{=}CH_2}$ | $a_w$ (alkenes) — $V_w(\mathrm{CH_3})$ | 20.86 | 21.07 |
| $-\mathrm{OH}$ | $a_w$ (alcohols) — $V_w(\mathrm{CH_3})$ | 5.74 | 8.04 |
| $-\mathrm{NH_2}$ | $a_w$ (prim. amines) — $V_w(\mathrm{CH_3})$ | 10.22 | 10.54 |
| $=\mathrm{NH}$ | $a_w$ (sec. amines) — $2V_w(\mathrm{CH_3})$ | 5.92 | 8.08 |
| $=\mathrm{O}$ | $a_w$ (alkane ethers) — $2V_w(\mathrm{CH_3})$ | 5.21 | 5.20 |
| $-\mathrm{Cl}$ | $a_w$ (chlorinated hydrocarbons) — $V_w(\mathrm{CH_3})$ | 11.47 | 11.62 |
| $-\mathrm{Br}$ | From $V_w$ of brominated and iodinated hydrocarbons minus $V_w(\mathrm{CH_3})$ and $V_w(\mathrm{CH_2})$ group contributions | 13.78 | 14.4 |
| $-\mathrm{I}$ | | 17.44 | 19.18 |

[a] $a_w$ and $b_w$ parameters from Table 5.
[b] From ref. 8.

TABLE 7

Hexane — entropy of evaporation and fluctuation volume

| $T$ (K) | $(\Delta S_v)_T$ [a]<br>(u.s.) | $(V_w)_T$ [b]<br>($cm^3$ $mol^{-1}$) | $(V_e)_T$ [b]<br>($cm^3$ $mol^{-1}$) | $(V_0)_T$ [c]<br>($cm^3$ $mol^{-1}$) | $(V_g)_T$ [d]<br>($cm^3$ $mol^{-1}$) | $\frac{(\Delta S_v)_T}{R \ln\left(\frac{V_g}{V_0}\right)_T}$ |
|---|---|---|---|---|---|---|
| 341.90 = $T_B$ | 20.17 | 70.66 | 70.66 | 0.93 | 28056 | 0.98 |
| 336.90 | 20.71 | 70.44 | 69.60 | 0.91 | 32432 | 0.99 |
| 331.90 | 21.28 | 70.24 | 68.58 | 0.87 | 37824 | 1.00 |
| 326.90 | 21.85 | 70.04 | 67.60 | 0.84 | 44066 | 1.01 |
| 298.16 | 25.45 | 68.94 | 62.60 | — | — | — |

[a] From eqn. (4).

[b] From eqns. (1) and (3)–(5).

[c] From eqn. (7) assuming $(S)_T = (S)_{298} \left|\frac{(V_w)_T}{(V_w)_{298}}\right]^{2/3}$

[d] $V_g = (RT)/p$, with $p$ calculated by $\ln p = -B/(C + T)$, and $A$, $B$, $C$ from ref. 14.

Bowden and Jones [19] type equation

$$(V^0)_T = [(\Delta H_v)_{298}/(\Delta H_v)_T]^n (V^0)_{298} \qquad (5)$$

where $n = 0.7445$, $0.7524$ and $0.6145$ for alkanes, alkenes and alcohols, respectively, it is possible, by means of eqn. (3), to find the following exponential correlation between vaporization entropy $(\Delta S_v)_T$ and the $(V_w/V_e)_T$ ratio

$$(\Delta S_v)_T = A \exp[B(V_w/V_e)_T] \qquad (6)$$

where $A = 1.9079$ and $B = 2.3615$ for alkanes and alkenes (with a correlation coefficient of 0.997) and $A = 2.6106$ and $B = 2.3143$ for alcohols (with a correlation coefficient of 0.991). The interdependence established by eqn. (6), however, is not to be expected only on the basis of eqn. (3).

(b) Assuming 1.70 Å for the carbon radius, 1.50 Å for the oxygen radius and average bond lengths [20] of 1.08 Å for C—H, 1.53 Å for C—C and 1.43 Å for C—O, the contribution to surface area $(S)_{298}$ from calculated $(V_w)_{298}$ values, are $2.13 \times 10^9$, $1.34 \times 10^9$, $2.68 \times 10^9$ cm$^2$ mol$^{-1}$, respectively, for $-CH_3$, $=CH_2$ and $-CH_2OH$ groups.

Furthermore, assuming that the surface area increases with temperature as $(V_w)^{2/3}$, it is possible to check that at $T_B$ the so-called fluctuation volume, i.e., the volume swept out by the centre of gravity of the molecule as a result of its thermal vibrations, if calculated according to Bondi [1] as

$$(V_0)_{T_B} = \tfrac{4}{3}\pi(V_e/S)^3_{T_B} N_A \qquad (7)$$

is, for alkanes, in good agreement with the fluctuation volume $(V_l)_{T_B}$ calculated by the equation

$$(V_l)_{T_B} = \{V_{(g)} \exp[\Delta S_v/R]\}_{T_B} \qquad (8)$$

As illustrated in Table 7 for hexane, for example, this agreement can also be observed at least down to 15° below the boiling point if $(Vg)_T$ values are calculated from the vapour pressure—temperature data, using an Antoine-type [21] equation.

Conversely, analogous calculations for alcohols reveal, in the same temperature range, a mean constant ratio between $(\Delta S_v)_T$ and $R \ln(V_g/V_0)_T$ equal to 1.24.

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