Atomic Dimensions from the Coefficients of Compressibility and Thermal Expansion

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properties of any phosphorus compound whose entropy and heat of formation are known.
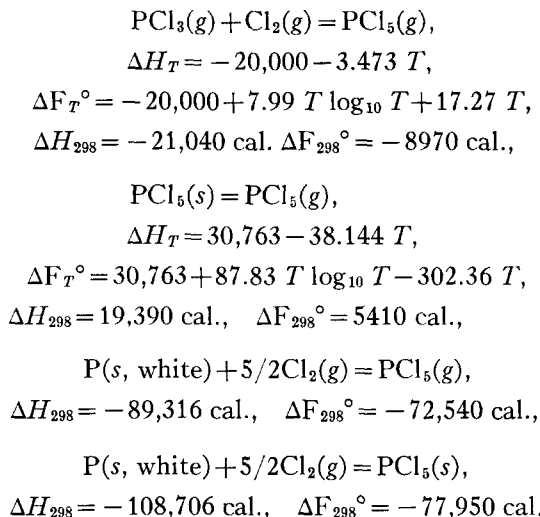
Phosphorus trichloride

The heats of formation[7] and vaporization[8] of PCl_3 are 75,900 cal. and -7620 cal., respectively, and the free energy of vaporization is 1080 cal. at 25°C. The entropy of $PCl_3(g)$ has been calculated[1] to be 74.7 cal./deg. One may then write:

$$P(s, \text{white}) + 3/2 Cl_2(g) = PCl_3(l),$$
$$\Delta H = -75,900 \text{ cal.,} \quad \Delta F°_{298} = -64,650 \text{ cal.,}$$
$$P(s, \text{white}) + 3/2 Cl_2(g) = PCl_3(g),$$
$$\Delta H = -68,280 \text{ cal.,} \quad \Delta F°_{298} = -63,570 \text{ cal.}$$
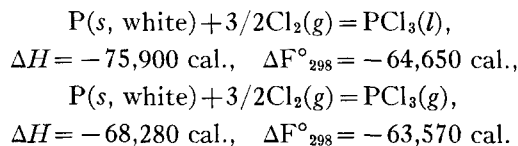
Phosphorus pentachloride

Holland[9] has made careful equilibrium measurements on the reaction $PCl_3(g) + Cl_2(g) = PCl_5(g)$ over the temperature range 440°–630° and his results have been recalculated by Nernst.[10] The vapor pressures of $PCl_5(s)$ have been carefully measured by Smith and Lombard.[11] From these results, together with those obtained above, the following thermochemical equations may be written:

[7] Berthelot and Longuinine, Ann. d. chim. phys. (5) **6**, 307 (1875); Thomsen, Ber. **16**, 37 (1883); J. Ogier, Comptes rendus **87**, 210 (1878).
[8] Regnault, Mem. de. l'acad. Sciences (France) **26**, 339 (1862).
[9] C. Holland. Zeits. f. Elektrochemie **18**, 234 (1913).
[10] W. Nernst. Zeits. f. Elektrochemie **22**, 37 (1916).
[11] Alex. Smith and R. H. Lombard, J. Am. Chem. Soc. **37**, 2055 (1915).

$$PCl_3(g) + Cl_2(g) = PCl_5(g),$$
$$\Delta H_T = -20,000 - 3.473\,T,$$
$$\Delta F_T° = -20,000 + 7.99\,T \log_{10} T + 17.27\,T,$$
$$\Delta H_{298} = -21,040 \text{ cal.} \quad \Delta F_{298}° = -8970 \text{ cal.,}$$

$$PCl_5(s) = PCl_5(g),$$
$$\Delta H_T = 30,763 - 38.144\,T,$$
$$\Delta F_T° = 30,763 + 87.83\,T \log_{10} T - 302.36\,T,$$
$$\Delta H_{298} = 19,390 \text{ cal.,} \quad \Delta F_{298}° = 5410 \text{ cal.,}$$

$$P(s, \text{white}) + 5/2 Cl_2(g) = PCl_5(g),$$
$$\Delta H_{298} = -89,316 \text{ cal.,} \quad \Delta F_{298}° = -72,540 \text{ cal.,}$$

$$P(s, \text{white}) + 5/2 Cl_2(g) = PCl_5(s),$$
$$\Delta H_{298} = -108,706 \text{ cal.,} \quad \Delta F_{298}° = -77,950 \text{ cal.}$$

From its heat of solution, Thomsen[12] obtained the value $-106,600$ cal. for the heat of formation of $PCl_5(s)$. The agreement is satisfactory.

If we take Giauque's[13] value, 53.31 cal./deg., for the entropy of $Cl_2(g)$, there is then obtained for the standard virtual entropies of $PCl_5(s)$ and $PCl_5(g)$, 40.8 and 87.7 cal./deg., respectively. An electron diffraction determination of the structure of PCl_5 combined with Raman data would lead to an independent determination of these quantities.

[12] J. Thomsen, "Systematisk gennemförte termokemiske undersögelsers numeriske og teortiske resultater" (1882–1886). International Critical Tables, Vol. V, p. 180.
[13] Giauque, J. Am. Chem. Soc. **54**, 1731 (1932).

Atomic Dimensions from the Coefficients of Compressibility and Thermal Expansion

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Starting from the equation of state $p - K(V - V_0)/V_0 = RT/V - V_0$, the relation $\alpha_a/\beta = R/(V - V_0)$ is derived, where V_0 is identified with the actual volume occupied by one mole of atoms or molecules. Values of the radii of atoms for different elements are calculated from this relation and compared to the values obtained from crystal analysis. Possibility of using the relation $\alpha_a/\beta = R/(V - V_0)$ to estimate molecular dimensions in the liquid state is also referred to.

THE estimation of the size of atoms or molecules from the van der Waals equation for gases

$$p + a/V^2 = RT/(V - b) \tag{1}$$

is well known. Here b represents 4 times the actual volume of the molecules in 1 mole, and may be calculated from the relation

$$b = RT_K/8P_K, \tag{2}$$

where T_K and P_K are, respectively, the critical temperature and pressure.

A similar procedure for the calculation of atomic dimensions may also be pursued in the cases of solids or liquids if a proper equation of state for those substances is known. In a paper published about five years ago,[1] the writer then suggested an equation of state of the form

$$p - K(V - V_0)/V_0 = RT/(V - V_0) \qquad (3)$$

for the liquid and solid states. Here p is the external pressure applied, V the molecular volume at absolute temperature T, V_0 the molecular volume at absolute zero, R the gas constant, and K an arbitrary constant.

If to a mass of molecular volume V two different pressures p_1 and p_2 are applied, we have evidently

$$\begin{aligned} p_1 - K(V_1 - V_0)/V_0 &= RT/(V_1 - V_0), \\ p_2 - K(V_2 - V_0)/V_0 &= RT/(V_2 - V_0). \end{aligned} \qquad (4)$$

Eliminating K from the Eqs. (4), we obtain

$$\begin{aligned} p_1/(V_1 - V_0) &- p_2/(V_2 - V_0) \\ &= RT(1/(V_1 - V_0)^2 - 1/(V_2 - V_0)^2). \end{aligned} \qquad (5)$$

Since in the case of liquids and solids the compressibility is usually small, V_1 and V_2 can differ only by an insignificant amount for ordinary magnitudes of applied pressures. We may therefore write approximately V for both V_1 and V_2 and reduce (5) to the form

$$p_1 - p_2 = RT(V_2 - V_1)/(V - V_0)^2. \qquad (6)$$

Multiplying both sides by V_2 and rearranging, we have

$$-V_2(p_1 - p_2)/(V_1 - V_2) = RTV_2/(V - V_0)^2. \qquad (7)$$

Denote the coefficients of compressibility and average thermal expansion respectively by β and α_a, it is seen that according to the usual definition, we have

$$\begin{aligned} 1/\beta &= -V_2(p_1 - p_2)/(V_1 - V_2); \\ 1/\alpha_a &= TV/(V - V_0) = TV_2/(V - V_0). \end{aligned} \qquad (8)$$

Eq. (7) becomes then

$$\alpha_a/\beta = R/(V - V_0); \quad \text{or} \quad V_0 = V - \beta R/\alpha_a. \qquad (9)$$

Here α_a is to be noted as the average thermal expansion.

As the thermal pressure $RT/(V - V_0)$ vanishes when T equals zero, it may be safely assumed that at that condition all the atoms (or molecules) are as closely packed as possible and that V_0 differs very little from the volume actually occupied by the atoms. If N is the Loschmidt number, the radius r of the atom may then be calculated as

$$r = \left[\frac{3V_0}{4\pi N}\right]^{\frac{1}{3}} = \left[\frac{3}{4\pi N}\left(V - \frac{\beta R}{\alpha_a}\right)\right]^{\frac{1}{3}} \qquad (10)$$

with possibly a small error. Values obtained thus are tabulated in Table I. A glance at the table shows clearly that the values of r_2 calculated from Eq. (10) agree with crystal data very well in spite of approximations.

Eq. (9) may also be applied to molecules in a liquid state. For spherical molecules, V_0/N gives directly an estimation of the radius of the

TABLE I. *Atomic radii from compressibility and expansion.*

ELE-MENTS	α ($\times 10^5$ per deg.)	β ($\times 10^{12}$ c.g.s.u)	V (cc)	V_0 (cc)	r_1 CRYSTAL DATA ($\times 10^{-8}$ cm)	r_2 CALCU-LATED ($\times 10^{-8}$ cm)
Na	22.0	15.4	23.7	17.63	1.92	1.91
K	25.0	31.5	45.4	33.90	2.36	2.36
Rb	30.0	40.0	56.25	41.16	2.53	2.54
Cs	28.3	61.0	71.0	53.0	—	2.76
Ca	7.1	5.5	25.3	18.71	1.97	1.94
P	36.0	20.3	17.0	12.3	—	1.70
Mg	7.8	2.7	13.3	10.02	1.60	1.60
Bi	4.0	2.8	21.2	14.95	—	1.81
Al	7.2	1.3	10.1	8.33	1.43	1.48
Cu	5.0	0.75	7.12	5.84	1.28	1.32
Cd	7.4	1.9	13.6	11.13	1.52	1.64
Fe	3.6	0.60	7.10	5.72	1.27	1.31
Ni	4.2	0.27	6.67	5.52	1.24	1.30
Co	$\alpha/\beta = 68 \times 10^6$		6.9	5.67	1.25	1.31
Zn	8.7	1.7	9.21	7.58	1.37	1.44
Mo	1.1	0.26	10.7	8.74	1.40	1.51
I_2	25.0	13.0	25.7	21.38	—	2.02
Ag	5.7	1.01	10.3	8.84	1.44	1.50
Pt	2.7	0.40	9.12	7.89	1.38	1.46
Tl	9.0	2.6	17.2	14.79	1.71	1.80
Pb	8.8	2.2	18.3	15.99	1.74	1.85
Pd	3.8	0.58	9.24	8.01	1.37	1.47
Au	4.3	0.60	10.0	9.09	1.44	1.53
Li	19.0	8.8	13.0	9.01	1.57	1.52
Sb	3.3	2.2	18.1	12.56	—	1.70
S	18.0	12.5	15.5	9.73	—	1.57

α = Coefficient of thermal expansion.
β = Coefficient of compressibility.
V = Gram molecular vol. at T = 290°C.
V_0 is Gram molecular vol. calculated from Eq. (9).
α for the temperature range 0→100°C is used instead of α_a as defined in Eq. (8), because values of the latter are unavailable.
r_1 are taken from the data cited by V. M. Goldschmidt in the paper "Crystal Structure and Chemical Constitution." J. Faraday Soc , March (1929). Values of r from different authorities often differ somewhat.
α, β, and V are taken from *Smithsonian Physical Tables.*

[1] G. F. Djang, "Physical Constants and Molecular Forces," Science J. of Univ. of Shanghai (1930).

individual molecules. For molecules of a non-spherical shape, V_0/N can help at least to determine one dimension of the molecules. For instance, in the case of ring or chain form compounds, the value V_0/N gives the length of the chain or the size of the ring when the depth of the molecule in question is known, or *vice versa*. Further data are being gathered in this direction.

DISCUSSION

From the conception of spherical atoms used in the derivation of Eq. (10), the value r calcu-lated from $[3V_0/4\pi N]^{\frac{1}{3}}$ should be appreciably larger than the real radius of the atom. Therefore it is rather surprising that the agreement between the calculated values and the crystal data should be as close as indicated in the table. The agreement is perhaps due to the fact that at absolute zero temperature the actual dimensions of the atoms are so reduced that this reduction just about counterbalances the additional part included in V_0. Anyhow, though theoretical explanations may be yet to be found, the formula seems to be proving a very helpful guidance in the work of crystal analysis.

The Structure of Rubrene and Some Remarks on the "Ortho-Effect"

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RECENTLY W. H. Taylor[1] has described x-ray measurements of rubrene, modification B. The data

$$C_{2h}^5 \quad a = 17.9A, \ b = 10.1A, \ c = 8.8A,$$
$$\beta = 120°; \ n = 2;$$

plane of the molecule nearly parallel to (010);

have been found. As Taylor pointed out, they are compatible with the rubrene formula (I), origin-ally developed by Moureu and his co-workers.[2] Meanwhile the experiments of Eck and Marvel[3] and of Koelsch and Richter[4] have shown that formula (I) cannot be correct, and recently

I   II

Dufraisse and Velluz[5] have proved that rubrene has structure (II); the same conclusion was reached by experiments in our laboratory, which will be reported elsewhere.

Is it possible to reconcile formula II with the x-ray data? Consideration of the models cor-responding to I and II reveals that the available x-ray data cannot give an exclusive proof for one of the two formulae; but packing of the molecules I into a three-dimensional structure with the above parameters seems more complicated. Therefore, also from x-ray data, formula II seems more likely (Figs. 1–4). The model of II still allows for two possibilities, but only the second one (II$_2$) of them leads in a simple way to the arrangement C_{2h}^5.

It may be noted that the formation of rubrene-peroxide is in accordance with formula II. The model shows that between the positions 9 and 10 of the anthracene nucleus a bridge of two carbon or similar atoms (e.g., oxygen) may be extended without any strain.[6] The peroxide of rubrene, therefore, is the next analog of the peroxides of

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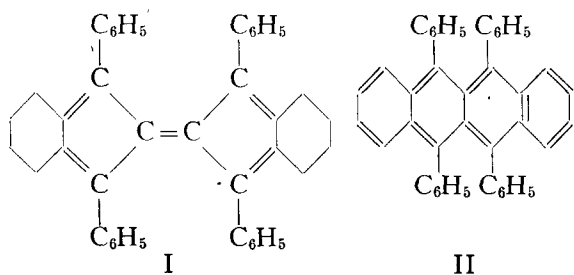
[1] Taylor, Zeits. f. Krist. A93, 151 (1936).
[2] Willemart, Comptes rendus 187, 385 (1928); Moureu, Dufraisse and Enderlin, ibid., p. 406.
[3] Eck and Marvel, J. Am. Chem. Soc. 57, 1898 (1935).
[4] Koelsch and Richter, J. Am. Chem. Soc. 57, 2010 (1935).

[5] Dufraisse and Velluz, Comptes rendus 201, 1394 (1935).
[6] Compare Bergmann and Fujise, Liebig's Annalen 480, 188 (1930); Diels and Alder, Liebig's Annalen 486, 191 (1931); Ber. d. D. Chem. Ges. 64, 2117 (1931); Clar, Ber. d.