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Boiling Point and the Refraction (Polarizability) of Exposed Atoms

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Boiling points for an unprecedented variety of substances can herewith be predicted by a method which is both 1, practical even for species with few or no measured properties, and 2, in agreement with this principle form theory: The London forces between molecules, and the refraction of light, both depend on polarizability and thus mainly on the outer electrons of atoms. The London forces on molecular surfaces, however, should not reflect the effects of sufficiently well-shielded internal atoms, and we use an objective geometric criterion to exclude them. Addition of the molar refractions (or atomic polarizabilities) of the other atoms, with an adjustment for electronegativity differences, gives the effective total refraction. We aim for great generality but emphasize inorganic substances at present. Boiling points are calculated for 193 substances from a proportionality to the 3/4 power of the total refractions, with a standard deviation <4%, up to at least 800 K. Values for 29 others are predicted for possible future experimental checking. Objective criteria for the exclusion of highly polar and other substances are presented, and the boiling temperatures for 19 of these are examined.

We wish to understand various properties in theory and also to be able to predict them in practice. In theory the critical temperature may be more interesting than the bp (boiling temperature) at an arbitrary pressure, but the bp is related, usually much better known, and more important in practice. Here we present a semiempirical, but theoretically reasonable, relationship that can be exploited to estimate bp's, even for unknown substance, from existing tables of the molar refractions, electronegativities, and atomic radii of the elements.

The treatment of unknown substances, and intermolecular contact in the liquid, preclude the use of relationships such as the equation due to London,[1a)]

$$U = -3\alpha^2 h\nu_0/4r^6, \tag{1}$$

which require the prior observation of several molecular properties.

The old idea of a connection between bp and molar mass *per se* still appears in recent writing,[2)] especially on organic chemistry[3—5)] and chemical education,[6—8)] so we note in passing that this connection was disproved long ago.[9,10a)]

We have long had purely empirical predictors of bp's, especially for certain classes of organic compounds.[11—13)] The limitations have been 1, application to few types of substances; 2, the absence of a reasonable relation to other properties; 3, the implied prediction of negative, imaginary or complex absolute bp's, or the absence of any prediction, at the bottom of the scale; and 4, the need for a large number, up to 80 in Kinney's well-known approach,[13)] of empirical constants.

Many earlier and recent workers[14—18)] have shown how to use topological properties to predict some physical characteristics, but limitations 1 and 2 seem self-evident. Concerning the third, it was well stated, apparently with no irony intended, that "There should be no absurdities in the limit of large or small molecules."[14)] Some topological indices, however, cannot be applied to CH_4, or even up to C_4H_{10}. Granted, we already know their bp's, but the lack of any basic distinction between these compounds and the other saturated hydrocarbons, plus the arbitrary structures of some of the indices, indicate the inadequacy of topology for real understanding.

Accuracy can of course be improved by restricting scope, and by choosing an independent variable closely related to bp, e.g., the gas chromatographic retention index, which is intimately related to volatility.[19)]Myers uses the London equation to calculate bp's for 42 already-observed molecules classified by shape.[20)]Correia's analysis of alkyl halides[21)] also is not directed toward predictions. Meissner uses a parameter depending on the functional group present, added to the total molar refraction to the 1.47 power, all divided by the parachor, which varies with the fourth root of the surface tension.[22)]

The Present Correlation, and the Criteria for Exclusion and Inclusion

The dispersion energy between distant, identical molecules varies as the square of the polarizability α (or refraction R) at constant distance r, as in the London equation. This must fail in a liquid, however, where the distances between molecular centers are small and proportional to the cube root of the volume, which varies directly with refraction, as shown by one form[1b)] of the Lorenz–Lorentz equation,

$$R = V(n^2-1)/(n^2+2), \tag{2}$$

where R is the molar refraction, n is the index of refrac-

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tion, and V is the molar volume. The distances between the surface layers (of individual molecules) mainly involved in both the refraction of light and the intermolecular attractions are even smaller in a way which is still difficult to handle *a priori.* The increase of distance (between molecular centers) with polarizability, however, must reduce the desired functional relationship to less than the second power. Moreover we are concerned here with bp's rather than the dispersion energies themselves.

One of the empirical aspects of the present study is the appearance of this theoretically expected correlation as a direct proportion between the bp and the 3/4 power of the total, for the exposed atoms, of the molar electric polarizability or optical refraction. Eq. 3 is the correlation to be used for actual predictions, as in Fig. 1, which shows 212 substances, not all numbered, mostly those listed in the tables as included or excluded:

$$T_e/\mathrm{K} = f_T(R_t \ \mathrm{mol\,cm^{-3}})^p \text{ or : } (\mathrm{dln}\ T_e)/(\mathrm{dln}\ R_t) = p. \quad (3)$$

T_e is the estimated bp. R_t is the total molar refraction for the exposed atoms, with an adjustment for electronegativity differences to be explained with Eq. 7. Statistical treatment with the SAS package for nonlinear relationships shows the factor f_T, for conversion to the boiling temperature, to be 31.4 for most groups of substances. The exponent p is likewise found to be 0.75. (Table 10 will give the statistics.)

For the statistical analysis and handling of errors we correlate ln (T_o) with ln (R_t) and define the relative error as

$$E \equiv \ln\ (T_e/T_o), \quad (4)$$

which is intermediate between $(T_e-T_o)/T_o$ and $(T_e-T_o)/T_e$; T_o is the observed bp. This avoids limiting either the positive or negative error to 100% while the other is unlimited.

A strict dichotomy between exposed and shielded atoms would of course be insupportable. Some must be intermediate and have a fractional exposure of their central atoms M, as will be examined with Table 2.

Classes Excluded. We could simply exclude all potentially polar substances (those of low molecular symmetry) but have chosen to include those with low polarities. Dipole moments, μ, of a given magnitude must be less important for larger molecules (those with larger R_t's), and we exclude those for which

$$\mu > 0.05(R_t \ \mathrm{mol\,cm^{-3}})\ \mathrm{D}, \quad (5)$$

where the debye, $\mathrm{D} \equiv 10^{-18}$ Fr cm, and the franklin, $\mathrm{Fr} = 3.3\times10^{-10}$ C, or $\mathrm{D} = 3.3\times10^{-30}$ C m. Dipole moments below this threshold are found to be too small to invalidate our method. No separate treatment of hydrogen bonding is required here. We have tried and failed, even with the exclusion of hydrogen bonding, to correlate the bp's of highly polar substances with the reported magnitudes of their dipole and quadruple moments by adding a term or terms for those moments.

Quadrupole and especially octopole moments are known seldom and very imprecisely,[23,24] but we use the former to exclude substances in which their influence may be large. The quadruple moments, θ, of such excluded substances are given, where reported, in the footnotes of the main Tables 4, 5, 6, 7, 8, and 9. Our criterion for exclusion is that

$$|\theta| > 0.4(R_t \ \mathrm{mol\,cm^{-3}})\mathrm{B}, \quad (6)$$

where the buckingham, $\mathrm{B} \equiv 10^{-26}\mathrm{Fr\,cm^2} = 3.3\times10^{-40}$ C m^2. Ideally, we might exclude anything with unknown quadruple or octopole moments, but this would be too restrictive even for species known to exist and would eliminate most unknown ones. Instead, we note that large moments are expected, if symmetry permits, when similar substances have high values. The linear carbon oxide C_5O_2, for example, would be excluded by this criterion alone because CO_2 has a high θ. The reasons for other exclusions will be noted in the tables or the text. (Readers will find several substances excluded in spite of fitting well, and a few, most notably WCl_6 in Table 9, included even with a poor fit.) We need accurate measurements, however, of additional multipole moments.

The thresholds for the exclusion of highly dipolar and quadrupolar substances are not adjustable constants in the same sense as the others. We set these limits above zero, even at the possible expense of a slightly higher standard deviation, to permit wide coverage. Lowering well-placed thresholds should not, except for the random effects of removing any acceptable substances, greatly change the quality of the correlation.

We are not prepared to do the calculations for very large or complicated molecules, even if not very polar, unless they are flat and therefore fully or almost fully exposed to each other. The criterion here is whether the molecule is either simple enough for the use of the geometric standard, or planar.

We are also not yet able to deal with multiple bonding in general. Mostly flat aromatics (in Table 6) and transitional organometallics (in Table 9b) are exceptions. In each of these two cases we have enough similar compounds to support an appropriate treatment.

For some substances, for example OsF_6, IrF_6, and PtF_6, special effects such as the interaction of unpaired electrons in neighboring molecules must be considered. Where such effects apply to few cases that could otherwise be handled, they are excluded from our correlation, but the instance just mentioned will be looked at later. Ring strain, as in P_4, is another such special effect, as is the quantum influence in He, Ne, and H_2.

Nonmolecular substances such as NaCl and metals are of course excluded, as are molecular substances for which *independent* evidence shows significant associa-

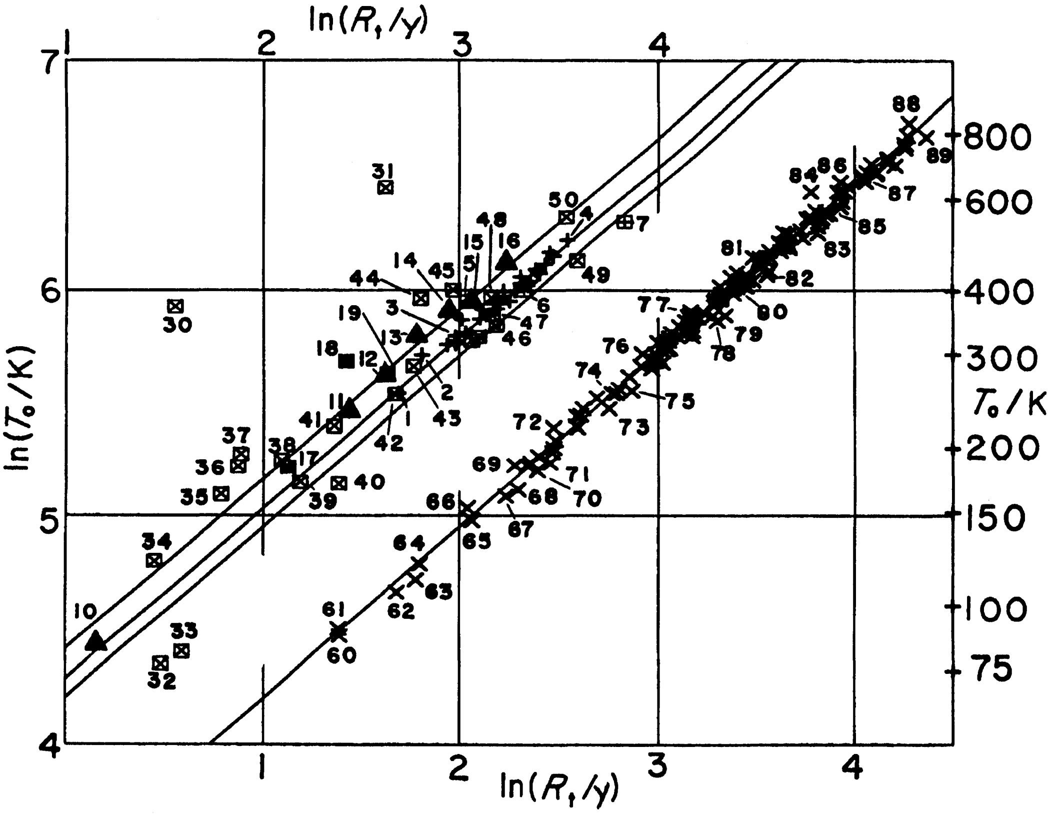

Fig. 1. Natural log of the observed boiling temperature, T_o, vs. natural log of the total exposed refraction, R_t. Left-hand part, using upper abscissa: halogens, organometallics and excluded substances. Right-hand part, using lower abscissa: others. Right-hand ordinate: antilog of the left, no displacement. Upper line: calcd for halogens. Second line: organometallics. Third and fourth lines (identical but with the fourth displaced horizontally to avoid crowding): others. The following symbols and numerical codes are for the examples. Symbols in squares represent exclusions for reasons discussed in the text. The unit y≡ $\mathrm{cm^3\,mol^{-1}}$. +: **1**, BMe_3 (Me≡CH_3); **2**, $SiMe_4$; **3**, $ZnMe_2$; **4**, Sb_2Me_4. ⊞: **5**, $PbMe_4$; **6**, Al_2Me_6; **7**, Sn_2Et_6. ▲: **10**, F_2; **11**, Cl_2; **12**, BrCl; **13**, Br_2; **14**, ICl; **15**, IBr; **16**, I_2. ■: **17**, ClF; **18**, BrF; **19**, Cl_2O. ⊠: **30**, H_2O; **31**, Hg; **32**, N_2; **33**, CO; **34**, NO; **35**, O_3; **36**, N_2O; **37**, CO_2; **38**, C_2H_2; **39**, BF_3; **40**, C_2H_4; **41**, AsF_5; **42**, C_2N_2; **43**, ClF_3; **44**, XeF_2; **45**, OsO_4; **46**, PtF_6; **47**, C_6H_5F; **48**, C_5H_5N, pyridine; **49**, Al_2Cl_6; **50**, P_4. ×: **60**, Ar; **61**, O_2; **62**, OF_2, **63**, CH_4; **64**, Kr; **65**, CF_4; **66**, NF_3; **67**, SiH_4; **68**, Xe; **69**, C_2H_6; **70**, B_2H_6; **71**, PH_3; **72**, SeF_6; **73**, C_3F_8; **74**, CF_3SF_5; **75**, SbH_3; **76**, Ge_2H_6; **77**, C_4H_4S, thiophene; **78**, PCl_3; **79**, $Ru(CO)_5$; **80**, $CoCp(CO)_2$ (Cp≡cyclopentadienyl); **81**, CBr_4; **82**, C_6F_5I; **83**, Si_2Br_6; **84**, WCl_6; **85**, p-$C_6H_4(NO_2)_2$; **86**, GeI_4; **87**, S_8; **88**, As_4S_4; **89**, $C_{22}H_{14}$, picene. In the figure but not the tables: **7**, **17**, **18**, **33**—**38**, **40**, **42**.

Table 1. Minimal Distances between Atoms in Two Symmetrical MX_j Molecules in Symmetrical Contact

Planar (and Linear)	Regular Polyhedral	Bipyramidal
	d_1, M–X Distances with X–X contact	
$(w_X^2-c^2)^{1/2}-w_s$.	$(w_X^2-zc^2/3)^{1/2}+sc-w_s$.	$(w_X^2-2c^2/q)^{1/2}+tc-w_s$.
	d_2, M–M Distances with X–X contact	
$(w_X^2-qc^2)^{1/2}-w_M$.	$(w_X^2-zc^2/3)^{1/2}+2sc-w_M$.	$(w_X^2-zc^2/q)^{1/2}+2tc-w_M$.
	d_3, M–M Distances with M–X contact	
$(w_X^2-c^2)^{1/2}-w_M$.	$(w_X^2-zc^2/3)^{1/2}+sc-w_M$.	$(w_s^2-2c^2/q)^{1/2}+tc-w_M$.

c≡sum of the single-bond covalent radii of M and X, r_M+r_X, or actual M–X bond length. w_M,w_X≡2 times the van der Waals radius of M or X, respectively. w_s≡sum of the van der Waals radii of M and X, $(w_M+w_X)/2$. $q\equiv3+\cos\phi$. $v\equiv2-2\cos\phi/2$. $z\equiv2-2\cos\phi$. $s^2\equiv(1+2\cos\phi)/3$. $t^2\equiv(1+\cos\phi)/(3+\cos\phi)$. $\phi\equiv\angle$XMX for adjacent X atoms. In bipyramidal molecules it refers only to the equatorial angles, the others being 90°.

Table 2. Fractions of Exposure

M_iX_j	c/pm	d_1/pm	d_2/pm	d_3/pm	d_{av}/pm	e_M/%
2a. Linear						
$ZnMe_2$	202	−60	−130	−59	−82.9	100.0
$CdMe_2$	218	−86	−187	−82	−118.2	100.0
$HgMe_2$	221	−91	−198	−86	−125.0	100.0
2b. Trigonal planar						
BF_3	$130^{a)}$	−37	−45	−37	−39.8	91.9
BCl_3	$175^{a)}$	−26	−6	−29	−20.1	1.6
BBr_3	193	−16	19	−22	−6.7	0.0
$AlBr_3$	239	−93	−104	−91	−96.1	100.0
BI_3	212	−2	52	−12	12.2	0.0
AlI_3	258	−79	−71	−81	−77.0	100.0
GaI_3	257	−77	−68	−80	−75.0	100.0
BMe_3	156	9	50	5	21.7	0.0
$GaMe_3$	201	−58	−62	−58	−59.3	100.0
$InMe_3$	220	−89	−112	−85	−95.2	100.0
2c. Tetrahedral						
B_2H_6	$126^{a,b)}$	−42	−49	−35	−41.8	100.0
CH_4	$109^{a)}$	−36	−47	−31	−38.1	84.1
SiH_4	148	−89	−127	−72	−96.0	100.0
GeH_4	152	−94	−136	−76	−102.1	100.0
SnH_4	170	−123	−176	−95	−131.2	100.0
CF_4	148	9	52	10	23.9	0.0
SiF_4	$154^{a)}$	−33	−29	−27	−29.6	45.1
Al_2Cl_6	224	−20	28	−15	−2.2	0.0
Ga_2Cl_6	223	−19	30	−14	−0.7	0.0
CCl_4	176	40	121	37	65.8	0.0
$SiCl_4$	217	−11	42	−7	8.2	0.0
$GeCl_4$	221	−16	34	−11	2.3	0.0
$SnCl_4$	$230^{a)}$	−37	−2	−28	−22.6	13.0
$TiCl_4$	231	−30	14	−22	−12.7	0.0
$ZrCl_4$	244	−48	−13	−37	−32.7	59.4
$HfCl_4$	243	−47	−11	−35	−31.1	52.0
Fe_2Cl_6	215	−8	46	−5	11.1	0.0
CBr_4	191	56	157	51	88.1	0.0
$SiBr_4$	232	6	79	7	30.5	0.0
$GeBr_4$	236	1	71	2	24.7	0.0
$SnBr_4$	254	−24	35	−18	−2.4	0.0
$TiBr_4$	246	−13	51	−9	9.8	0.0
$ZrBr_4$	259	−31	24	−23	−10.0	0.0
$HfBr_4$	258	−30	26	−22	−8.5	0.0
CI_4	210	77	203	69	116.3	0.0
SiI_4	251	27	126	24	58.7	0.0
GeI_4	255	22	118	19	52.9	0.0
SnI_4	273	−3	81	−1	26.0	0.0
TiI_4	265	8	98	8	38.1	0.0
ZrI_4	278	−10	71	−6	18.4	0.0
HfI_4	277	−8	73	−5	19.9	0.0
XeO_4	$174^{a)}$	−45	−43	−37	−41.9	100.0
OsO_4	$171^{a)}$	−41	−36	−33	−36.4	76.3
CMe_4	154	67	161	63	97.3	0.0
$SiMe_4$	195	22	89	22	44.5	0.0
$GeMe_4$	199	18	82	18	39.1	0.0
$SnMe_4$	217	−4	48	−1	14.5	0.0
$PbMe_4$	231	−21	22	−16	−5.2	0.0
Al_2Me_6	202	14	76	15	35.1	0.0
$Ni(CO)_4$	$184^{a)}$	−29	−6	−22	−19.0	0.0
2d. Trigonal bipyramidal						
PF_5	181	−5	10	1	1.9	0.0
AsF_5	193	−19	−16	−10	−14.8	0.0
SbF_5	212	−42	−59	−27	−42.9	100.0
PCl_5	209	30	82	32	47.9	0.0
$SbCl_5$	240	−6	16	3	4.1	0.0
$NbCl_5$	233	2	31	9	14.4	0.0
$TaCl_5$	233	2	31	9	14.4	0.0
$NbBr_5$	248	21	71	25	39.1	0.0
$TaBr_5$	248	21	71	25	39.1	0.0
NbI_5	248	48	122	48	72.4	0.0
TaI_5	248	48	122	48	72.4	0.0
$AsMe_5$	199	45	109	45	66.7	0.0
$SbMe_5$	218	26	74	29	42.7	0.0
$Fe(CO)_5$	193	−4	13	2	3.5	0.0
$Ru(CO)_5$	202	−15	−7	−6	−9.1	0.0
$Os(CO)_5$	203	−16	−9	−7	−10.6	0.0
2e. Octahedral						
AlH_6 $^{c)}$	155	−46	−51	−32	−42.9	100.0
SF_6	173	34	103	37	58.0	0.0
SeF_6	188	21	83	27	43.5	0.0
TeF_6	208	2	56	13	23.4	0.0
MoF_6	201	9	66	18	30.6	0.0
WF_6	201	9	66	18	30.6	0.0
UF_6	213	−3	49	9	18.2	0.0
OsF_6	197	12	71	20	34.6	0.0
IrF_6	197	12	71	20	34.6	0.0
PtF_6	201	9	66	18	30.6	0.0
$As_2F_{11}^-$	193	16	76	23	38.6	0.0
$(SbF_5)_k$	212	−2	50	10	19.3	0.0
WCl_6	229	49	150	53	83.9	0.0
$Cr(CO)_6$	195	5	54	13	24.1	0.0
$Mo(CO)_6$	207	17	84	25	42.0	0.0
$W(CO)_6$	207	17	84	25	42.0	0.0
WMe_6	207	72	182	73	108.9	0.0
2f. Pentagonal Bipyramidal						
IF_7	204	21	102	30	51.2	0.0
ReF_7	199	26	108	33	55.4	0.0

a) Experimental. b) Average. c) In $Al(BH_4)_3$.

tion in the liquid, or dissociation in the vapor. Individual examples of the latter, even when they happen to fit well, are noted below. In addition we find that *transitional*-element compounds are nonmolecular, not only when fully exposed, as expected, but also when intermediate.

Finally, we naturally exclude many organic substances here, because of their overwhelming numbers; we include only the simpler ones.

The preceding groupings differ somewhat from those of Hildebrand and Scott,[25] but we agree broadly that "in dealing with intermolecular potentials one should recognize distinct types of molecules"; they mention those with permanent dipoles, hydrogen bonds, action as electron donors or acceptors, π electrons, outer but nonbonding electron pairs, and only bonding [outer]

Table 3. Constituent Molar Refractions, Electronegativities, and Covalent Radii

van der Waals radius of CH_3, Pauling: $1/2w_{\mathrm{Me}}/\mathrm{pm}$: 200

	Symbol:	H	He	B	C	N	O	F	Ne	Al	Si	P	S	Cl
Batsanov:	R/y[a]:	1.02	0.50	3.5	2.08	2.20	1.99	1.60	0.95	9.9	9.06	8.6	7.6	5.71
Teachout & Pack min.:	R/y:	1.68	0.49	8.65	2.37	2.62	1.85	1.35	0.64	13	10.6	9.8	8.70	5.8
Teachout & Pack max.:	R/y:	1.68	0.57	12.9	5.3	3.3	2.25	1.51	1.23	28	17.2	11.1	9.8	6.58
Miller & Bederson:	R/y:	1.68	0.52	7.64	4.44	2.77	2.02	1.41	1.00	21.0	13.6	9.16	7.32	5.50
Allred et al.:	x:	2.1		2.01	2.50	3.07	3.50	4.10		1.47	1.74	2.06	2.44	2.83
Berry et al.:	r/pm:	30	50	79	77	74	74	71	70	125	118	110	102	99

	Symbol:	Ar	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Batsanov:	R/y[a]:	4.00	10.7	8.2	7.2	7.3	7.0_5	6.6	6.5_5	7.0_5	8.9	11.6	11.08	10.3
Teachout & Pack min.:	R/y:	3.96	56.5	48.2	29.0	36.8	32.0	28.5	25.7	23.0	20.5	13	8.3	10
Teachout & Pack max.:	R/y:	6.16	56.5	48.2	41.9	36.8	32.0	28.5	66	55	20.5	23.5	17.6	13.2
Miller & Bederson:	R/y:	4.14	34.3	28.8	17.2	21.7	18.9	17.2	16.4	15.4	17.9	20.5	15.3	10.9
Allred et al.:	x:	3.21[b]	1.32	1.45	1.56	1.60	1.64	1.70	1.75	1.75	1.66	1.82	2.02	2.20
Berry et al.:	r/pm:	95	132	122	118	117	116	116	115	117	125	124	122	122

	Symbol:	Se	Br	Kr	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
Batsanov:	R/y[a]:	10.8	8.09	6.04	13.9	10.8_5	9.4	8.4	8.1	8.2	8.8	10.1	12.7	13.8[c]
Teachout & Pack min.:	R/y:	11.4	8.6	6.26	64.6	55.0	23	39.9	35.1	31.3	28.3	25.5	23.3	11.4
Teachout & Pack max.:	R/y:	11.4	9.56	8.76	64.6	55.0	46.2	39.9	35.1	31.3	28.3	25.5	23.3	16.4
Miller & Bederson:	R/y:	9.51	7.69	6.26	45	35	33	25.2	21.7	19.2	17.4	15.9	15.1	11.4
Allred et al.:	x:	2.48	2.74	2.91[b]	1.22	1.23	1.30	1.36	1.42	1.45	1.35	1.42	1.46	1.49
Berry et al.:	r/pm:	117	114	110	145	134	130	127	125	125	128	134	141	143

	Symbol:	Sn	Sb	Te	I	Xe	Hf	Ta	W	Re	Os	Ir	Pt	Au
Batsanov:	R/y[a]:	14.4[c]	14.5[d]	13.0[c]	12.67[c]	9.90	13.4	10.8_5	9.5	8.8	8.4	8.5	9.0	10.1
Teachout & Pack min.:	R/y:	14.6	12.2	10.4	8.93	7.54	57.3	43	18	37.8	34.8	31.5	29.0	27.0
Teachout & Pack max.:	R/y:	15.1	13	10.4	13.6	15.1	57.3	48.9	42.4	37.8	34.8	31.5	29.0	27.0
Miller & Bederson:	R/y:	11.1	10.1	9.8	9.8	10.2	38	33	25	23	20	18	15.9	14.4
Allred et al.:	x:	1.72	1.82	2.01	2.21	2.40[b]	1.23	1.33	1.40	1.46	1.52	1.55	1.44	1.42
Berry et al.:	r/pm:	140	141	137	133	130	144	134	130	128	126	126	130	134

	Symbol:	Hg	Tl	Pb	Bi	Po	At	Rn	Th	Pa	U
Batsanov:	R/y[a]:	12.4[c]	15.2[c]	16.1[c]	16.8[d]			12.54[e]	19.8	15.0	12.5
Teachout & Pack min.:	R/y:	13	8.8	15.8	14.0	12.6	11.0	9.66			
Teachout & Pack max.:	R/y:	24.7	16.1	15.8	14.0	12.6	11.0	15.9			
Miller & Bederson:	R/y:	12.9	8.8	9.3	10.1	11.6	12.9	15.9	126	121	116
Allred et al.:	x:	1.44	1.44	1.55	1.67	1.76	1.90	2.02[b]	1.11	1.14	1.22
Berry et al.:	r/pm:	144	155	154	152	153	150	145	165	150	142

Other R's used in subsequent tables:

Table No.	Symbol	R/y	Description
6, 9	C	2.86_5	R(C, aromatic), empirical value
6	NO_2	8.44	experimental $R_t(N_2O_4)/2$
6	F	1.02	empirically ≈ R(H) in aromatic fluorides
6—8	Me	4.81	Methyl: $e_M(C)R(C) + 3R(H)$
6—8	Et	7.32	Ethyl, empirical value
9	Cp	19.43	$5R$(C, aromatic) + $5R$(H), in metallocenes
9	CO	4.07	$R(C) + R(O)$, in metallic carbonyls

a) y≡$\mathrm{cm}^3\,\mathrm{mol}^{-1}$, also in subsequent tables. b) Extrapolated from the three previous elements. c) Reduced 10% from the original. d) Reduced 20% from the original. e) Predicted here from the boiling point.

Table 4. Main Groups, Shielded

No.	M_iX_j	R_s/y	Δx	T_o/K	T_e/K	E/%
1	CF_4	6.40	1.60	145	149	2.4
2	PF_5	8.00	2.04	193	191	−1.1
3[e]	AsF_5	8.00	1.90	220	186	−16.9
4	C_2F_6	9.60	1.60	196	202	2.8
5	SF_6	9.60	1.66	207	204	−1.6
6	SeF_6	9.60	1.62	218	203	−7.4
7	TeF_6	9.60	2.09	229	221	−3.4
8	IF_7	11.20	1.89	248	239	−3.7
9	C_3F_8	12.80	1.60	237	251	5.6
10	S_2F_{10}	16.00	1.66	302	300	−0.8
11[p]	$Se2F_{10}$	16.00	1.62		298	
12	Te_2F_{10}	16.00	2.09	326	326	−0.2
13	CF_3SF_5	12.80	1.66	254	253	−0.3
14	$(CF_3)_2SF_4$	16.00	1.66	293	300	2.3
15	$CF_2(SF_5)_2$	19.20	1.66	333	344	3.2
16	CCl_4	22.84	0.33	350	335	−4.5
17	$GeCl_4$	22.84	0.81	356	347	−2.6
18	PCl_5	28.55	0.77	433	409	−5.8
19	$SbCl_5$	28.55	1.01	413	420	1.6
20	C_2Cl_6	34.26	0.33	459	455	−1.0
21[e]	Al_2Cl_6	34.26	0.82	456	472	3.3
22	Ga_2Cl_6	34.26	1.01	474	482	1.6
23	C_3Cl_8	45.68	0.33	543	565	3.9
24	BBr_3	24.27	0.73	363	360	−0.8
25	CBr_4	32.36	0.24	463	434	−6.5
26	$GeBr_4$	32.36	0.72	460	447	−2.9
27	$SnBr_4$	32.36	1.02	475	462	−2.8
28	BI_3	38.01	0.20	483	489	1.3
29	CI_4	50.68	0.29	580	610	5.0
30	GeI_4	50.68	0.19	648	608	−6.4
31	AnI_4	50.68	0.49	621	616	−0.8

[e] excluded, also in subsequent tables. [p] predicted, likewise in the following tables. NOTES on numbered entries, as in later tables: 13: $R_t = R_t(CF_3) + R_t(SF_5)$, with C and S shielded. 14: $R_t = 2R_t(CF_3) + R_t(SF_4)$. 15: $R_t = R_t(CF_2) + 2R_t(SF_5)$.

Table 5. Main Groups, Exposed

No.	M_iX_j	R_s/y	Δx	T_o/K	T_e/K	E/%
5a. General						
1[e]	He	0.50		4	19	148.4
2[e]	Ne	0.95		27	30	10.7
3	Ar	4.00		87	89	2.2
4	Kr	6.04		120	122	1.3
5	Xe	9.90		166	177	6.3
6[p]	Rn	12.54 est		211		
7[e]	Hg	13.80		630	227	−101.9
8[e]	H_2	2.04		20	54	97.4
9	O_2	3.98		90	89	−1.4
10	S_8	60.80		671	696	3.6
11[e]	P_4	44.24		553	547	−1.1
12[p]	As_4	55.96			653	
13	PH_3	11.66	0.04	187	200	6.7
14	P_2H_4	21.28	0.04	325	315	−3.1
15	AsH_3	13.36	0.10	218	222	1.7
16	SbH_3	17.56	0.28	256	274	6.7
17	BiH_3	19.86	0.43	295	303	2.5
18[e]	H_2O	4.03	1.40	373	101	−130.3
19	HI	13.69	0.11	238	226	−5.0
20[e]	BF_3	8.90	—	172	163	−5.3
21	NF_3	7.00	1.03	153	146	−4.9
22	N_2F_4	10.80	1.03	200	202	1.0
23	OF_2	5.19	0.60	106	111	4.7
24[e]	ClF_3	15.94	—	285	253	−11.7
25[e]	XeF_2	13.10	1.70	387	260	−39.9
26	PCl_3	25.73	0.77	350	378	7.6
27	PBr_3	32.87	0.68	446	451	1.1
28[p]	PI_3	46.61	0.15		570	
29	GaI_3	49.61	0.39	619	603	−2.7
30	P_4S_3	57.20	0.38	680	671	−1.4
31	P_4S_7	70.40	0.38	796	784	−1.5
32	As_4S_4	71.60	0.24	838	790	−5.9
33[p]	P_4Se_3	66.80	0.42		756	
5b. Halogens						
34	F_2	3.20		85	93	8.9
35	Cl_2	11.42		239	243	1.9
36	Br_2	16.18		332	316	−4.8
37	I_2	25.34		458	444	−3.1
38	BrCl	13.80	0.09	278	281	0.9
39	ICl	18.38	0.62	371	357	−3.7
40	IBr	20.76	0.53	389	389	−0.1
41[e]	Cl_2O	13.41	0.67	277	283	2.0
42[p]	Br_2O	18.17	0.76		358	

11[e]: R(3–ring) = 2.46y = $4R$(3–ring, *cyclo*–C_3H_6); see Ref.[28b)]. 12[p]: R(3–ring) = 3.07y = $5R$(3–ring, *cyclo*–C_3H_6); Ref.[28b)] and Table 3. 18[e]: $\mu = 1.85$D. 20[e]: $\theta = -14.6$B. 20[e], 24[e]: Observed R_t replaces R_s. 24[e]: Independent evidence of association in condensed phases. 25[e]: $\theta = -19$B. 31: Two P's are shielded, two exposed.

electrons.

Exceptional Inclusions. Some groups of compounds that would be excluded by geometry or difficulty in calculation have been included by, we will argue, reasonable extensions of our principles. All of the following types could be omitted, however, with no damage except to breadth of coverage.

CF_3SF_5 in Table 4 will exemplify those that, strictly speaking, are not handled by our simple geometry, but are very similar to those that are.

Indene and the others in Table 6b are planar and aromatic except for one or two methylene groups. Likewise the mono- and polyphenylbenzenes at the end of 6d are not quite flat, but nearly so.

The ethyl group, as in organometallics in Table 7, is not easily amenable to our geometric treatment, but is included to illustrate a purely empirical extension.

Each of the Tables 4, 5, 6, 7, 8, and 9 includes one or more bp's that is/are predicted here, but not yet confirmed by experiment. Several not known to be confirmed at the beginning of this study have been found confirmed since then. Most of the tables also give several examples of excluded substances, together with the reason(s) for exclusion unless these have been discussed in the test.

The Geometric Criterion for Shielding

Table 1 gives the formulas for the distances between spherical atomic surfaces in two symmetrical

Table 6. Aromatic Compounds

No.	$M_iX_jY_k$	R_s/y	Δx	T_o/K	T_e/K	E/%	Name
6a. Fully unsaturated homocycles							
1	C_6H_6	23.31	0.40	353	341	−3.5	Benzene
2	$C_{10}H_8$	36.81	0.40	491	481	−2.0	Naphthalene
3	$C_{12}H_8$	42.54	0.40	544	537	−1.3	Acenaphthylene
4	$C_{14}H_{10}$	50.31	0.40	611	609	−0.3	Phenanthrene
5	$C_{14}H_{10}$	50.31	0.40	613	609	−0.6	Anthracene
6	$C_{16}H_{10}$	56.04	0.40	656	661	0.8	Fluoranthene
7	$C_{16}H_{10}$	56.04	0.40	666	661	−0.7	Pyrene
8	$C_{18}H_{12}$	63.81	0.40	708	729	2.9	Benz[*a*]anthracene
9	$C_{18}H_{12}$	63.81	0.40	712	729	2.4	Triphenylene
10	$C_{18}H_{12}$	63.81	0.40	721	729	1.1	Chrysene
11	$C_{18}H_{12}$	63.81	0.40	723	729	0.8	Naphthacene
12	$C_{20}H_{12}$	69.54	0.40	754	778	3.1	Benzo[*b*]fluoranthene
13	$C_{20}H_{12}$	69.54	0.40	754	778	3.1	Benzo[*k*]fluoranthene
14	$C_{20}H_{12}$	69.54	0.40	766	778	1.6	Benzo[*e*]pyrene
15	$C_{20}H_{12}$	69.54	0.40	769	778	1.2	Benzo[*a*]pyrene
16	$C_{22}H_{14}$	77.31	0.40	793	843	6.1	Picene
17	$C_{24}H_{12}$	81.02	0.40	798	873	9.0	Coronene
18[p]	C_{60}	171.90			<1524		Buckminsterfullerene
6b. Almost fully unsaturated homocycles							
19	C_9H_8	33.16	0.40	455	445	−2.1	Indene
20	$C_{12}H_{10}$	43.01	0.40	552	541	−2.0	Acenaphthene
21	$C_{13}H_{10}$	46.66	0.40	567	576	1.5	Fluorene
22	$C_{17}H_{12}$	60.16	0.40	675	697	3.3	Benzo[*b*]fluorene
23	$C_{17}H_{12}$	60.16	0.40	680	697	2.5	Benzo[*a*]fluorene
6c. Heterocycles							
24[e]	C_5H_5N	21.62	0.97	389	339	−13.7	Pyridine
25	C_4H_4O	17.53	1.40	305	307	0.7	Furan
26	C_4H_4S	23.14	0.40	357	339	−5.2	Thiophene
27	C_4H_4Se	26.34	0.40	383	374	−2.4	Selenophene
28	C_4H_4Te	28.54	0.49	424	399	−6.0	Tellurophene
28[e]	C_4H_4Te	32.08	—	424	430	1.3	Tellurophene
29	C_8H_6O	31.03	1.03	447	448	0.2	Benzofuran
30	C_8H_6S	36.64	0.40	494	480	−3.0	Benzothiophene
31[p]	C_8H_6Se	39.84	0.40		511		Benzoselenophene
32[p]	C_8H_6Te	42.04	0.45		534		Benzotellurophene
6d. Substituted benzenes							Substituent(s)
33[e]	C_6H_5F	23.31	0.40	358	341	−4.9	Fluoro
34	$C_6H_4F_2$	23.31	0.40	362	341	−6.0	1,4-Difluoro
35	$C_6H_3F_3$	23.31	0.40	349	341	−2.2	1,3,5-Trifluoro
36	$C_6H_2F_4$	23.31	0.40	367	341	−7.4	1,2,4,5-Tetrafluoro
37	C_6HF_5	23.31	0.40	358	341	−4.9	Pentafluoro
38	C_6F_6	23.31	0.40	355	341	−3.9	Hexafluoro
39	C_6H_6Cl	28.00	0.73	405	401	−0.9	Chloro
40	C_6F_5Cl	28.00	0.73	396	401	1.4	Chloropentafluoro
41	$C_6H_4Cl_2$	32.69	0.73	446	451	1.1	1,4-Dichloro
42	$C_6H_3Cl_3$	37.38	0.73	482	499	3.6	1,3,5-Trichloro
43	C_6H_5Br	30.38	0.64	429	423	−1.3	Bromo
44	C_6F_5Br	30.38	0.64	408	423	3.8	Bromopentafluoro
45	$C_6H_4Br_2$	37.45	0.64	492	496	0.7	1,4-Dibromo
46	$C_6H_3Br_3$	44.52	0.64	551	565	2.5	1,3,5-Tribromo
47	C_6H_5I	34.96	0.40	462	463	0.2	Iodo
48	C_6F_5I	34.96	0.40	435	463	6.2	Iodopentafluoro
49	$C_6H_4I_2$	46.61	0.40	558	575	3.0	1,4-Diiodo
50	C_6H_5Me	27.10	0.40	384	382	−0.5	Methyl
51	C_6F_5Me	27.10	0.40	391	382	−2.2	Methylpentafluoro
52	C_6H_5Et	29.61	0.40	409	409	−0.1	Ethyl
53	$C_6H_5C_2H_3$	31.08	0.40	418	424	1.3	Vinyl
54	$C_6H_4(NO_2)_2$	38.15	1.40	571	553	−3.3	1,4-Dinitro
55[p]	$C_6H_3(NO_2)_3$	45.57	1.40		632		1,3,5-Trinitro
56	$C_6H_5C_6H_5$	44.58	0.40	529	556	5.0	Phenyl
57	$C_6H_4(C_6H_5)_2$	65.85	0.40	700	747	6.4	1,4-Diphenyl
58[p]	$C_6H_3(C_6H_5)_3$	87.12	0.40		922		1,3,5-Triphenyl

17: Added too late for Fig. 1 or overall statistical treatment. 24[e]: μ=2.19D, and we used the R for ordinary (non-conjugated) N. 28[e]: The observed R_t replaces R_s. 33[e]: μ=1.58D.

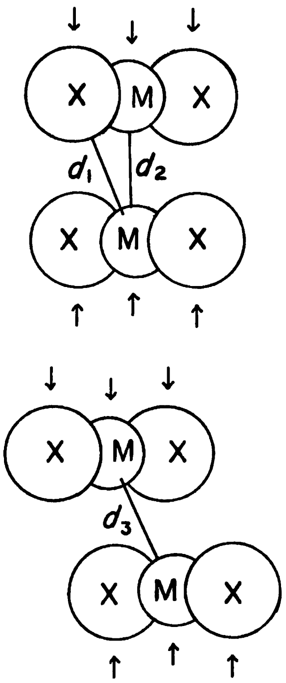

Fig. 2. Definitions of the three interatomic distances for two molecules in contact, illustrated by linear MX_2 rotated +45° and −45° around a vertical axis perpendicular to X–M–X. Upper: push together vertically until each X rests on the two X's in the adjacent molecule. Lower: push together vertically until the upper M touches and is directly above the lower left X.

Table 7. Main-Group Organometallics

No.	M_iX_j	R_s/y	Δx	T_o/K	T_e/K	$E/\%$
7a. Exposed						
1	$ZnMe_2$	18.52	0.84	319	323	1.2
2	$CdMe_2$	22.32	1.04	379	381	0.4
3	$HgMe_2$	22.02	1.06	369	378	2.3
4	$SeMe_2$	20.42	0.40	331	336	1.2
5	$TeMe_2$	22.62	0.49	360	364	1.2
6	$ZnEt_2$	23.54	0.84	391	387	−1.1
7^p	$CdEt_2$	27.34	1.04		443	
8	$HgEt_2$	27.04	1.06	432	441	2.0
9	$SeEt_2$	25.44	0.40	383	396	3.3
10	$TeEt_2$	27.64	0.49	411	424	3.2
7b. Intermediate						
11	PMe_3	18.56	0.44	314	313	−0.4
12	$AsMe_3$	19.37	0.40	326	322	−1.1
13	$SbMe_3$	21.39	0.68	354	354	0.2
14	$BiMe_3$	22.49	0.83	383	373	−2.6
15	PEt_3	26.08	0.44	401	404	0.8
16	$AsEt_3$	26.90	0.40	414	413	−0.3
17	$SbEt_3$	28.91	0.68	432	445	2.9
18^p	$BiEt_3$	30.02	0.83		464	
19	$GaEt_3$	27.52	0.68	416	429	3.1
20^p	$InEt_3$	28.58	1.01		457	
21	$TlEt_3$	29.25	1.06	465	468	0.6
22^p	P_2Me_4	27.49	0.44		421	
23	As_2Me_4	29.12	0.40	438	439	0.1
24	Sb_2Me_4	33.15	0.68	497	493	−0.8
25^p	Bi_2Me_4	35.36	0.83		525	
7c. Shielded						
26	BMe_3	14.43	0.49	253	260	2.5
27	BEt_3	21.96	0.49	368	356	−3.3
28	$SiMe_4$	15.79	0.76	300	284	−5.5
29	$GeMe_4$	19.24	0.48	316	322	1.9
30	$SnMe_4$	19.24	0.78	351	330	−6.1
31^e	$PbMe_4$	22.86	0.95	383	383	0.0
$31^{e'}$	$PbMe_4$	19.24	0.95	383	336	−13.0
32^e	Al_2Me_6	25.36	1.03	403	418	3.7
33	$SiEt_4$	25.83	0.76	425	412	−3.2
34	$GeEt_4$	29.28	0.49	433	443	2.2
35	$SnEt_4$	29.28	0.78	448	453	1.2
36	$PbEt_4$	29.28	0.95	473	462	−2.4
37^p	$AsMe_5$	24.05	0.40		380	
38	$SbMe_5$	24.05	0.68	400	387	−3.2
39^p	$TeMe_6$	28.86	0.49		436	
40^p	WMe_6	28.86	1.10		466	

31^e: $w_M(CH_3) = 376.4$ pm and $e_M(Pb) = 23.2\%$; $31^{e'}$: $w_M(CH_3) = 400.0$ pm and $e_M(Pb) = 0\%$. 32^e: Independent evidence of dissociation in the vapor. Assume the two 5-coordinate bridge C's shielded.

MX_i molecules in closest symmetrical contact. This is a modified form of an earlier proposal.[10b)] See Fig. 2 for the visually simple case of MX_2. For methane as a more important example, "X–X" contact would have six H atoms in the two molecules staggered around the middle of an H–C C–H axis, taken as vertical here. Three H atoms would be in contact with the other three, and the "M–M" distance between the two C atoms, and the "M–X" distance between the C and nearby H atoms in adjacent molecules might be found to be either >0 (not in contact), 0 (barely touching) or <0 (overlapping). For M–X contact we displace one of the molecules horizontally, and perhaps vertically, until one H in one molecule is in contact just above or below the C, and equidistant from the three H's, in the other.

One purpose is the prediction of bp's for unknown substances where possible, so we calculate single-bond distances from a complete table of single-bond covalent radii,[26)] instead of using measured distances. For multiple bonds, as in XeO_4 and OsO_4, the measured values are smaller and must be used here. (These tetroxides are included for comparison, even though their multiple bonding and perhaps high octopole moments still preclude calculating their bp's.) For the singly-bonded intermediate substances in Table 8c also, we need to calculate the actual exposure factors. For greater accuracy in these few cases, the actual bond distances should be used. For the first few saturated aliphatic hydrocarbons, however, the exposure factor for methane is assumed to be adequate.

Pauling found van der Waals radii to be 75—83 pm larger than the single-bond covalent values;[27a)] we simply increase the latter by 80 pm to arrive at the former, and do not treat this as an adjustable constant. The van der Waals radius of the roughly spherical methyl

Table 8. Miscellaneous Main-Group Compounds

No.	M_iX_j	R_s/y	Δx	T_o/K	T_e/K	E/%
8a. Exposed boranes and tetrahedral hydrides						
1	B_2H_6	10.90	0.09	181	190	4.9
2	B_4H_{10}	19.76	0.09	291	298	2.3
3	B_5H_9	21.13	0.10	321	314	−2.4
4	B_5H_{11}	23.17	0.09	336	336	0.0
5	B_6H_{10}	24.54	0.09	355	351	−1.2
6	B_6H_{12}	26.58	0.09	359	373	3.7
7^{p}	B_9H_{15}	36.80	0.09		477	
8	$B_{10}H_{14}$	38.17	0.09	486	490	0.8
9^{p}	$B_{10}H_{16}$	40.21	0.09		510	
10	$Al(BH_4)_3$	19.41	0.63	317	302	−5.0
11	$Zr(BH_4)_4$	25.88	0.88	396	384	−3.1
12	$Hf(BH_4)_4$	25.88	0.87	391	384	−2.0
13	SiH_4	8.82	0.36	161	164	1.5
14	Si_2H_6	15.61	0.36	258	252	−2.6
15	Si_3H_8	22.39	0.36	326	330	1.2
16	GeH_4	10.62	0.08	185	187	0.7
17	Ge_2H_6	19.19	0.08	302	292	−3.6
18	Ge_3H_8	27.77	0.08	384	385	0.3
19	SnH_4	13.52	0.38	220	226	2.6
20^{p}	Sn_2H_6	24.99	0.38		359	
8b. Shielded silicon halides						
21	$SiCl_4$	19.39	1.09	331	317	−4.4
22	Si_2Cl_6	27.36	1.09	418	411	−1.8
23	Si_3Cl_8	35.33	1.09	484	498	2.9
24	$SiBr_4$	28.91	1.00	426	423	−0.6
25	Si_2Br_6	41.64	1.00	513	558	8.3
26	SiI_4	47.23	0.47	563	583	3.5
27^{p}	Si_2I_6	69.12	0.47		778	
8c. Intermediate compounds						
28	CH_4	5.83	0.40	112	120	7.0
29	C_2H_6	9.62	0.40	185	175	−5.3
30	C_3H_8	13.41	0.40	231	225	−2.8
31	C_4H_{10}	17.20	0.40	273	271	−0.5
32	C_5H_{12}	20.99	0.40	309	315	1.9
33	CMe_4	19.24	0.40	283	295	4.3
34	CEt_4	29.28	0.40	419	405	−3.5
35	SiF_4	7.05	2.36	187	186	−0.9
36	Si_2F_6	10.90	2.36	254	258	1.4
37^{p}	Si_3F_8	14.75	2.36		324	
38	BCl_3	17.46	0.82	286	284	−0.9
39	$SnCl_4$	24.95	1.11	387	384	−0.7

Table 9. Shielded Transitional-Element Compounds

No.	$M_iX_jY_k$	R_s/y	Δx	T_o/K	T_e/K	E/%
9a. Halides						
1	MoF_6	12.39	2.80	308	313	1.4
2	WF_6	12.42	2.70	290	306	5.4
3	UF_6	13.31	2.88	330	336	1.7
4	ReF_7	13.81	2.64	342	327	−4.4
5^{e}	OsF_6u_2	13.37	2.58	320	315	−1.5
6^{e}	IrF_6u_3	14.03	2.55	327	325	−0.6
7^{e}	PtF_6u_4	14.82	2.66	342	347	1.3
8	$TiCl_4$	26.02	1.51	409	422	3.0
9	$NbCl_5$	31.77	1.60	514	498	−3.2
10	$TaCl_5$	31.77	1.50	515	489	−5.1
11	WCl_6	37.08	1.43	620	544	−13.1
12	$TiBr_4$	35.54	1.42	503	526	4.3
13	$NbBr_5$	43.67	1.51	635	623	−1.8
14	$TaBr_5$	43.67	1.41	593	613	3.3
15	TiI_4	53.86	0.89	650	668	2.8
16	ZrI_4	54.81	0.99	704	685	−2.7
17^{p}	HfI_4	54.66	0.98		683	
9b. πBonded						
18	$Ni(CO)_4$	16.28	1.75	316	309	−2.3
19	$Fe(CO)_5$	20.35	1.86	376	373	−0.8
20	$Ru(CO)_5$	20.35	2.08	358	390	8.4
21	$Os(CO)_5$	20.35	1.98	408	382	−6.7
22	$Cr(CO)_6$	24.42	1.94	418	435	3.9
23	$Mo(CO)_6$	24.42	2.20	429	458	6.5
24	$W(CO)_6$	24.42	2.10	448	449	0.2
25a	CoCp	19.42	0.80	$CoCp(CO)_2$, part a		
25b	$Co(CO)_2$	8.14	1.80	$CoCp(CO)_2$, part b		
25	$CoCp(CO)_2$	30.99	—	414	418	1.2
26a	MnCp	19.42	0.90	$MnCp(CO)_3$, part a		
26b	$Mn(CO)_3$	12.21	1.90	$MnCp(CO)_3$, part b		
26^{p}	$MnCp(CO)_3$	36.93	—		478	
27	$FeCp_2$	38.85	0.86	522	521	−0.3
28	$RuCp_2$	38.85	1.08	551	535	−3.1
29^{p}	$OsCp_2$	38.85	0.98		528	
30^{p}	WCp_2H_2	40.89	1.10		557	
31^{p}	$Cr(C_6H_6)_2$	46.62	0.94		603	

5^{e}, 6^{e}, 7^{e}: u_u is only a reminder to include $R(u)$ for unpaired electrons. 25: $R_t = R_t(\mathrm{CoCp}) + R_t(\mathrm{Co(CO)_2})$, where Co is shielded. Cp is cyclopentadienyl here and below. 25, 26^{p}: R_t replaces R_s. Shielding of M is assumed, not proved by calculation, here and below. 26^{p}: $R_t = R_t(\mathrm{MnCp}) + R_t(\mathrm{Mn(CO)_3})$, where Mn is shielded.

group was estimated to be about 200 pm.[27b)] Covalent radii will be included in Table 3.

Using Table 1, we find the three minimal distances mostly for symmetrical molecules MX_i. A simple average, d_{av}, of the three turns out to be adequate for classifying the central atoms. They behave as if completely exposed when this average is less than d_{min} (the minimal distance permitting any effective shielding), which is found to be about −42 pm; completely shielded, if more than d_{max} (the maximal distance permitting any effective exposure), −20 pm; and intermediate, otherwise. For the last case, we calculate a fraction of exposure of the M atom, e_M, by linear interpolation between 0% at d_{max} and 100% at d_{min}.

We treat somewhat less symmetrical molecules, such as S_2F_{10}, as having the same bond angles and distances as their simpler homologs. And in carbonyls, the van der Waals radius of C is the proper value for the CO group.

Table 2 gives some results; e.g., the C in CH_4 is 84% exposed.

Refraction and Electronegativity

Table 3 presents the values we use for molar refraction R (omitting the so-far unneeded left side of the periodic chart), mostly by Batsanov;[28a)] for electronegativity x, by Allred et al.;[29,30)] and for covalent radius r, by Berry et al.[26)] These sources are valued especially

Table 10. Summary of Constants and Statistical Results

Param/unit	Value (adj p)	Value (set p)	Table No.
d_{min}/pm	−41.6±1.4	−41.8±1.4	2
d_{max}/pm	−19.7±1.5	−19.7±1.6	2
$R_{\mathrm{c,arom}}$/y	2.865±0.041	2.877±0.039	3, 6, 9b
R_{Et}/y	7.32±0.14	7.33±0.14	3, 6d, 7, 8c
p	0.7545±0.0055	3/4	4—9
f_x	0.0891±0.0050	0.0886±0.0049	4—9
f_T	31.37±0.58	31.82±0.18	4, 5a, 6, 8, 9
f_T	38.71±0.77	39.17±0.54	5b
f_T	34.09±0.68	34.56±0.37	7
e_{M}	0	0	4, 7c, 9b
e_{M}	1	1	5, 6, 7a
e_{M}	1/2	1/2	7b
e_{B}	0.683±0.023	0.682±0.023	8a
$e_{\mathrm{Si,Ge,Sn}}$	0.562±0.026	0.560±0.025	8a
e_{Si}	−0.381±0.029	−0.378±0.029	8b
e_{M}	0.297±0.035	0.302±0.035	9a
e_{M}'s	from Table 2	—	8c

Table No.	No. Incl.	No. Pred.	No. Excl.	Totals	σ/% [a)]
4	28	1	2	31	3.5
5	27	5	10	42	4.2
6	51	5	2	58	3.2
7	30	8	2	40	2.6
8	34	5	0	39	3.5
9	23	5	3	31	4.8
Totals	193	29	19	241	3.7

a) Not changed significantly if $p \equiv 3/4$.

for completeness.

Refraction. Batsanov's refractions are for infinite wavelength. Other values, derived by the author (by multiplying by $4\pi N/3$, where N is Avogadro's constant) from more recent compilations of atomic polarizabilities,[31,32] are included for comparison. These are clearly too divergent for our purposes. The present work, by offering new evidence of a different, and often considerably more accessible, type (i.e., bp's), may point to better refractions for some of the elements. Our use of most of Batsanov's values, together with some parameters derived here, allows relatively small errors in correlating bp's.

Batsanov's values in the lower right part of the periodic chart are large in relation to those of the elements to their left. We have reduced them 10 or 20%, as shown. *Part* of the rationale for these crude reductions is of course to minimize the errors in our calculations, although another part is to improve the periodicity of the refractions themselves.

The bottom of Table 3 gives some group R values used later. The derivation of these should be self-explanatory. Larger ligands, such as ethyl, are found to contribute less to bp's than expected from the additivity of refractions. This is reasonable, because some of the atoms in these folded groups attached to central atoms holding several such ligands must be relatively well shielded, even though their motions make simple geometric criteria difficult to apply.

One might proceed by either 1, developing a much more complex theory of shielding, 2, omitting compounds having "large" ligands, or 3, introducing some pure empiricism for ligands as required. For the time being we are taking mainly route 2, using route 3 with ethyl as an example of the possibilities. The value for ethyl in Table 3, then, is a "bp number",[13] as much as a (partial) molar refraction.

Electronegativity. When chemical bonds are polarized, the separation of charges increases the responsiveness of the molecules (compared to that expected form the sum of the isolated neutral atoms) to the electric fields arising from neighboring molecules, or from light, and this increase varies approximately with the square of the electronegativity difference, where this difference, Δx, is $x_{\mathrm{X}}-x_{\mathrm{M}}$ for $\mathrm{M}_i\mathrm{X}_j$. For compounds of more than two elements, our work simply takes the largest difference, that between the most extreme electronegativities. Our correction is in Eq. 2:

$$R_{\mathrm{t}} = R_{\mathrm{s}}[1 + f_x(\Delta x)^2]. \qquad (7)$$

R_{s} is the sum of elemental molar refractions, excluding any shielded elements; f_x is the electronegativity factor, 0.089, and the adjustment for this is included even when M is shielded. This equation is treated as empirical, although it agrees rather well, if increased about 12%, with measured values of the total R when Δx's must be considered.[10c] This indicates that f_x is not merely an arbitrary adjustment for boiling points; it represents a real phenomenon in refractions. Because of the problems in some measurements of total R and the dependence of our R_{t}'s on optimizing several parameters for large groups of substances, these calculations, like Batsanov's and other's, could often prove more reliable than experiments for the R's of individual compounds. Further discussion of the refractions themselves,[28] however, is beyond the scope of this paper.

We would expect a higher electronegativity for a given element at a higher oxidation state,[33] at least if the attached atoms have high electronegativities, and an adjustment for this would improve our final results in some cases. Overall, however, the benefit is not striking; some of it should already be absorbed in the empirical constant f_x. Also, really complete tables of multi-valued electronegativities do not yet exist; we thus use a single-valued table.

We combine Eqs. 3 and 7 to get Eq. 8, which is used for all our calculations. The method of arriving at R_{s}, though usually straightforward, will be shown in each subsequent section.

$$T_{\mathrm{e}}/\mathrm{K} = f_T\{R_{\mathrm{s}}[1 + f_x(\Delta x)^2]\ \mathrm{mol\,cm^{-3}}\}^p. \qquad (8)$$

Shielded Main-Group Halides

Table 4 presents the halides of main-group elements (except Si, in Table 8b), M_iX_j, which are shielded. We have, then, simply Eq. 9:

$$R_s = jR_X. \tag{9}$$

Entry numbers (in the first column) with the superscript "e" in any of these tables show substances that are *excluded* from the overall correlation for reasons discussed in the text or mentioned in footnotes. Entry numbers with "p" represent *predictions* of bp's where these are not known. The relative error, in the last column, is based on the unrounded T_e and T_o. Most values of R_s and Δx are obtained very easily. To remove any doubt in more complicated cases, however, we list them all. Bp's and multipole moments have been taken from a great variety of sources.

AsF_5, entry No. 3^e, is largely monomeric, but various lines of evidence are equivocal as to whether polymerization is significant. It is, however, a much more potent fluoride-ion acceptor than PF_5;[34] moreover, the polymeric ion $As_2F_{11}^-$ has been isolated.[35] It is therefore excluded from this correlation, and its high bp now constitutes new evidence of some polymerization.

Al_2Cl_6, No. 21^e, fits well but it sublimes and changes the coordination number of Al from 6 to 4 in doing so. The formula Al_2Cl_6 therefore does not actually apply to the condensed phase, and it is excluded here.

Exposed Substances, General

Here we clearly have:

$$R_s = iR_M + jR_X. \tag{10}$$

He, Ne and H_2, in Table 5, are "quantum liquids"[36,37a] and therefore excluded. We used the bp of Rn to predict the R shown here. Hg is excluded by its metallic bonding.

O_2 is included as not having a double bond in the ordinary sense. The T_o for S_8 is not the ordinary 717.8 K recorded for elemental sulfur, which, at the bp, is a mixture mostly of longer open chains, not well-formed 8-membered rings. We arrived at the temperature used here by extrapolating from the vapor pressure of the liquid up to 433 K, where it is still a clear yellow and the rings are intact. The bp of XeF_2 is also extrapolated.

Chemists are familiar with highly dipolar molecules, and these are barely illustrated here, with H_2O. Many highly quadrupolar compounds, even BF_3, also have much multiple bonding. We do not yet have a good method of predicting what this contributes to the total refraction, so in these cases we use the measured values of the latter, when available (even though we exclude the final results).

The halogens all have high bp's, and we find f_T to be 38.7 for them. One possible explanation is that their quadrupole moments are poorly known[23,24] and may be somewhat larger than reported. Cl_2O is not quite a halogen, so is excluded from the statistical determination of parameters, but it does fit and is listed as such. On this basis a prediction is made for Br_2O, whose bp would have to be extrapolated.

Exposed Aromatics

Here we may have more than two elements, in $M_iX_jY_k$ (i.e., $C_iH_jY_k$), so

$$R_s = iR_M + jR_X + kR_Y. \tag{11}$$

Note that carbon is the aromatic carbon near the bottom of Table 3. The aromatic hydrocarbons mostly fit better using our calculated, rather than the measured, refractions. In general, the calculated values in this work benefit from the use of atomic refractions, some of which are derived from various measurements whose errors may cancel. Bp's, too, are of course subject to error, but not to such a great degree.

In Table 6a we estimate an upper limit of 1.5 kK for the (extrapolated) bp of fully exposed C_{60}, No. 18^p, even though it is well outside the confirmed range for our correlation. The molecules' roundness must reduce contact among them and must lower the resultant bp. This limit agrees crudely with the report of sublimation at about 600°C and an enthalpy of sublimation of 39 $\mathrm{kcal\,mol^{-1}}$ or higher.[38] A good bp for C_{60} should enable estimates for the other fullerenes, including the endohedral compounds. The almost fully unsaturated homocycles in 6b are also treated as completely exposed.

Among the heterocyclics in Table 6c, tellurophene fits (accidentally?) much better (in No. 28^e) with its measured than with its calculated refraction (in No. 28) but the latter is counted here for consistency. This suggests, however, that the measured value may be more accurate in this case, and that it may be revealing a real anomaly in the refraction. The effect of differences of electronegativity apparently does not spread significantly beyond the ring of origin, as in the benzo compounds, Nos. 29—32^p. We compute $(\Delta x)^2$ separately for each ring, and take the average.

Fluorine in the aromatic fluorides in Table 6d behaves (in relation to bp's) almost the same as hydrogen, as is well known but not explained,[39] and is therefore treated as equivalent here. It is interesting, moreover, that the θ's of C_6H_6 and C_6F_6 are nearly equal although of opposite sign.[40] (We could improve the fit a little by allowing separate adjustments for effective values of both the refraction and the electronegativity of aromatic fluorine, but prefer not to do so.)

At the highest bp's in sections 6a and 6d of this table (Table 6), the calculated values are a little too high. The low orientational entropy of very large, flat molecules in the liquid should be relevant but has not been considered. These large ones could arguably therefore be excluded for now. Extrapolating the errors for biphenyl, No. 56, and *p*-terphenyl, No. 57, however, suggests an E of about 8% for 1,3,5-triphenylbenzene, No. 58$^{\mathrm{p}}$. On this basis we expect a T_{o} near 850 to 860 K for the last case. This prediction showed the report of 459°C, 717 mm, Beilstein Ref. B5^3, 2563,[41)] to be suspect, and Beilstein indeed has no such report.

Main-Group Organometallics

Zn, Cd, and Hg are best considered as transitional elements for some purposes, but as main-group elements in this paper.

Many of the central atoms in the compounds in Table 7 retain unshared pairs of outer electrons and thus have a different structure from that assumed by our geometric criterion for shielding. We get good results, quite reasonably, by assuming exposure for MX_2, intermediate status for MX_3 and M_2X_4, and shielding for MX_4 (or higher) and M_2X_6, unless proved otherwise, as with the complete shielding found in Table 2b for the small B atom in BMe_3 and, *a fortiori*, in BEt_3.

Here then we take

$$R_{\mathrm{s}} = e_{\mathrm{M}} i R_{\mathrm{M}} + j R_{\mathrm{X}} + k R_{\mathrm{Y}}, \qquad (12)$$

where e_{M} is of course 1 for the exposed compounds in Table 7a, and 0 for the shielded ones in Table 7c; 1/2 is the assigned value for the intermediate compounds in Table 7b. The success of this simple approach in the intermediate group may seem surprising at first for pyramidal molecules like PMe_3, which must be exposed on one side, although shielded on the other.

We also note that the methyl group is not really spherical, and the estimate of 200 pm for its van der Waals radius[27b)] is rather crude. A value of 188.2 pm fits our data best, but by actually affecting only $PbMe_4$, which can thus be made to fit perfectly (though with extreme sensitivity to the value chosen). This would be improper, however, so we exclude $PbMe_4$ here, and leave the radius at 200 pm.

We have no explanation at this time of the need for a higher bp factor, f_T, namely 34.1, for this rather large group of compounds.

Miscellaneous Main-Group Compounds

The tetrahedral hydrides in Table 8a have their central atoms of Si, Ge, and Sn fully exposed, and of B practically fully exposed, according to our geometric criterion. We nevertheless find it necessary to treat these compounds in an intermediate manner. We have then:

$$R_{\mathrm{s}} = e_{\mathrm{M}} i R_{\mathrm{M}} + j R_{\mathrm{X}}. \qquad (13)$$

For the central elements we use empirical values for e_{M}. We find 0.68 for e_{B} and 0.56 for $e_{\mathrm{Si,Ge,Sn}}$ taken together.

The geometric calculation for a hypothetical molecule AlH_6, the central part of $Al(BH_4)_3$, shows it to be (barely) completely exposed. In the real $Al(BH_4)_3$, of course, the large BH_4 ligands, more difficult to consider in this calculation, provide much more shielding, and this justifies assuming the Al to be completely shielded; likewise Zr and Hf in the tetrakis(tetrahydroborate)s.

The low bp's of the Si halides (as in Table 8b) and other compounds of Si, especially in comparison to those of C and Ge, have often been noted and explained in various ways. Hildebrand and Scott,[37b)] for example, relate the phenomenon to the large volumes of Si compounds, and deny "any unique character on the part of [$SiCl_4$]". Because refraction, however, is directly related to volume,[1c)] we could also rationalize the opposite result. And the large volumes themselves need some explanation, because the covalent radius of Si is between those of C and Ge, though much closer to the latter. The same authors, moreover, find their own "δ" values for CCl_4, $SiCl_4$, $GeCl_4$, and $SnCl_4$ to be 8.6, 7.6, 8.1, and 8.7, respectively.[37c)] Myers' treatment,[20)] however, shows no anomaly for Si. Our purpose and approach are different, so we merely note that this empirical calculation for elements like Si may or may not reflect a fundamental problem.

Our actual procedure is to subtract from R_{s} a fixed amount for each Si atom, *even when shielded*, as if it makes a certain amount of the ligand's polarizability unavailable to attract its neighbors, or as if it reduces the ligand's polarizability (which should be experimentally testable). In Eq. 13 for Table 8b e_{Si} is found to be −0.38. (Note that $e_{\mathrm{Si,exp}} - e_{\mathrm{Si,sh}}$, $0.56-(-0.38)$, should be and is about 1.0.) For e_{M} in the (intermediate) Si fluorides in Table 8c, we clearly have to subtract the 0.38, not from the *zero* for *shielded* halides, but from the *0.45* for the *intermediate* Si_iF_j's (for SiF_4 in Table 2). The e_{M} for these silicon fluorides is thus 0.07.

Shielded Transitional-Element Compounds

In Table 8 we examined some main-group hydrides and Si halides whose central atoms add less than expected to, or subtract from, the calculated effect of the outer atoms in determining bp's. The transitional-element halides, in Table 9a, show the opposite effect. Even though shielded, the central atoms appear to project a fraction of their influence (through their *d* orbitals?) to the outside world. (This stronger influence also appears in the fact, alluded to above, that intermediate molecules of transitional elements apparently always polymerize to infinite structures and are thus excluded from this work.) Therefore we again need Eq. 12; for Table 9a here, e_{M} is found to be 0.30.

For OsF_6, IrF_6, and PtF_6, an additional effect proportional to u, the number of *unpaired* electrons per molecule (2, 3, and 4 respectively), is seen and even expected because there should be some tendency for such electrons even in different molecules to pair with each other. The addition to R_{s} is found here to be $(0.64\pm0.15)u$ cm^3 mol^{-1}, and these three fluorides then fit quite well, but the inclusion of this further empirical constant seems unwarranted for so little added coverage; they are therefore excluded.

For WCl_6, entry No. 11, the best substantiated[42)] bp, 620 K, is unique in our tables in being 13% "too high", although 573 K (5% "high"), is also reported.[43)] This is worth reinvestigation. The shielding ought to be enough to prevent any dimerization even in the liquid; vapor densities support this in the vapor.[42)]

The additional atoms (O or H, not in contact with M) in the ligands of the π-bonded compounds in Table 9b are not covered by Tables 1 and 2 but are found, as expected, to provide complete shielding (so that $e_M=0$) for the central atoms.

We also note that formulas such as those sometimes written as $W(CPD)_2H_2$ or $W(CP)_2H_2$, for example, can be both shortened and clarified as, say, $WCpd_2H_2$ or WCp_2H_2. (Could we construe CPD briefly as carbon phosphide deuteride?)

Statistics, and Further Work Needed

Table 10 lists the constants derived from this study, with standard uncertainties. Most of this work has assumed an adjustable exponent p, but the factor f_T has strikingly lower uncertainties when p is set at exactly 3/4; this suggests taking it as fixed in the future.

A similar approach to related variables, such as the enthalpy of vaporization,[5)] should be fruitful. We still need reasonable interpretations of the differences among the three f_T's, the value of p, and the reduced effective R and/or x for F in aromatic compounds. More efforts may be justified to include other types of multiply bonded and more highly multipolar compounds, and those with more complicated molecular structures. The low entropy of large, flat molecules in their liquid forms should be allowed for. At least the bp of WCl_6, and perhaps the refraction of tellurophene, should be rechecked carefully, and the predicted values in other cases should be determined experimentally where possible. Detailed information on the refractions of ligands on silicon could help us interpret the lower-than-expected values of e_M for Tables 8a and 8b. Likewise an empirical fitting for the covalent or van der Waals radius of the unique H atom (and/or the Si atom) might permit us to abandon these harder-to-explain special e_M's at least for Table 8a.

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