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# AM1* parameters for vanadium and chromium

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**Abstract** Our extension of the AM1 semiempirical molecular orbital technique, AM1*, has been parameterized for the elements V and Cr. The basis sets for both metals contain one set each of $s$-, $p$- and $d$-orbitals. AM1* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, V, Cr, Cu, Zn, Br, Zr, Mo and I. The performance and typical errors of AM1* are discussed for V and Cr and compared with available NDDO Hamiltonians.

## Introduction

We have introduced AM1* [1–4] as an extension of AM1 [5] with $d$-orbitals for the elements P, S, Cl [1], Al, Si, Ti and Zr [2], Cu and Zn [3], Br and I [4]. Molybdenum is also available as a slight modification of Voityuk and Rösch's AM1(d) parameter set [6]. AM1* is intended to retain the advantages of AM1 (good energies for hydrogen bonds, higher rotation barriers for $\pi$-systems than MNDO [7, 8] or PM3 [9–11]) for the elements H, C, N, O and F and to improve performance over AM1 compounds that contain second-row elements and heavier. As a continuation of this work, we now report AM1* parameters for vanadium and chromium. Both vanadium and chromium are important in the chemistry of catalytic reactions [12–14]. Because the experimental data for heats of formation of compounds of these two metals are relatively sparse, we have also used a series of model compounds whose heats of formation we have derived from DFT calculations [15].

## Theory

AM1* for the two new elements uses the same basic theory as outlined previously [1, 2]. As for other element-H interactions, the core-core repulsion potential for the V-H and Cr-H interactions used a distance-dependent term $\delta_{ij}$, rather than the constant term used for core-core potentials for most other interactions in AM1* [1]. This distance-dependent $\delta_{ij}$ was also used for the Mo-H interaction in AM1(d) [6] and for Ti-H, Cu-H, Zn-H, Br-H, Zr-H, Mo-H and I-H in AM1* [2–4]. The core-core terms for V-H and Cr-H are thus:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 \left[1 + r_{ij}\delta_{ij}\exp\left(-\alpha_{ij}r_{ij}\right)\right] \quad (1)$$

where all terms have the same meaning as given in reference [1].

For the remaining core-core terms (i.e. those between V or Cr with all elements except hydrogen) the standard MNDO/d interaction term (Eq. 2) is used:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 \left[1 + \delta_{ij}\exp -\alpha_{ij}r_{ij}\right]. \quad (2)$$

The parameterization techniques were those reported in references [1] and [2] and will not be described further here.

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## Parameterization data

The target values used for parameterization and their sources are defined in Table S1 of the Supplementary Material. We have used both reaction energies and heats of formation as we did for the Ti, Zr, Cu, Zn and Br, I parameterizations [2–4] and have also used a small series of model compounds whose heats of formation we have derived from DFT calculations. As before, [1–3] we checked that experimental values for heats of formation were reasonable using DFT calculations.

DFT calculations used the Gaussian 03 suite of programs [16] with the LANL2DZ basis set and standard effective core potentials [17–20] augmented by a set of polarization functions [21] (designated LANL2DZ + pol) and the B3LYP hybrid functional [22–24].

Experimental parameterization data for vanadium and chromium were taken largely from the NIST Webbook, [25] but also from the OpenMopac collection [26] and the other experimental and theoretical sources given in the Supplementary Material.

The energetic parameterization data and their sources are given in Table S1 of the Supplementary Material. In addition to the energetic data, geometries, dipole moments and ionization potentials taken from the above sources, crystal structures from the Cambridge Structural Database (CSD) [27] were used in the parameterization to ensure that not only the energetic and electronic properties for the "prototype" compounds, but also the structures of large vanadium and chromium compounds are well produced.

The heat of formation for $VCl_2^-$ was changed significantly from the NIST value ($-284.2\pm5.0$ kcal mol$^{-1}$, claimed to be taken from [28]). Examination of the original literature revealed that the calculations are based on work on $VCl_2$ [29]. In this work, the following heat of reaction (gas phase) is reported

$$VCl_2 \rightarrow V + 2Cl \quad \Delta H_{298}^0 = 239.5 \text{ kcal mol}^{-1}.$$
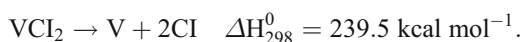
Using the standard heats of formation of vanadium (123.20 kcal mol$^{-1}$) and chlorine (28.992 kcal mol$^{-1}$) atoms, [25] we obtain $\Delta H°_f(VCl_2)=-58.3$ kcal mol$^{-1}$. This value is not included in the NIST WebBook. The two different values given for the electron affinity of $VCl_2$ ($-0.3$ and 1.2 eV) [28] give $\Delta H°_f(VCl_2^-)=-51.4$ or $-86.0$ kcal mol$^{-1}$. The NIST value of $-284.2\pm5.0$ kcal mol$^{-1}$ is close to the sum of the heat of reaction given above and the electron affinity of 1.2 eV ($-267.2$ kcal mol$^{-1}$), so that this may be the source of the error.

We have derived a heat of formation for $VCl_2^-$ of $-58.8$ kcal mol$^{-1}$ using DFT calculations (see Supporting Information) which is also close to the PM5 [30] and PM6 [31] heats of formation ($-52.1$ and $-94.5$ kcal mol$^{-1}$,

respectively) for $VCl_2^-$. We have used this value for the parameterization. Neither $VCl_2$ nor $VCl_2^-$ were used for the parameterization of PM6 [31].

## Results

The optimized AM1* parameters are shown in Table 1. Geometries were optimized with the new AM1* parameterization using VAMP 10.0 [32], while the PM5 calculations used LinMOPAC2.0 [30] and those with PM6 used MOPAC2007 [33]. The three programs give essentially identical results for the Hamiltonians that are available in all three.

### Vanadium

Heats of formation

The calculated heats of formation for our training set of vanadium compounds are shown in Table 2. We have compared our results with Stewart's recently published PM6 method [33] and also unpublished PM5 method implemented in LinMopac [31].

Statistically, AM1* reproduces heats of formation for the training set of vanadium compounds better than PM6 and far better than PM5. As before, however, we note that this comparison is not strictly valid as it is based on the current parameterization data, which sometimes differ from those used for PM5 and PM6. The mean unsigned error (MUE) for the AM1* parameterization dataset is 22.6 kcal mol$^{-1}$, compared with 25.3 and 59.0 kcal mol$^{-1}$ for PM6 and PM5, respectively. The parameterization data set for PM5 has not been published, but clearly does not cover the range of compounds used for AM1*. AM1* tends to overestimate heats of formation of vanadium-containing compounds by only 2.2 kcal mol$^{-1}$ while PM6 and PM5 tend to give more positive systematic errors with MSEs of 6.0 and 12.9 kcal mol$^{-1}$, respectively. The largest positive errors for AM1* are found for the molecules $VCl_2$ (88.9 kcal mol$^{-1}$), $VCl$ (73.5 kcal mol$^{-1}$), $VCl_3^-$ (71.9 kcal mol$^{-1}$), $VCl_3$ (60.9 kcal mol$^{-1}$), $VCl_4$ (60.4 kcal mol$^{-1}$), and $V_2C_{22}N_4H_{20}O_8$ (CEKHUV) (50.9 kcal mol$^{-1}$). The largest negative errors are found for $V_2Cl_9^-$ ($-131.0$ kcal mol$^{-1}$), $V(NH_3)_6^{2+}$ ($-104.7$ kcal mol$^{-1}$), and $V(CN)_5$ ($-72.2$ kcal mol$^{-1}$). Generally, large errors in AM1* come from chlorinated compounds and also from the compounds that contain original AM1 elements. As before, we attribute this to a weakness in the AM1* parameterization for the chlorine and also general weakness of the original AM1 parameterization. In addition, as we have faced in our previous AM1* parameterizations, oxygen-containing compounds

**Table 1** AM1* parameters for the elements V and Cr

| Parameter | V | Cr |
|---|---|---|
| $U_{ss}$ [eV] | −32.5007313 | −21.5000000 |
| $U_{pp}$ [eV] | −22.8176012 | −15.0000000 |
| $U_{dd}$ [eV] | −34.6990829 | −56.0000000 |
| $\zeta_s$ [bohr$^{-1}$] | 2.3438708 | 1.5551176 |
| $\zeta_p$ [bohr$^{-1}$] | 1.8676559 | 17.0408948 |
| $\zeta_d$ [bohr$^{-1}$] | 1.5941826 | 2.1098056 |
| $\beta_s$ [eV] | −1.1782158 | −8.6646957 |
| $\beta_p$ [eV] | −1.3164040 | −34.3489849 |
| $\beta_d$ [eV] | −2.9814499 | −15.0408921 |
| $g_{ss}$ [eV] | 6.6351662 | 8.1213983 |
| $g_{pp}$ [eV] | 14.5104896 | 15.1012780 |
| $g_{sp}$ [eV] | 9.6218429 | 14.1688433 |
| $g_{p2}$ [eV] | 5.9416348 | 14.6285467 |
| $h_{sp}$ [eV] | 3.3478389 | 3.1759218 |
| $z_{sn}$ [bohr$^{-1}$] | 1.6228539 | 12.5465123 |
| $z_{pn}$ [bohr$^{-1}$] | 0.7296035 | 0.6411768 |
| $z_{dn}$ [bohr$^{-1}$] | 1.0967084 | 1.4560578 |
| $\rho$(core) [bohr$^{-1}$] | 1.9933766 | 1.3878582 |
| $\Delta H^\circ_f$(atom) [kcal mol$^{-1}$] | 122.9 | 95.0 |
| $F^0_{sd}$ [eV] | 6.7975092 | 4.0400000 |
| $G^2_{sd}$ [eV] | 1.6923888 | 5.5000000 |
| $\alpha(ij)$ | | |
| H | 3.6013897 | 2.8199706 |
| C | 3.7725836 | 3.7290093 |
| N | 2.4888949 | 3.3339752 |
| O | 2.6735090 | 3.5657676 |
| F | 3.0683228 | 5.0646274 |
| Al | 3.2984193 | 1.3373658 |
| Si | 3.3162937 | 0.8315555 |
| P | 3.8585547 | 2.2001523 |
| S | 4.0661894 | 1.1565308 |
| Cl | 3.3918803 | 4.2139509 |
| Ti | 1.7021094 | 2.3540000 |
| V | 5.2583117 | 1.9587210 |
| Cr | 1.9587210 | 1.8584457 |
| Cu | 3.7398185 | 2.3450000 |
| Zn | 3.6692571 | 2.4225000 |
| Br | 3.4607221 | 2.4900000 |
| Zr | 2.9324325 | 1.9546000 |
| Mo | 1.3354356 | 1.9985000 |
| I | 3.6466767 | 2.0965000 |
| $\delta(ij)$ | | |
| H | −10.0286441 | −4.6277736 |
| C | 52.7142817 | 24.8021840 |
| N | 4.5648766 | 8.7064523 |
| O | 6.6835854 | 9.7960490 |
| F | 12.1347506 | 98.3067342 |
| Al | 43.9618494 | 1.0379731 |
| Si | 47.3637663 | 0.1916771 |

**Table 1** (continued)

| Parameter | V | Cr |
|---|---|---|
| **P** | 121.0494602 | 2.9142566 |
| **S** | 105.6181605 | 0.2808183 |
| **Cl** | 40.9704281 | 92.6763694 |
| **Ti** | 0.6073749 | 4.5000000 |
| **V** | 38.9295618 | 3.0959306 |
| **Cr** | 3.0959306 | 1.7368306 |
| **Cu** | 107.0552941 | 3.6560000 |
| **Zn** | 83.5135611 | 3.0320000 |
| **Br** | 44.6144240 | 3.0600000 |
| **Zr** | 5.1029965 | 4.1854000 |
| **Mo** | 0.9513533 | 3.2166000 |
| **I** | 138.6470845 | 1.4262000 |

give systematic errors. Errors for some oxygenated compounds are found as −52.4, −34.6, −22.1 and −23.4 kcal mol$^{-1}$ for $V(H_2O)_6^{2+}$, $V(H_2O)_6^{3+}$, $VO_3^-$ and $VO_2^-$, respectively. These results are analogous to those obtained for other elements and we attribute the performance limits to the fact that AM1* uses the unchanged AM1 parameterization for the elements H, C, N, O and F, which limits the possible accuracy of the parameterization. However, this does not explain the large errors for $VC_4H_8S_5$ (CUSPOV) (−68.4 kcal mol$^{-1}$), $VBr_4O^-$ (−41.5 kcal mol$^{-1}$), VI (39.5 kcal mol$^{-1}$), HVZr (−33.6 kcal mol$^{-1}$), $V_2Br_4$ (−36.6 kcal mol$^{-1}$) and $VBr_4^+$ (24.4 kcal mol$^{-1}$). With the exception of the hydrogen in HVZr, the carbon and the hydrogen in $VC_4H_8S_5$ and the oxygen in $VBr_4O^-$, these compounds contain only "pure" AM1* elements. This is likely to be a consequence of our sequential parameterization strategy, in contrast to the simultaneous parameterization used for PM6 [33], aggravated by using the original AM1 parameters for H, C, N, O and F. Nevertheless, on aggregate AM1* performs comparably to or better than the other available methods for the heats of formation of vanadium compounds.

Ionization potentials and dipole moments

A comparison of the calculated and experimental Koopmans' theorem ionization potentials and dipole moments are shown in Table 3.

For the ionization potentials, AM1* performs marginally better than both PM6 and PM5. The MUE for the AM1* is found 1.41 eV, compared with 1.52 and 1.70 eV for PM5 and PM6, respectively. AM1* and PM5 overestimate ionization potentials of the test set of vanadium compounds by 0.17 eV and 0.12 eV, respectively, and PM6 underestimate them by 0.24 eV. All the serious large AM1* errors are found for the oxygen-containing compounds $VO_2$

**Table 2** Calculated AM1*, PM6 and PM5 heats of formation and errors compared with our target values for the vanadium-containing compounds used to parameterize AM1* (all values kcal mol$^{-1}$)

| Compound | Target $\Delta H^o_f$ | AM1* $\Delta H^o_f$ | Error | PM6 $\Delta H^o_f$ | Error | PM5 $\Delta H^o_f$ | Error |
|---|---|---|---|---|---|---|---|
| V$^-$ | 110.8 | 113.7 | 2.9 | 135.6 | 24.8 | 183.0 | 72.2 |
| V | 122.9 | 122.9 | 0.0 | 122.9 | 0.0 | 116.0 | -6.9 |
| V$^+$ | 277.4 | 256.8 | -20.6 | 244.3 | -33.1 | 306.0 | 28.6 |
| V$_2$ | 187.4 | 176.9 | -10.5 | 188.5 | 1.1 | 295.2 | 107.8 |
| VH | 125.9 | 114.8 | -11.1 | 86.0 | -39.9 | 133.5 | 7.6 |
| VH$_2$ | 72.4 | 107.0 | 34.6 | 93.0 | 20.6 | 159.3 | 86.9 |
| V(CO)$_3^-$ | -62.2 | -82.7 | -20.5 | -62.6 | -0.4 | -38.2 | 24.0 |
| V(CO)$_4^-$ | -129.0 | -141.6 | -12.6 | -111.7 | 17.3 | -62.9 | 66.2 |
| V(CO)$_5^-$ | -186.6 | -184.7 | 1.9 | -204.7 | -18.2 | -140.9 | 45.6 |
| V(CO)$_6^-$ | -265.3 | -234.3 | 31.0 | -262.3 | 3.0 | -183.9 | 81.4 |
| VC$_{10}$H$_{10}$ | 48.6 | 35.2 | -13.4 | 49.6 | 1.0 | 33.8 | -14.8 |
| VC$_{12}$H$_{12}$ | 25.6 | 30.1 | 4.5 | 42.2 | 16.6 | 29.5 | 3.9 |
| VC$_{14}$H$_{22}$ (COGXOL) | 28.7 | 9.9 | -18.8 | 13.6 | -15.1 | 16.1 | -12.6 |
| VC$_4$O$_{10}$ (AOXOVA) | -409.0 | -409.9 | -0.9 | -430.1 | -21.1 | -487.1 | -78.1 |
| VC$_4$H$_2$O$_{10}$ (AOXVAN10) | -541.4 | -541.9 | -0.5 | -529.3 | 12.1 | -619.2 | -77.8 |
| VC$_4$H$_4$O$_{10}$ (DABKEW) | -498.7 | -549.5 | -50.8 | -534.2 | -35.5 | -641.1 | -142.4 |
| VC$_6$H$_6$O$_{10}$ (AJUJEU) | -551.0 | -561.7 | -10.7 | -569.5 | -18.5 | -657.1 | -106.1 |
| VC$_6$H$_{15}$O$_4$ (Vanadium(V) tri-ethoxide oxide) | -242.5 | -260.4 | -17.9 | -273.4 | -30.9 | -235.6 | 6.9 |
| VC$_{10}$H$_{14}$O$_5$ (Vanadium(V)diacetylacetonate oxide) | -293.0 | -256.7 | 36.3 | -267.4 | 25.6 | -301.6 | -8.6 |
| VC$_{11}$H$_{12}$O (BEYRIG) | 1.5 | 16.0 | 14.5 | -7.0 | -8.5 | 14.1 | 12.6 |
| VC$_{12}$H$_8$O$_5^{2-}$ (BOBWOE) | -244.4 | -220.4 | 24.0 | -215.0 | 29.4 | -263.0 | -18.6 |
| VC$_{12}$H$_{10}$O$_2^+$ (CCPZRB) | 88.2 | 99.6 | 11.4 | 102.1 | 13.9 | 125.8 | 37.6 |
| VC$_{14}$H$_{14}$O$_4^+$ (BOBHIJ) | -20.4 | 1.2 | 21.6 | -44.1 | -23.7 | -0.4 | 20.0 |
| VC$_{18}$H$_{12}$O$_6^{2-}$ (BOBWEU) | -275.3 | -247.3 | 28.0 | -254.4 | 20.9 | -318.3 | -43.0 |
| VN | 125.0 | 113.1 | -11.9 | 133.5 | 8.5 | 128.4 | 3.4 |
| V(NH$_3$)$_6^{2+}$ | 238.8 | 134.2 | -104.7 | 255.5 | 16.7 | 60.9 | -177.9 |
| V(CN)$_5$ | 270.2 | 198.0 | -72.2 | 236.0 | -34.2 | 285.3 | 15.1 |
| VC$_{10}$N$_2$H$_{12}$O$_8$ (Vanadium(III) EDTA) | -401.6 | -396.4 | 5.3 | -444.1 | -42.5 | -555.0 | -153.4 |
| VC$_{12}$N$_6$H$_{18}^{2+}$ (BEQQIX) | 370.1 | 368.8 | -1.3 | 357.3 | -12.8 | 180.7 | -189.4 |
| VC$_{14}$N$_3$H$_{13}$O$_5$ (CAGSAE) | -206.6 | -202.1 | 4.5 | -219.3 | -12.7 | -310.8 | -104.2 |
| VC$_{18}$N$_2$H$_{12}$O$_4^-$ (BALLIJ) | -190.2 | -146.0 | 44.2 | -162.8 | 27.4 | -224.5 | -34.3 |
| VC$_{30}$N$_6$H$_{24}$ (DPYRDV) | 132.2 | 167.1 | 34.9 | 118.6 | -13.6 | -49.7 | -181.9 |
| V$_2$C$_{22}$N$_4$H$_{20}$O$_8$ (CEKHUV) | -352.9 | -302.0 | 50.9 | -311.2 | 41.7 | -467.1 | -114.2 |
| VO | 30.5 | 16.9 | -13.7 | 24.3 | -6.2 | 49.8 | 19.3 |
| VO$^-$ | 4.7 | 21.9 | 17.2 | 33.8 | 29.1 | 60.3 | 55.6 |
| VO$_2$ | -55.6 | -68.5 | -12.9 | -41.0 | 14.6 | 18.2 | 73.8 |
| VO$_2^-$ | -101.8 | -125.2 | -23.4 | -69.1 | 32.7 | -21.0 | 80.8 |
| VO$_3^-$ | -167.5 | -189.6 | -22.1 | -137.7 | 29.8 | -59.2 | 108.3 |
| V(H$_2$O)$_6^{3+}$ (COLNUM) | 378.2 | 343.6 | -34.6 | 341.1 | -37.1 | 301.4 | -76.8 |
| V(H$_2$O)$_6^{2+}$ | 30.9 | -21.5 | -52.4 | 24.3 | -6.6 | -61.4 | -92.3 |
| VF | -19.8 | 4.5 | 24.3 | 14.0 | 33.8 | 32.3 | 52.1 |
| VF$_2^-$ | -168.0 | -150.9 | 17.1 | -91.8 | 76.2 | -88.9 | 79.1 |
| VF$_3$ | -201.0 | -235.4 | -34.4 | -192.8 | 8.2 | -126.8 | 74.2 |
| VF$_3^-$ | -247.0 | -250.0 | -3.0 | -196.4 | 50.6 | -188.9 | 58.1 |
| VF$_4^-$ | -380.9 | -343.9 | 37.0 | -288.2 | 92.7 | -263.8 | 117.1 |
| VF$_5$ | -348.7 | -325.6 | 23.1 | -351.7 | -3.0 | -245.3 | 103.4 |
| VF$_5^-$ | -446.0 | -451.2 | -5.2 | -376.7 | 69.3 | -320.8 | 125.2 |
| VOF$^-$ | -113.0 | -127.3 | -14.3 | -86.5 | 26.5 | -59.4 | 53.6 |
| VOF$_2^-$ | -221.0 | -222.4 | -1.4 | -198.5 | 22.5 | -166.1 | 54.9 |
| VAlH$_2$ | 99.1 | 103.8 | 4.7 | 54.6 | -44.5 | 107.4 | 8.3 |
| HVAlH$_2$ | 109.6 | 114.1 | 4.6 | 56.5 | -53.0 | 142.0 | 32.5 |
| VSiH$_3$ | 89.0 | 105.8 | 16.8 | 152.9 | 63.9 | 131.2 | 42.1 |
| HVSiH$_3$ | 89.2 | 87.1 | -2.1 | 137.1 | 47.9 | 153.2 | 64.0 |
| VPH$_2$ | 66.2 | 78.4 | 12.2 | 71.5 | 5.4 | 58.4 | -7.8 |
| HVPH$_2$ | 65.7 | 64.4 | -1.3 | 44.9 | -20.8 | 121.8 | 56.1 |

**Table 2** (continued)

| | | AM1* | | PM6 | | PM5 | |
|---|---|---|---|---|---|---|---|
| **VP** | 95.0 | 105.7 | 10.7 | 117.4 | 22.4 | 124.9 | 30.0 |
| **VS$^+$** | 218.0 | 237.0 | 19.0 | 255.0 | 37.0 | 338.4 | 120.3 |
| **VSH** | 42.7 | 63.2 | 20.5 | 80.0 | 37.3 | 92.3 | 49.6 |
| **HVSH** | 42.9 | 52.0 | 9.1 | 52.6 | 9.7 | 116.8 | 73.8 |
| **VC$_4$H$_8$S$_5$ (CUSPOV)** | -28.8 | -97.2 | -68.4 | -17.1 | 11.7 | 23.8 | 52.6 |
| **VC$_4$H$_8$S$_4$O (CAVWAX)** | -110.6 | -150.0 | -39.4 | -114.9 | -4.3 | -31.5 | 79.1 |
| **VC$_9$H$_{15}$S$_6$O$_4$ (BIRYOO10)** | -209.8 | -166.8 | 43.0 | -216.4 | -6.6 | -110.5 | 99.3 |
| **VC$_{10}$H$_{11}$SO$_3$ (CUDNIY)** | -109.0 | -101.2 | 7.8 | -115.4 | -6.4 | -145.9 | -36.9 |
| **VC$_{12}$H$_{18}$N$_2$O$_2$S (BAWBUW)** | -125.3 | -97.3 | 28.0 | -113.6 | 11.7 | -51.6 | 73.7 |
| **VCl** | 13.1 | 86.6 | 73.5 | 51.6 | 38.5 | 41.6 | 28.5 |
| **VOCl$^-$** | -74.0 | -55.3 | 18.7 | -67.5 | 6.5 | -57.4 | 16.6 |
| **V(C$_5$H$_5$)$_2$Cl (DCPVCL)** | 4.3 | 0.6 | -3.7 | 11.4 | 7.1 | -7.2 | -11.5 |
| **VCl$_2$** | -58.3 | 30.6 | 88.9 | -28.5 | 29.8 | -28.9 | 29.4 |
| **VCl$_2^-$** | -58.8 | -47.7 | 11.2 | -52.1 | 6.7 | -94.5 | -35.7 |
| **VCl$_3$** | -72.8 | -12.0 | 60.9 | -59.3 | 13.5 | -82.3 | -9.5 |
| **VCl$_3^-$** | -136.0 | -64.1 | 71.9 | -105.9 | 30.1 | -167.2 | -31.2 |
| **VC$_{20}$N$_2$H$_{24}$Cl$_3$O (AFUGAJ)** | -98.0 | -111.9 | -13.9 | -127.8 | -29.8 | -186.3 | -88.3 |
| **VCl$_4$** | -126.0 | -65.6 | 60.4 | -114.1 | 11.9 | -130.3 | -4.3 |
| **VCl$_5$** | -131.2 | -131.2 | 0.0 | -147.3 | -16.1 | -147.7 | -16.5 |
| **V$_2$Cl$_6$** | -170.2 | -163.4 | 6.8 | -160.7 | 9.5 | -279.5 | -109.3 |
| **V$_2$Cl$_9^-$ (DOTPAD)** | -350.1 | -481.1 | -131.0 | -345.1 | 5.0 | -470.3 | -120.2 |
| **VOCl$_2^-$** | -141.0 | -123.2 | 17.8 | -137.3 | 3.7 | -142.1 | -1.1 |
| **HVTi** | 153.0 | 152.9 | -0.1 | 180.1 | 27.1 | 341.5 | 188.5 |
| **VCr** | 141.7 | 176.5 | 34.8 | 277.3 | 135.6 | 132.1 | -9.6 |
| **VCu** | 147.5 | 150.9 | 3.4 | 172.7 | 25.2 | 146.0 | -1.4 |
| **HVCu** | 112.1 | 111.5 | -0.6 | 143.9 | 31.9 | 191.2 | 79.1 |
| **VZn** | 125.3 | 124.3 | -1.0 | 12.8 | -112.5 | 135.6 | 10.4 |
| **HVZn** | 97.0 | 101.9 | 4.9 | -30.7 | -127.7 | 138.9 | 41.9 |
| **VBr$_3$** | -43.5 | -33.5 | 10.0 | -28.9 | 14.6 | -3.0 | 40.5 |
| **VBr$_4$** | -80.5 | -75.7 | 4.8 | -74.2 | 6.3 | -19.6 | 60.9 |
| **VBr$_4^+$** | 91.5 | 115.9 | 24.4 | 106.1 | 14.6 | 201.4 | 109.9 |
| **VBr$_4$O$^-$** | -211.6 | -253.1 | -41.5 | -213.2 | -1.6 | -172.9 | 38.7 |
| **V$_2$Br$_4$** | -27.3 | -63.9 | -36.6 | -44.2 | -16.9 | -78.2 | -50.9 |
| **HVZr** | 173.6 | 140.1 | -33.6 | 118.3 | -55.3 | 201.1 | 27.5 |
| **VMo** | 190.5 | 190.5 | 0.0 | 206.5 | 16.0 | 313.0 | 122.5 |
| **HVMo** | 205.6 | 206.0 | 0.4 | 206.8 | 1.2 | 354.4 | 148.8 |
| **VI** | 76.0 | 115.5 | 39.5 | 76.7 | 0.7 | 89.1 | 13.1 |
| **VI$_3$** | 6.2 | 5.1 | -1.1 | 36.8 | 30.6 | -2.9 | -9.1 |
| **VI$_4$** | -29.3 | -27.4 | 1.9 | -37.2 | -7.9 | -35.6 | -6.3 |
| **VI$_5$** | -8.2 | -8.2 | 0.0 | -3.2 | 5.0 | -15.3 | -7.1 |
| | | **AM1*** | | **PM6** | | **PM5** | |
| ***N*=95** | | | | | | | |
| **Most positive error** | | | 88.9 | | 135.6 | | 188.5 |
| **Most negative error** | | | -131.0 | | -127.7 | | -189.4 |
| **MSE** | | | 2.2 | | 6.0 | | 12.9 |
| **MUE** | | | 22.6 | | 25.3 | | 59.0 |
| **RMSD** | | | 33.2 | | 35.7 | | 75.7 |

Errors are classified by coloring the boxes in which they appear. Green indicates errors lower than 10 kcal mol$^{-1}$, yellow 10–20 kcal mol$^{-1}$ and pink those greater than 20 kcal mol$^{-1}$. The coded-names within parentheses indicate the CSD-names of the compounds

(−3.73 eV), VBrO$_2$ (3.12 eV), VClO2 (2.84 eV), VIO$_2$ (2.11 eV) and VOF$_3$ (−1.60 eV). These errors may be an indirect result of using the original AM1 parameters for oxygen, although the fact that the three methods agree well argues against this interpretation.

AM1* shows almost no systematic error for the dipole moments of vanadium compounds. Its MSE is 0.09 Debye, whereas PM6 gives a negative MSE (−0.41 Debye) and PM5 a positive one (0.56 Debye). The mean unsigned error for AM1* is 0.98 Debye, compared with 1.28 and 1.42 Debye for PM5 and PM6, respectively. Particularly large errors, more than 1.0 Debye, for AM1* are found for the fluorine- and/or oxygen-containing compounds VF (−2.89 Debye), VOF$_3$ (1.59 Debye), VO$_2$F (−1.40 Debye)

**Table 3** Calculated AM1*, PM6 and PM5 Koopmans' theorem ionization potentials and dipole moments for vanadium-containing compounds

| Compound | Target | AM1* | Error | PM6 | Error | PM5 | Error |
|---|---|---|---|---|---|---|---|
| **Koopmans' Theorem Ionization Potentials for Vanadium Compounds (eV)** | | | | | | | |
| VCp$_2$ | 6.81 | 7.59 | 0.78 | 7.72 | 0.91 | 7.74 | 0.93 |
| VN | 8.00 | 7.35 | -0.65 | 7.11 | -0.89 | 7.27 | -0.73 |
| VO | 7.24 | 7.61 | 0.37 | 7.03 | -0.21 | 8.06 | 0.82 |
| VO$_2$ | 12.70 | 8.97 | -3.73 | 8.18 | -4.52 | 9.03 | -3.67 |
| V(CO)$_6$ | 7.52 | 7.43 | -0.09 | 7.20 | -0.32 | 7.59 | 0.07 |
| VOF$_3$ | 13.88 | 12.28 | -1.60 | 11.17 | -2.71 | 12.48 | -1.40 |
| VS | 8.40 | 7.83 | -0.57 | 7.63 | -0.77 | 8.19 | -0.21 |
| VClO$_2$ | 7.70 | 10.54 | 2.84 | 10.50 | 2.80 | 10.23 | 2.53 |
| VOCl$_3$ | 11.84 | 11.04 | -0.80 | 11.00 | -0.84 | 11.23 | -0.61 |
| VBrO$_2$ | 7.40 | 10.52 | 3.12 | 10.04 | 2.64 | 10.13 | 2.73 |
| VIO$_2$ | 6.80 | 8.91 | 2.11 | 9.22 | 2.42 | 9.57 | 2.77 |
| VI$_3$ | 6.36 | 6.59 | 0.23 | 4.98 | -1.38 | 4.59 | -1.77 |
| | | **AM1*** | | **PM6** | | **PM5** | |
| *N=12* | | | | | | | |
| MSE | | 0.17 | | -0.24 | | 0.12 | |
| MUE | | 1.41 | | 1.70 | | 1.52 | |
| **Dipole Moments for Vanadium Compounds (Debye)** | | | | | | | |
| VN | 6.28 | 6.89 | 0.61 | 3.24 | -3.04 | 2.90 | -3.38 |
| VO | 3.10 | 4.28 | 1.18 | 5.07 | 1.97 | 3.76 | 0.66 |
| VF | 4.00 | 1.11 | -2.89 | 3.67 | -0.33 | 3.75 | -0.26 |
| VO$_2$F | 3.51 | 2.11 | -1.40 | 4.19 | 0.68 | 5.41 | 1.90 |
| VOF$_3$ | 0.25 | 1.83 | 1.59 | 1.84 | 1.59 | 0.47 | 0.22 |
| VCl | 4.82 | 4.86 | 0.04 | 3.59 | -1.23 | 5.85 | 1.03 |
| VClO$_2$ | 3.38 | 3.74 | 0.36 | 3.46 | 0.08 | 5.00 | 1.62 |
| VOCl$_3$ | 0.57 | 1.30 | 0.73 | 1.82 | 1.25 | 0.22 | -0.35 |
| VBr | 5.02 | 5.89 | 0.87 | 3.43 | -1.59 | 7.12 | 2.10 |
| VBrO$_2$ | 3.29 | 2.68 | -0.61 | 2.54 | -0.76 | 5.17 | 1.88 |
| VIO$_2$ | 3.32 | 3.86 | 0.54 | 0.24 | -3.08 | 4.04 | 0.72 |
| | | **AM1*** | | **PM6** | | **PM5** | |
| *N=11* | | | | | | | |
| MSE | | 0.09 | | -0.41 | | 0.56 | |
| MUE | | 0.98 | | 1.42 | | 1.28 | |

The errors are color coded as follows: green up to 0.5 eV or 0.5 Debye; yellow between 0.5 and 1.0; pink larger than 1.0

and VO (1.18 Debye). These large errors, once again, may be a consequence of using original AM1 parameters for oxygen and fluorine.

Geometries

The geometrical parameters used to parameterize AM1* for vanadium and a comparison of the AM1*, PM6 and PM5 results are shown in Table 4.

AM1* performs slightly better than both PM6 and PM5 for bond angles and significantly better for bond lengths. The AM1* MUE for bond lengths is 0.09 Å, compared with 0.14 Å and 0.20 Å for PM6 and PM5, respectively. PM6 and PM5 overestimate bond lengths to vanadium systematically, with MSEs of 0.05 Å and 0.09 Å, respectively. AM1* shows no systematic error for bond lengths to vanadium. AM1* tends to overestimate the bond angles by 1.4°, whereas PM5 underestimates them by 2.4°. PM6 with an MSE of −0.1° shows no significant systematic error. AM1* performs slightly better for the bond angles to

vanadium with a mean unsigned error of 5.2°, compared with 6.7° and 7.7° for PM6 and PM5, respectively. These differences are, however, hardly significant.

**Chromium**

Heats of formation

The calculated heats of formation for our training set of chromium compounds are shown in Table 5.

Table 5 shows that, for this set of compounds AM1* gives the best results for the heats of formation of chromium compounds. Its MUE (25.1 kcal mol$^{-1}$) is significantly lower than those for PM6 and PM5, 38.4 and 55.9 kcal mol$^{-1}$, respectively. PM6 and PM5 generally predict heats of formation to be too negative with mean signed errors of −23.5 and −43.2 kcal mol$^{-1}$, respectively, whereas AM1* tends to overestimate them by around nine kcal mol$^{-1}$. The largest positive errors for AM1* are found

**Table 4** Calculated AM1*, PM6 and PM5 bond lengths and angles for vanadium-containing compounds

| Compound | Variable | Target | AM1* | Error | PM6 | Error | PM5 | Error |
|---|---|---|---|---|---|---|---|---|
| VH | V-H | 1.72 | 1.58 | -0.14 | 1.09 | -0.63 | 1.82 | 0.10 |
| VH$_2$ | V-H | 1.78 | 1.59 | -0.19 | 1.30 | -0.48 | 1.85 | 0.08 |
| VH$_3$ | V-H | 1.67 | 1.59 | -0.09 | 1.21 | -0.46 | 1.89 | 0.22 |
| | H-V-H | 120.0 | 120.0 | 0.0 | 122.0 | 2.0 | 119.5 | -0.5 |
| VC$_{10}$H$_{10}$ (Bicyclopentadienyl vanadium) | V-C | 2.28 | 2.26 | -0.02 | 2.35 | 0.07 | 2.41 | 0.13 |
| VC$_{10}$H$_{10}$ (CPNDYV) | V-C | 2.24 | 2.25 | 0.01 | 2.36 | 0.12 | 2.40 | 0.16 |
| VC$_{12}$H$_{12}$ (Dibenzene vanadium) | V-C | 2.21 | 2.24 | 0.03 | 2.45 | 0.24 | 2.40 | 0.19 |
| VC$_{12}$H$_{12}$ (CPLHLV01) | V-C(Cp) | 2.25 | 2.26 | 0.00 | 2.36 | 0.11 | 2.38 | 0.13 |
| | V-C(C6) | 2.18 | 2.25 | 0.07 | 2.36 | 0.18 | 2.40 | 0.22 |
| VC$_{14}$H$_{22}$ (COGXOL) | V-C1 | 2.20 | 2.17 | -0.03 | 2.31 | 0.11 | 2.40 | 0.20 |
| | V-C2 | 2.24 | 2.30 | 0.06 | 2.47 | 0.23 | 2.42 | 0.18 |
| | C-V-C | 162.0 | 143.6 | -18.4 | 177.0 | 15.1 | 145.5 | -16.5 |
| | V-C3 | 2.24 | 2.30 | 0.06 | 2.37 | 0.13 | 2.49 | 0.25 |
| VN | V#N | 1.61 | 1.66 | 0.05 | 1.50 | -0.12 | 1.69 | 0.08 |
| V(CN)$_5$ | V-C | 1.97 | 2.06 | 0.09 | 2.05 | 0.08 | 2.02 | 0.05 |
| V(NH$_3$)$_6$$^{2+}$ | V-N | 2.27 | 2.04 | -0.23 | 2.27 | 0.00 | 2.16 | -0.11 |
| VC$_{12}$N$_6$H$_{18}$$^{2+}$ (BEQQIX) | V-N | 2.11 | 2.00 | -0.11 | 2.08 | -0.03 | 2.01 | -0.10 |
| | N-C | 1.12 | 1.17 | 0.05 | 1.16 | 0.04 | 1.16 | 0.04 |
| | C-C | 1.45 | 1.44 | -0.01 | 1.43 | -0.02 | 1.43 | -0.02 |
| VC$_{30}$N$_6$H$_{24}$ (DPYRDV) | V-N | 2.10 | 2.09 | -0.01 | 2.15 | 0.05 | 2.07 | -0.03 |
| | N-V-N | 79.8 | 82.2 | 2.4 | 79.8 | 0.0 | 80.8 | 1.0 |
| VO | V-O | 1.59 | 1.70 | 0.11 | 1.55 | -0.04 | 1.58 | -0.01 |
| VO$^-$ | V-O | 1.64 | 1.75 | 0.11 | 1.61 | -0.02 | 1.74 | 0.10 |
| VO$_2$ | V-O | 1.59 | 1.71 | 0.12 | 1.57 | -0.02 | 1.62 | 0.03 |
| | O-V-O | 110.0 | 131.6 | 21.6 | 115.5 | 5.5 | 102.2 | -7.8 |
| VO$_2$$^-$ | V-O | 1.64 | 1.73 | 0.08 | 1.63 | -0.01 | 1.66 | 0.02 |
| VO$_3$$^-$ | V-O | 1.64 | 1.74 | 0.10 | 1.63 | -0.02 | 1.67 | 0.03 |
| VO(H$_2$O)$_5$ | V=O | 1.59 | 1.71 | 0.12 | 1.54 | -0.05 | 1.56 | -0.03 |
| | V-O(eq) | 2.02 | 2.09 | 0.07 | 2.20 | 0.18 | 2.08 | 0.06 |
| | V-O(ax) | 2.22 | 2.11 | -0.11 | 2.42 | 0.20 | 2.22 | 0.00 |
| VH$_{12}$O$_6$$^{3+}$ (COLNUM) | V-O | 1.99 | 2.08 | 0.09 | 2.19 | 0.20 | 2.01 | 0.02 |
| V(H$_2$O)$_6$$^{2+}$ | V-O | 2.16 | 2.09 | -0.07 | 2.22 | 0.06 | 2.12 | -0.04 |
| VCH$_5$O$_3$ (Methylvanadium(V)oxidehydroxide) | V-C | 2.03 | 2.08 | 0.05 | 2.10 | 0.07 | 2.14 | 0.11 |
| | V=O | 1.59 | 1.74 | 0.15 | 1.58 | -0.01 | 1.59 | 0.00 |
| | V-O | 1.79 | 1.88 | 0.09 | 1.74 | -0.05 | 1.76 | -0.03 |
| V(CO)$_3$$^-$ | V-C | 1.94 | 2.00 | 0.07 | 1.93 | -0.01 | 2.15 | 0.21 |
| | C-V-C | 120.0 | 121.3 | 1.3 | 124.4 | 4.4 | 119.2 | -0.8 |
| V(CO)$_4$$^-$ | V-C | 1.99 | 2.00 | 0.00 | 2.06 | 0.07 | 2.08 | 0.09 |
| | C-V-C | 90.0 | 90.0 | 0.0 | 90.0 | 0.0 | 90.0 | 0.0 |
| V(CO)$_5$$^-$ | V-C | 1.96 | 1.99 | 0.04 | 1.94 | -0.02 | 2.06 | 0.10 |
| | V-C | 1.94 | 1.97 | 0.03 | 1.90 | -0.04 | 2.13 | 0.19 |
| | C-V-C | 120.0 | 120.1 | 0.1 | 120.1 | 0.1 | 130.4 | 10.4 |
| | C-V-C | 180.0 | 179.9 | -0.1 | 179.9 | -0.1 | 159.0 | -21.0 |
| VC$_{11}$H$_{12}$O (BEYRIG) | V-O | 1.96 | 1.99 | 0.03 | 1.67 | -0.29 | 1.85 | -0.11 |
| | V-C(Cp) | 2.26 | 2.29 | 0.03 | 2.43 | 0.17 | 2.38 | 0.12 |
| | V-C(O) | 2.09 | 2.68 | 0.59 | 2.97 | 0.88 | 2.92 | 0.83 |
| VC$_{32}$N$_4$H$_{34}$O (CAKMAC10) | V=O | 1.58 | 1.74 | 0.16 | 1.57 | -0.01 | 1.59 | 0.01 |
| | V-N | 2.03 | 2.00 | -0.03 | 2.03 | 0.00 | 2.05 | 0.02 |
| | O-V-N | 106.0 | 104.3 | -1.7 | 104.5 | -1.5 | 101.4 | -4.6 |
| VC$_{12}$H$_{10}$O$_2$$^+$ (CCPZRB) | V-C | 1.95 | 2.05 | 0.10 | 2.06 | 0.11 | 2.06 | 0.11 |
| | C-O | 1.15 | 1.17 | 0.02 | 1.14 | -0.01 | 1.14 | -0.01 |
| | V-C(Cp) | 2.24 | 2.23 | -0.01 | 2.32 | 0.08 | 2.31 | 0.07 |
| VC$_{14}$H$_{14}$O$_4$$^+$ (BOBHIJ) | V-C(O) | 1.93 | 2.05 | 0.12 | 2.06 | 0.13 | 2.06 | 0.13 |
| | C-O | 1.18 | 1.18 | 0.00 | 1.15 | -0.03 | 1.15 | -0.03 |

**Table 4** (continued)

| Compound | Bond/Angle | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **VC$_{18}$N$_2$H$_{12}$O$_4$$^-$ (BALLIJ)** | V=O | 1.64 | 1.75 | 0.11 | 1.61 | -0.03 | 1.63 | -0.01 |
| | V-O | 1.97 | 2.11 | 0.14 | 2.13 | 0.16 | 2.10 | 0.13 |
| | V-N | 2.31 | 2.19 | -0.12 | 2.41 | 0.10 | 2.16 | -0.15 |
| | O=V-O | 95.7 | 94.5 | -1.2 | 98.6 | 2.9 | 93.9 | -1.8 |
| | O=V-N | 163.0 | 166.9 | 3.9 | 161.8 | -1.2 | 168.2 | 5.2 |
| **VC$_{10}$H$_{14}$O$_5$ (ACACVO)** | V=O | 1.56 | 1.73 | 0.17 | 1.59 | 0.03 | 1.58 | 0.01 |
| | V-O | 1.97 | 1.95 | -0.02 | 2.03 | 0.06 | 2.05 | 0.08 |
| | O-V-O | 104.5 | 92.3 | -12.2 | 105.9 | 1.3 | 85.9 | -18.6 |
| **VC$_{12}$H$_8$O$_5$$^{2-}$ (BOBWOE)** | V-O | 1.96 | 2.02 | 0.06 | 2.09 | 0.13 | 2.03 | 0.07 |
| | V=O | 1.61 | 1.74 | 0.13 | 1.59 | -0.02 | 1.60 | -0.01 |
| | O-V-O | 83.0 | 85.9 | 2.9 | 76.9 | -6.2 | 85.8 | 2.8 |
| | O-V=O | 104.0 | 110.7 | 6.7 | 109.2 | 5.2 | 107.3 | 3.3 |
| **VC$_{15}$NH$_{19}$O$_5$ (CUCWUS)** | V=O | 1.57 | 1.73 | 0.16 | 1.58 | 0.01 | 1.58 | 0.01 |
| | V-O | 2.01 | 2.03 | 0.02 | 1.86 | -0.15 | 1.90 | -0.11 |
| | V-N | 2.48 | 2.11 | -0.37 | 2.44 | -0.04 | 2.09 | -0.39 |
| | O=V-O | 98.2 | 96.9 | -1.3 | 104.6 | 6.3 | 92.3 | -5.9 |
| **VC$_{14}$N$_3$H$_{13}$O$_5$ (CAGSAE)** | V=O | 1.59 | 1.73 | 0.14 | 1.56 | -0.03 | 1.58 | -0.01 |
| | V-O(C) | 1.99 | 1.99 | 0.00 | 1.90 | -0.09 | 2.09 | 0.10 |
| | V-N | 2.33 | 2.16 | -0.17 | 2.56 | 0.23 | 2.22 | -0.11 |
| | V-N' | 2.11 | 2.06 | -0.05 | 2.12 | 0.01 | 2.05 | -0.06 |
| | O-V-O | 101.1 | 96.1 | -5.0 | 101.6 | 0.5 | 99.6 | -1.5 |
| **V(CO)$_6$** | V-C | 2.01 | 2.02 | 0.01 | 2.00 | -0.01 | 2.02 | 0.01 |
| **V(CO)$_6$$^-$** | V-C | 1.93 | 1.98 | 0.05 | 1.95 | 0.02 | 1.95 | 0.02 |
| | C-O | 1.14 | 1.19 | 0.05 | 1.16 | 0.02 | 1.18 | 0.04 |
| | C-V-C | 180.0 | 180.0 | 0.0 | 140.5 | -39.5 | 179.8 | -0.2 |
| | C-V-C | 90.0 | 90.0 | 0.0 | 87.2 | -2.8 | 90.00 | 0.00 |
| **VC$_{18}$H$_{12}$O$_6$$^{2-}$ (BOBWEU)** | V-O | 1.92 | 2.00 | 0.08 | 1.93 | 0.01 | 2.10 | 0.18 |
| | O-V-O | 80.5 | 84.8 | 4.3 | 77.5 | -3.0 | 79.1 | -1.4 |
| **VC$_{10}$N$_2$H$_{12}$O$_8$ (Vanadium(III) EDTA)** | V-N | 2.19 | 2.08 | -0.11 | 2.26 | 0.07 | 2.07 | -0.12 |
| | V-O | 2.03 | 2.03 | 0.00 | 2.00 | -0.03 | 1.99 | -0.04 |
| | N-V-N | 87.3 | 88.0 | 0.8 | 84.8 | -2.5 | 86.7 | -0.5 |
| **VC$_4$O$_{10}$$^{3-}$ (AOXOVA)** | V=O | 1.65 | 1.74 | 0.09 | 1.62 | -0.03 | 1.63 | -0.02 |
| | V-O | 1.99 | 1.98 | -0.01 | 1.91 | -0.08 | 2.17 | 0.18 |
| | O=V=O | 103.8 | 121.6 | 17.8 | 111.7 | 7.8 | 106.4 | 2.6 |
| | O-V=O | 95.3 | 101.3 | 6.0 | 108.2 | 12.9 | 85.6 | -9.7 |
| **VC$_4$H$_4$O$_{10}$$^-$ (DABKEW)** | V-O(H2) | 1.97 | 2.11 | 0.14 | 3.44 | 1.47 | 2.17 | 0.20 |
| | V-O(C2O3) | 2.00 | 2.00 | 0.00 | 2.00 | 0.00 | 1.97 | -0.03 |
| | O-V-O | 90.2 | 85.5 | -4.7 | 104.4 | 14.3 | 83.6 | -6.6 |
| **VC$_6$H$_6$O$_{10}$$^{2-}$ (AJUJEU)** | V-O | 2.00 | 2.03 | 0.03 | 2.05 | 0.05 | 2.05 | 0.05 |
| | O-V-O | 87.2 | 91.0 | 3.8 | 92.3 | 5.1 | 95.8 | 8.6 |
| | V=O | 1.59 | 1.75 | 0.16 | 1.60 | 0.01 | 1.16 | -0.43 |
| **VF** | V-F | 1.76 | 1.84 | 0.08 | 1.66 | -0.10 | 1.76 | 0.00 |
| **C$_6$H$_5$VF$^-$** | V-C | 2.18 | 2.07 | -0.12 | 2.06 | -0.13 | 2.22 | 0.04 |
| | V-F | 1.93 | 1.83 | -0.10 | 1.82 | -0.11 | 2.01 | 0.08 |
| **VO$_2$F** | V-F | 1.77 | 1.81 | 0.04 | 1.73 | -0.04 | 1.79 | 0.01 |
| | V=O | 1.61 | 1.73 | 0.12 | 1.58 | -0.03 | 1.62 | 0.01 |
| **VF$_2$$^-$** | V-F | 1.89 | 1.81 | -0.08 | 1.89 | 0.00 | 1.92 | 0.03 |
| **VF$_3$** | V-F | 1.75 | 1.81 | 0.06 | 1.70 | -0.05 | 1.75 | 0.00 |
| | F-V-F | 120.0 | 106.2 | -13.8 | 120.0 | 0.0 | 107.1 | -12.9 |
| **VF$_3$$^-$** | V-F | 1.84 | 1.85 | 0.00 | 1.86 | 0.02 | 1.85 | 0.01 |
| **VOF$_3$** | V=O | 1.57 | 1.73 | 0.16 | 1.56 | -0.01 | 1.59 | 0.02 |
| | V-F | 1.73 | 1.82 | 0.09 | 1.74 | 0.01 | 1.74 | 0.01 |
| | O=V-F | 107.5 | 112.5 | 5.0 | 109.6 | 2.1 | 105.1 | -2.4 |
| **VF$_4$$^-$** | V-F | 1.83 | 1.86 | 0.03 | 1.83 | 0.01 | 1.86 | 0.03 |
| **VF$_5$** | V-F(ax) | 1.73 | 1.84 | 0.11 | 1.74 | 0.01 | 1.75 | 0.02 |
| | V-F(eq) | 1.71 | 1.83 | 0.12 | 1.74 | 0.03 | 1.73 | 0.02 |
| **VF$_5$$^-$** | V-F | 1.76 | 1.85 | 0.09 | 1.79 | 0.03 | 1.77 | 0.01 |

**Table 4** (continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | V-F | 1.83 | 1.87 | 0.05 | 1.85 | 0.02 | 1.89 | 0.06 |
| **VF₆** | V-F | 1.81 | 1.86 | 0.05 | 1.80 | -0.01 | 1.80 | -0.01 |
| **VAlH₂** | V-Al | 2.67 | 2.36 | -0.31 | 2.05 | -0.61 | 2.43 | -0.24 |
| **VSiH₃** | V-Si | 2.62 | 2.34 | -0.28 | 2.56 | -0.05 | 2.59 | -0.03 |
| **VP** | V#P | 2.14 | 2.18 | 0.04 | 2.34 | 0.20 | 1.89 | -0.25 |
| **VPH₂** | V-P | 2.46 | 2.21 | -0.25 | 2.46 | 0.01 | 2.15 | -0.31 |
| **VC₁₂P₂H₂₄ (DACFUI)** | V-P | 2.46 | 2.31 | -0.15 | 2.46 | 0.00 | 1.94 | -0.52 |
| | P-V-P | 81.1 | 81.1 | 0.0 | 82.8 | 1.7 | 88.1 | 7.0 |
| | V-C(H3) | 2.22 | 2.00 | -0.22 | 2.16 | -0.06 | 2.43 | 0.21 |
| | V-C(C4) | 2.30 | 2.28 | -0.02 | 2.35 | 0.05 | 2.52 | 0.22 |
| **VS⁺** | V-S | 2.03 | 2.20 | 0.17 | 1.99 | -0.04 | 2.38 | 0.35 |
| **VSH** | V-S | 2.32 | 2.35 | 0.03 | 2.09 | -0.23 | 2.46 | 0.14 |
| **HVSH₂** | V-S | 2.35 | 2.30 | -0.04 | 2.25 | -0.10 | 2.45 | 0.10 |
| **VC₁₂N₂H₁₈SO₂ (BAWBUW)** | V-S | 2.07 | 2.20 | 0.13 | 2.13 | 0.06 | 2.21 | 0.14 |
| | V-O | 1.95 | 2.04 | 0.09 | 1.73 | -0.22 | 2.00 | 0.05 |
| | S-V-O | 109.6 | 113.6 | 4.0 | 105.6 | -4.0 | 111.2 | 1.6 |
| | V-N | 2.03 | 2.00 | -0.03 | 2.17 | 0.14 | 1.95 | -0.08 |
| **VC₁₀H₁₁SO₃ (CUDNIY)** | V-S | 2.47 | 2.18 | -0.29 | 2.28 | -0.19 | 2.75 | 0.28 |
| | V-C(O) | 1.88 | 1.99 | 0.11 | 2.00 | 0.12 | 2.00 | 0.12 |
| | V-C(Cp) | 2.23 | 2.23 | 0.00 | 2.34 | 0.11 | 2.39 | 0.16 |
| **VC₂₀N₄H₁₆SO₅ (ASAVAR)** | V-O | 1.58 | 1.74 | 0.16 | 1.58 | 0.00 | 1.59 | 0.01 |
| | V-O' | 1.96 | 1.86 | -0.10 | 1.70 | -0.26 | 1.76 | -0.20 |
| | O-V-O' | 105.0 | 98.5 | -6.5 | 105.8 | 0.7 | 98.7 | -6.3 |
| | V-N | 2.10 | 2.09 | -0.01 | 2.06 | -0.04 | 1.98 | -0.12 |
| **V(PH₂)(NH₂)(SH)** | V-P | 2.45 | 2.30 | -0.15 | 2.46 | 0.01 | 1.80 | -0.65 |
| | V-N | 1.85 | 1.81 | -0.04 | 1.78 | -0.07 | 1.73 | -0.12 |
| | V-S | 2.28 | 2.29 | 0.01 | 2.22 | -0.06 | 2.43 | 0.15 |
| **VC₄H₈S₄O²⁻ (CAVWAX)** | V=O | 1.63 | 1.76 | 0.13 | 1.58 | -0.05 | 1.58 | -0.05 |
| | V-S | 2.38 | 2.44 | 0.06 | 2.42 | 0.04 | 2.71 | 0.33 |
| | O=V-S | 104.0 | 107.7 | 3.7 | 102.8 | -1.2 | 101.8 | -2.2 |
| **VC₄H₈S₅ (CUSPOV)** | V-S | 2.35 | 2.31 | -0.04 | 2.29 | -0.06 | 2.45 | 0.10 |
| | S-V-S | 85.8 | 89.8 | 4.0 | 88.3 | 2.4 | 95.1 | 9.3 |
| | V=S | 2.10 | 2.28 | 0.18 | 2.36 | 0.26 | 2.99 | 0.89 |
| **VC₉H₁₅S₆O₄ (BIRYOO10)** | V-S | 2.47 | 2.47 | 0.00 | 2.43 | -0.04 | 2.54 | 0.07 |
| | S-V-S | 69.1 | 72.0 | 2.9 | 73.4 | 4.3 | 70.8 | 1.7 |
| | V-S | 2.62 | 2.53 | -0.09 | 2.60 | -0.02 | 2.82 | 0.20 |
| | V=O | 1.58 | 1.74 | 0.16 | 1.54 | -0.04 | 1.55 | -0.03 |
| **V(C₅H₅)₂Cl (DCPVCL)** | V-Cl | 2.39 | 2.30 | -0.09 | 2.23 | -0.16 | 2.32 | -0.07 |
| | V-C | 2.27 | 2.27 | 0.00 | 2.39 | 0.12 | 2.40 | 0.13 |
| **VClO₂** | V-Cl | 2.19 | 2.20 | 0.01 | 2.18 | -0.01 | 2.20 | 0.01 |
| | V=O | 1.60 | 1.72 | 0.12 | 1.56 | -0.04 | 1.60 | 0.00 |
| **VC₁₁P₂H₂₃Cl₂ (CECKIE)** | V-Cl | 2.40 | 2.29 | -0.11 | 2.57 | 0.17 | 2.31 | -0.09 |
| | Cl-V-Cl | 126.1 | 151.8 | 25.7 | 160.6 | 34.6 | 149.4 | 23.3 |
| | V-P | 2.51 | 2.25 | -0.26 | 2.50 | -0.01 | 2.00 | -0.51 |
| | V-C | 2.31 | 2.31 | 0.00 | 2.37 | 0.06 | 2.48 | 0.17 |
| **VC₁₂P₄H₃₂Cl₂ (DAJDOH)** | V-Cl | 2.44 | 2.22 | -0.22 | 2.67 | 0.23 | 2.38 | -0.06 |
| | V-P | 2.50 | 2.19 | -0.31 | 2.48 | -0.02 | 2.03 | -0.47 |
| | Cl-V-P | 88.2 | 88.8 | 0.6 | 89.3 | 1.1 | 98.6 | 10.4 |
| **VCl₂⁻** | V-Cl | 2.35 | 2.21 | -0.14 | 2.39 | 0.04 | 2.38 | 0.03 |
| **VCl₃** | V-Cl | 2.15 | 2.23 | 0.08 | 2.12 | -0.03 | 2.16 | 0.01 |
| **VCl₃⁻** | V-Cl | 2.29 | 2.30 | 0.01 | 2.35 | 0.06 | 2.30 | 0.01 |
| **VCl₃O** | V-O | 1.57 | 1.71 | 0.14 | 1.55 | -0.02 | 1.57 | 0.00 |
| | V-Cl | 2.14 | 2.21 | 0.07 | 2.16 | 0.02 | 2.15 | 0.01 |
| | O-V-Cl | 111.3 | 117.6 | 6.3 | 108.2 | -3.1 | 105.3 | -6.0 |
| **VC₂₀N₂H₂₄Cl₃O (AFUGAJ)** | V-Cl | 2.32 | 2.27 | -0.05 | 2.31 | -0.01 | 2.28 | -0.04 |
| | Cl-V-Cl | 170.9 | 166.3 | -4.5 | 164.0 | -6.8 | 119.9 | -51.0 |
| | V-O | 2.12 | 2.18 | 0.06 | 2.23 | 0.11 | 2.16 | 0.04 |

**Table 4** (continued)

| | | | AM1* | | PM6 | | PM5 | |
|---|---|---|---|---|---|---|---|---|
| | V-N | 2.13 | 1.97 | -0.16 | 2.11 | -0.02 | 2.04 | -0.09 |
| **VCl₄** | V-Cl | 2.14 | 2.22 | 0.08 | 2.16 | 0.02 | 2.13 | -0.01 |
| **VCl₄O⁻** | V-O | 1.56 | 1.72 | 0.16 | 1.55 | -0.01 | 1.57 | 0.01 |
| | V-Cl | 2.26 | 2.25 | -0.01 | 2.32 | 0.06 | 2.26 | 0.00 |
| | O-V-Cl | 103.3 | 107.2 | 3.9 | 104.9 | 1.6 | 103.0 | -0.3 |
| **VCl₅** | V-Cl(eq) | 2.19 | 2.20 | 0.01 | 2.17 | -0.02 | 2.13 | -0.06 |
| | V-Cl(ax) | 2.26 | 2.21 | -0.05 | 2.24 | -0.02 | 2.18 | -0.09 |
| **VCl₆⁻** | V-Cl | 2.33 | 2.23 | -0.10 | 2.29 | -0.04 | 2.22 | -0.11 |
| **V₂** | V-V | 1.77 | 1.57 | -0.20 | 1.70 | -0.07 | 1.70 | -0.07 |
| **V₂C₁₆H₁₆ (CAMXAP)** | V-C(C5) | 2.23 | 2.24 | 0.01 | 2.30 | 0.07 | 2.43 | 0.20 |
| | V-C(C4) | 2.26 | 2.23 | -0.03 | 2.35 | 0.09 | 2.40 | 0.14 |
| **V₂C₁₂H₂₀O₈ (BIWDIU)** | V=O | 1.59 | 1.73 | 0.14 | 1.59 | 0.00 | 1.59 | 0.00 |
| | V-O(C5) | 1.97 | 2.05 | 0.08 | 1.85 | -0.12 | 2.10 | 0.13 |
| | O-V-O | 108.1 | 105.1 | -3.0 | 109.0 | 0.9 | 80.5 | -27.6 |
| **V₂C₂₂N₄H₂₀O₈ (CEKHUV)** | V-O(C) | 1.95 | 2.02 | 0.07 | 2.07 | 0.12 | 1.99 | 0.04 |
| | V-O(br) | 2.20 | 2.19 | -0.01 | 1.99 | -0.21 | 2.25 | 0.05 |
| | O-V-O | 73.4 | 79.7 | 6.3 | 60.2 | -13.2 | 76.1 | 2.7 |
| | V-N | 2.13 | 2.07 | -0.06 | 2.16 | 0.03 | 2.02 | -0.11 |
| **V₂C₁₈H₁₀O₈F₁₂ (CPVFAC)** | V-O(t) | 1.62 | 1.74 | 0.12 | 1.62 | 0.00 | 1.63 | 0.00 |
| | V-V | 3.71 | 3.52 | -0.19 | 4.65 | 0.94 | 2.87 | -0.84 |
| | V-O | 2.31 | 2.14 | -0.17 | 6.62 | 4.31 | 2.03 | -0.28 |
| | O-V-V | 70.8 | 68.6 | -2.2 | 36.4 | -34.4 | 74.7 | 3.9 |
| | V-C | 2.39 | 2.35 | -0.04 | 2.44 | 0.05 | 2.73 | 0.34 |
| **V₂Cl₄** | V-Cl(t) | 2.17 | 2.23 | 0.06 | 2.08 | -0.09 | 2.16 | -0.01 |
| | V-Cl(b) | 2.34 | 2.24 | -0.10 | 2.46 | 0.12 | 2.20 | -0.14 |
| | Cl-V-Cl | 98.1 | 94.0 | -4.1 | 74.6 | -23.5 | 115.9 | 17.8 |
| **V₂Cl₉⁻ (DOTPAD)** | V-Cl(t) | 2.19 | 2.20 | 0.01 | 2.25 | 0.06 | 2.26 | 0.07 |
| | Cl-V-Cl | 96.6 | 101.1 | 4.5 | 102.2 | 5.6 | 90.3 | -6.3 |
| | V-Cl(br) | 2.46 | 2.46 | 0.00 | 2.52 | 0.06 | 2.49 | 0.03 |
| **HVTi** | V-Ti | 1.73 | 1.73 | 0.01 | 2.66 | 0.93 | 11.82 | 10.09 |
| **VCr** | V-Cr | 2.65 | 2.59 | -0.06 | 3.12 | 0.47 | 2.65 | 0.00 |
| **VCu** | V-Cu | 2.40 | 2.48 | 0.09 | 2.65 | 0.25 | 2.32 | -0.08 |
| **HVCu** | V-Cu | 2.48 | 2.46 | -0.02 | 2.72 | 0.24 | 2.31 | -0.17 |
| **VZn** | V-Zn | 2.67 | 2.64 | -0.03 | 2.02 | -0.65 | 2.35 | -0.32 |
| **HVZn** | V-Zn | 2.72 | 2.65 | -0.07 | 2.04 | -0.68 | 2.37 | -0.35 |
| **VBr** | V-Br | 2.39 | 2.39 | 0.00 | 2.25 | -0.14 | 2.50 | 0.11 |
| **VBrO₂** | V-Br | 2.33 | 2.28 | -0.05 | 2.30 | -0.04 | 2.46 | 0.13 |
| | V=O | 1.61 | 1.67 | 0.06 | 1.57 | -0.05 | 1.60 | -0.01 |
| **VBr₃** | V-Br | 2.33 | 2.29 | -0.04 | 2.27 | -0.06 | 2.42 | 0.09 |
| **VBr₄** | V-Br | 2.31 | 2.28 | -0.03 | 2.29 | -0.02 | 2.39 | 0.09 |
| **VBr₄⁺** | V-Br | 2.23 | 2.24 | 0.01 | 2.22 | -0.02 | 2.31 | 0.08 |
| **VBr₄O⁻** | V-Br | 2.48 | 2.34 | -0.14 | 2.48 | 0.00 | 2.51 | 0.04 |
| **VBr₆⁻** | V-Br | 2.50 | 2.31 | -0.19 | 2.47 | -0.03 | 2.47 | -0.03 |
| **HVZr** | V-Zr | 2.06 | 1.94 | -0.12 | 2.39 | 0.33 | 3.11 | 1.05 |
| **VMo** | V-Mo | 1.91 | 1.76 | -0.15 | 2.21 | 0.30 | 3.46 | 1.55 |
| **HVMo** | V-Mo | 1.87 | 1.96 | 0.09 | 2.18 | 0.31 | 3.72 | 1.85 |
| **VI** | V-I | 2.59 | 2.51 | -0.08 | 2.58 | -0.01 | 2.21 | -0.38 |
| **VIO₂** | V-I | 2.55 | 2.64 | 0.09 | 2.56 | 0.01 | 2.37 | -0.18 |
| | V=O | 1.60 | 1.67 | 0.07 | 1.56 | -0.04 | 1.60 | 0.00 |
| **VI₃** | V-I | 2.54 | 2.58 | 0.04 | 2.54 | 0.00 | 2.34 | -0.20 |
| **VI₄** | V-I | 2.52 | 2.58 | 0.06 | 2.69 | 0.17 | 2.33 | -0.19 |
| **VI₅** | V-I | 2.59 | 2.47 | -0.12 | 2.63 | 0.04 | 2.77 | 0.18 |
| | | | **AM1\*** | | **PM6** | | **PM5** | |
| *N=178* | | | | | | | | |
| **MSE bond length** | | | | 0.00 | | 0.05 | | 0.09 |
| **MUE bond length** | | | | 0.09 | | 0.14 | | 0.20 |
| *N=42* | | | | | | | | |
| **MSE bond angle** | | | | 1.4 | | -0.1 | | -2.4 |
| **MUE bond angle** | | | | 5.2 | | 6.7 | | 7.7 |

The coded-names within parentheses indicate the CSD-names of the compounds. The errors are color coded as follows: green up to 0.05 Å or 0.5°; yellow between 0.05–0.1 Å or 0.5–1.0°; pink larger than 0.1 Å or 1°

**Table 5** Calculated AM1*, PM6 and PM5 heats of formation and errors compared with our target values for the chromium-containing compounds used to parameterize AM1* (all values kcal mol$^{-1}$)

| Compound | Target $\Delta H^o_f$ | AM1* $\Delta H^o_f$ | Error | PM6 $\Delta H^o_f$ | Error | PM5 $\Delta H^o_f$ | Error |
|---|---|---|---|---|---|---|---|
| $Cr^-$ | 79.4 | 76.0 | -3.4 | 127.0 | 47.5 | 143.7 | 64.3 |
| $Cr$ | 95.0 | 95.0 | 0.0 | 94.3 | -0.7 | 95.0 | 0.0 |
| $Cr^+$ | 251.0 | 251.8 | 0.8 | 236.0 | -15.0 | 261.5 | 10.5 |
| $Cr^{2+}$ | 631.0 | 658.6 | 27.6 | 613.0 | -18.0 | 658.0 | 27.0 |
| $Cr^{3+}$ | 1345.0 | 1279.2 | -65.8 | 1202.8 | -142.2 | 1284.5 | -60.5 |
| $Cr_2$ | 148.0 | 147.4 | -0.6 | 123.2 | -24.8 | 184.6 | 36.6 |
| $Cr_2^-$ | 144.8 | 144.7 | -0.1 | 185.7 | 40.9 | 144.7 | -0.1 |
| $CrH$ | 99.9 | 96.9 | -3.0 | 30.4 | -69.5 | 20.4 | -79.4 |
| $CrH_2$ | 109.2 | 109.2 | 0.0 | -48.6 | -157.8 | -28.3 | -137.5 |
| $Cr(Cp)_2$ | 59.6 | 90.2 | 30.6 | 83.3 | 23.7 | 41.5 | -18.1 |
| $Cr(C_6H_6)_2$ | 56.0 | 31.4 | -24.6 | 73.3 | 17.3 | 57.7 | 1.7 |
| $CrN$ | 120.7 | 108.4 | -12.3 | 130.2 | 9.5 | -14.6 | -135.3 |
| $Cr(NH_3)_6^{2+}$ | 279.1 | 279.0 | -0.1 | 302.2 | 23.1 | 48.4 | -230.7 |
| $CrN_6C_{12}H_{30}^{3+}$ (SUKFEJ) | 597.6 | 618.4 | 20.8 | 538.3 | -59.3 | 521.1 | -76.5 |
| $CrO$ | 45.0 | 43.7 | -1.3 | 40.6 | -4.4 | 19.5 | -25.5 |
| $CrO^-$ | 23.9 | 16.7 | -7.2 | 30.5 | 6.6 | -5.5 | -29.4 |
| $CrO_2$ | -18.0 | -33.0 | -15.0 | -60.3 | -42.3 | -42.7 | -24.7 |
| $CrO_2^-$ | -70.0 | -54.7 | 15.3 | -67.6 | 2.4 | -122.6 | -52.6 |
| $CrO_3$ | -70.0 | -115.7 | -45.7 | -59.0 | 11.0 | -77.9 | -7.9 |
| $CrO_3^-$ | -158.4 | -140.1 | 18.3 | -146.0 | 12.4 | -200.6 | -42.2 |
| $CrO_4^{2-}$ | -186.0 | -185.7 | 0.3 | -175.7 | 10.3 | -227.4 | -41.4 |
| $HCrO_3^-$ | -270.5 | -135.4 | 135.1 | -192.4 | 78.1 | -253.2 | 17.3 |
| $Cr(H_2O)_6^{2+}$ | 58.1 | 34.8 | -23.3 | 29.0 | -29.1 | -55.7 | -113.8 |
| $Cr(CO)_3$ | -44.0 | -38.0 | 6.0 | -36.7 | 7.3 | -10.4 | 33.6 |
| $Cr(CO)_4$ | -102.0 | -75.5 | 26.6 | -92.1 | 9.9 | -36.2 | 65.8 |
| $Cr(CO)_4^-$ | -66.1 | -135.1 | -69.0 | -117.6 | -51.5 | -144.9 | -78.7 |
| $CrC_4H_4O_{10}^-$ (KOXACR) | -545.7 | -475.2 | 70.6 | -569.2 | -23.5 | -656.8 | -111.1 |
| $Cr(CO)_5$ | -154.0 | -158.1 | -4.1 | -162.4 | -8.4 | -140.4 | 13.6 |
| $Cr(CO)_6$ | -218.0 | -194.4 | 23.6 | -216.6 | 1.4 | -212.8 | 5.2 |
| $Cr(C_2O_4)_3^{3-}$ (AMOXCR) | -547.4 | -474.8 | 72.7 | -589.7 | -42.3 | -679.0 | -131.6 |
| $Cr(CO)_3(C_6H_6)$ | -83.7 | -82.7 | 1.0 | -75.4 | 8.3 | -84.6 | -0.9 |
| $Cr(CO)_3C_7H_8$ | -91.5 | -76.8 | 14.7 | -70.4 | 21.1 | -81.5 | 10.0 |
| $Cr(CO)_3(C_6H_5CH_3)$ | -90.6 | -90.6 | 0.0 | -87.9 | 2.7 | -92.0 | -1.4 |
| $Cr(CO)_3(C_6H_5\text{-}CHO)$ | -114.0 | -114.4 | -0.3 | -106.9 | 7.1 | -111.9 | 2.1 |
| $Cr(CO)_3(Ph\text{-}O\text{-}Me)$ | -117.0 | -120.8 | -3.8 | -121.2 | -4.2 | -119.9 | -2.9 |
| $Cr(CO)_4(C_7H_8)$ | -73.4 | -85.0 | -11.6 | -99.0 | -25.6 | -117.6 | -44.2 |
| $CrC_{12}H_{12}O_3$ (1,3,5-Trimethylbenzene chromium tricarbonyl) | -111.4 | -89.2 | 22.2 | -112.2 | -0.8 | -128.0 | -16.6 |
| $Cr(CO)_3C_{10}H_8$ | -61.7 | -65.0 | -3.3 | -65.2 | -3.5 | -63.4 | -1.7 |
| $CrC_{15}H_{18}O_3$ (Hexamethylbenzene chromium tricarbonyl) | -134.2 | -116.9 | 17.3 | -133.6 | 0.6 | -118.6 | 15.6 |
| $CrC_{16}H_{36}O_4$ (Cr(O-t-butyl)$_4$) | -309.6 | -288.4 | 21.2 | -300.8 | 8.8 | -324.3 | -14.7 |
| $Cr_2C_8H_{12}O_8$ (Chromium diacetate dimer) | -476.5 | -439.1 | 37.4 | -484.9 | -8.4 | -459.1 | 17.4 |
| $Cr_2(CO)_{10}^{2-}$ | -423.9 | -311.9 | 112.0 | -392.7 | 31.2 | -449.0 | -25.1 |
| $Cr(NO)_4$ | -32.6 | -32.4 | 0.2 | -22.2 | 10.4 | -212.8 | -180.2 |
| $CrC_{10}NH_5O_5$ (Cr(CO)$_5$(Py)) | -150.4 | -128.6 | 21.8 | -166.1 | -15.7 | -158.7 | -8.3 |
| $CrC_{10}NH_{10}O_5$ (Cr(CO)$_5$(Piperidine) | -200.0 | -153.3 | 46.7 | -192.6 | 7.4 | -196.6 | 3.4 |
| $Cr(CO)_3(C_6H_5\text{-}NMe_2)$ | -80.4 | -73.5 | 6.9 | -79.4 | 1.0 | -75.4 | 5.0 |
| $CrC_{14}N_2H_{10}O_4$ (Cr(CO)$_4$(Py)$_2$) | -92.7 | -50.8 | 41.9 | -97.8 | -5.1 | -94.8 | -2.1 |
| $CrC_{14}N_2H_{20}O_4$ (Cr(CO)$_4$(Piperidine)$_2$) | -189.0 | -113.3 | 75.7 | -166.9 | 22.1 | -184.9 | 4.1 |
| $(Cp)_2Cr_2(NO)_4$ | -29.0 | 39.0 | 68.0 | -17.4 | 11.6 | -223.1 | -194.1 |
| $Cr_2C_{24}N_4H_{24}O_4$ (Tetrakis(mu-(6-methyl-2(1H)-pyridinato) dichromium)) | -189.1 | -95.4 | 93.7 | -208.8 | -19.7 | -258.6 | -69.5 |
| $CrF$ | 9.7 | -8.8 | -18.5 | -13.9 | -23.6 | -33.8 | -43.5 |
| $CrF^-$ | -52.3 | 68.3 | 120.6 | 28.3 | 80.6 | -10.2 | 42.1 |
| $CrF_2$ | -79.0 | -64.2 | 14.8 | -105.6 | -26.6 | -131.4 | -52.4 |

**Table 5** (continued)

| | | AM1* | | PM6 | | PM5 | |
|---|---|---|---|---|---|---|---|
| $CrF_2^-$ | -152.2 | -118.1 | 34.1 | -117.9 | 34.3 | -157.2 | -5.0 |
| $CrF_3$ | -157.3 | -220.1 | -62.8 | -235.1 | -77.8 | -243.8 | -86.5 |
| $CrF_3^-$ | -255.9 | -234.0 | 21.9 | -239.2 | 16.7 | -269.5 | -13.6 |
| $CrF_4^-$ | -343.4 | -349.7 | -6.3 | -367.0 | -23.6 | -366.4 | -23.0 |
| $CrF_5^-$ | -417.2 | -417.5 | -0.3 | -453.6 | -36.4 | -439.6 | -22.4 |
| $CrF_6^{3-}$ | -249.8 | -165.8 | 84.0 | -233.7 | 16.1 | -285.4 | -35.6 |
| $CrOF$ | 15.5 | 36.1 | 20.6 | -77.8 | -93.3 | -93.5 | -109.0 |
| $CrOF^-$ | -88.0 | -73.7 | 14.3 | -115.4 | -27.4 | -140.2 | -52.2 |
| $CrO_2F$ | -131.8 | -147.4 | -15.6 | -148.9 | -17.1 | -103.5 | 28.3 |
| $CrO_2F^-$ | -173.0 | -156.4 | 16.6 | -210.1 | -37.1 | -235.5 | -62.5 |
| $CrOF_2$ | -148.9 | -178.8 | -29.9 | -202.6 | -53.7 | -195.4 | -46.5 |
| $CrOF_2^-$ | -196.0 | -195.6 | 0.4 | -248.5 | -52.5 | -257.0 | -61.0 |
| $CrO_2F_2$ | -219.6 | -242.1 | -22.5 | -244.6 | -25.0 | -236.0 | -16.4 |
| $CrF_5H_2O^{2-}$ (YASHAB) | -421.0 | -398.7 | 22.3 | -419.1 | 1.9 | -461.7 | -40.7 |
| $Cr_2F_9^{3-}$ (OCOLIB) | -601.3 | -598.7 | 2.6 | -594.0 | 7.3 | -599.4 | 1.9 |
| $CrC_2N_2H_{12}O_2F_2^+$ (BUTDAV) | -142.2 | -143.3 | -1.1 | -164.9 | -22.7 | -243.1 | -100.9 |
| $CrCl$ | 42.6 | 50.5 | 7.9 | 16.4 | -26.2 | -9.5 | -52.1 |
| $CrCl^-$ | -35.0 | 36.3 | 71.3 | 46.7 | 81.7 | 17.4 | 52.4 |
| $CrCl_2$ | -5.6 | 44.4 | 50.0 | -25.6 | -20.0 | -68.7 | -63.1 |
| $CrCl_2^-$ | -74.0 | -27.5 | 46.5 | -49.1 | 24.9 | -89.8 | -15.8 |
| $CrOCl$ | -59.2 | -13.6 | 45.6 | -33.8 | 25.4 | -52.8 | 6.4 |
| $CrOCl^-$ | -55.0 | -49.6 | 5.4 | -71.7 | -16.7 | -99.9 | -44.9 |
| $CrO_2Cl$ | -92.4 | -101.4 | -9.0 | -95.7 | -3.3 | -91.3 | 1.1 |
| $CrO_2Cl^-$ | -127.0 | -148.0 | -21.0 | -171.3 | -44.3 | -198.2 | -71.2 |
| $CrOCl_2$ | -79.6 | -70.5 | 9.1 | -91.6 | -12.0 | -100.9 | -21.3 |
| $CrOCl_2^-$ | -131.0 | -133.8 | -2.8 | -156.0 | -25.0 | -168.3 | -37.3 |
| $CrCl_2O_2$ | -127.0 | -125.1 | 1.9 | -148.2 | -21.2 | -130.4 | -3.4 |
| $CrCl_3$ | -33.6 | -37.2 | -3.7 | -66.4 | -32.8 | -92.6 | -59.0 |
| $CrCl_4$ | -110.7 | -68.0 | 42.7 | -95.7 | 15.0 | -104.7 | 6.0 |
| $Cr(CO)_4ClC_2H_3$ (CATYOL) | -134.9 | -120.1 | 14.8 | -132.6 | 2.3 | -115.5 | 19.4 |
| $CrC_{10}H_{15}Cl_2O$ (AFEHIC) | -126.0 | -128.7 | -2.7 | -126.2 | -0.2 | -118.1 | 7.9 |
| $CrC_4N_3H_{13}Cl_3$ (AMZCCR) | -106.2 | -100.0 | 6.2 | -110.2 | -4.0 | -221.4 | -115.2 |
| $CrAlH_2$ | 216.6 | 216.9 | 0.3 | 101.1 | -115.5 | 57.6 | -159.0 |
| $HCrAlH_2$ | 264.3 | 212.0 | -52.3 | -54.7 | -319.0 | 32.3 | -232.0 |
| $CrSiH_3$ | 204.9 | 208.3 | 3.4 | 187.9 | -17.0 | 38.4 | -166.5 |
| $HCrSiH_3$ | 199.6 | 193.3 | -6.3 | 149.9 | -49.7 | -76.8 | -276.4 |
| $Cr_2PH$ | 195.0 | 135.2 | -59.8 | 105.8 | -89.2 | 152.0 | -43.0 |
| $HCrPH_2$ | 158.5 | 110.9 | -47.6 | 54.8 | -103.7 | -15.8 | -174.3 |
| $Cr(PF_3)_6$ | -1430.9 | -1389.5 | 41.4 | -1431.7 | -0.8 | -1435.9 | -5.0 |
| $CrS$ | 116.6 | 113.7 | -2.8 | 53.8 | -62.7 | 109.8 | -6.8 |
| $CrSH$ | 149.9 | 150.8 | 0.9 | 71.7 | -78.2 | 127.0 | -22.9 |
| $HCrSH$ | 159.3 | 159.3 | 0.0 | -185.2 | -344.5 | 84.7 | -74.6 |
| $CrS_4C_4H_8^{2-}$ (CUWLIP) | -1.2 | 60.0 | 61.2 | -0.3 | 0.9 | 71.5 | 72.7 |
| $CrBr$ | 147.7 | 112.8 | -34.9 | 97.4 | -50.3 | 115.9 | -31.8 |
| $CrBr_2$ | 148.4 | 148.5 | 0.1 | 71.1 | -77.3 | 69.8 | -78.6 |
| $CrTi$ | 253.3 | 201.8 | -51.5 | 232.4 | -20.9 | 348.9 | 95.6 |
| $CrNi$ | 105.4 | 89.9 | -15.6 | 149.7 | 44.3 | -94.1 | -199.5 |
| $CrCu$ | 232.3 | 222.8 | -9.5 | 190.3 | -42.0 | -33.4 | -265.7 |
| $CrZn$ | 249.4 | 207.9 | -41.5 | 79.6 | -169.8 | 193.7 | -55.7 |
| $CrZr$ | 248.8 | 222.7 | -26.1 | 213.5 | -35.3 | 136.3 | -112.5 |
| $CrMo$ | 271.6 | 265.6 | -6.0 | 138.7 | -132.9 | 234.3 | -37.3 |
| $CrI$ | 135.6 | 135.6 | 0.0 | 89.4 | -46.2 | 87.6 | -48.0 |

for the compounds $HCrO_3^-$ (135.1 kcal mol$^{-1}$), $CrF^-$ (120.6 kcal mol$^{-1}$), $Cr_2(CO)_{10}^{2-}$ (112 kcal mol$^{-1}$), $Cr_2C_{24}N_4H_{24}O_4$ (tetrakis(mu-(6-methyl-2(1H)-pyridinato) dichromium) (93.7 kcal mol$^{-1}$), $CrF_6^{3-}$ (84 kcal mol$^{-1}$), Cr (CO)$_4$(piperidine)$_2$ (75.7 kcal mol$^{-1}$), $Cr(C_2O_4)_3^{3-}$ (AMOXCR) (72.7 kcal mol$^{-1}$) and $CrC_4H_4O_{10}^-$ (KOXACR) (70.6 kcal mol$^{-1}$). In addition, the chlorinated compounds $CrCl^-$, $CrCl_2$, $CrCl_2^-$, $CrOCl$ and $CrCl_4$ give positive errors

| N=105 | | | |
|---|---|---|---|
| **Most positive error** | 135.1 | 81.7 | 95.6 |
| **Most negative error** | -69.0 | -344.5 | -276.4 |
| **MSE** | 9.0 | -23.5 | -43.2 |
| **MUE** | 25.1 | 38.4 | 55.9 |
| **RMSD** | 37.9 | 65.9 | 82.7 |

Errors are classified by coloring the boxes in which they appear. Green indicates errors lower than 10 kcal mol$^{-1}$, yellow 10–20 kcal mol$^{-1}$ and pink those greater than 20 kcal mol$^{-1}$. The coded-names within parentheses indicate the CSD-names of the compounds

of more than 40 kcal mol$^{-1}$. The large negative errors are found for Cr(CO)$_4^-$ (−69 kcal mol$^{-1}$), Cr$^{3+}$ (−65.8 kcal mol$^{-1}$), Cr$_2$PH (−59.8 kcal mol$^{-1}$), HCrAlH$_2$ (−52.3 kcal mol$^{-1}$), CrTi (−51.5 kcal mol$^{-1}$), HCrPH$_2$ (−47.6 kcal mol$^{-1}$) and CrZn (−41.5 kcal mol$^{-1}$). Additionally, all three methods give very large negative errors for chromium tetra-, penta- and hexa-cations (not shown in Table 5 and not included in the statistics). AM1* errors are found to be −345.8 kcal mol$^{-1}$

**Table 6** Calculated AM1*, PM6 and PM5 Koopmans' theorem ionization potentials and dipole moments for chromium-containing compounds

| Compound | Target | AM1* | Error | PM6 | Error | PM5 | Error |
|---|---|---|---|---|---|---|---|
| **Koopmans' Theorem Ionization Potentials for Chromium Compounds (eV)** | | | | | | | |
| **CrCp$_2$** | 5.70 | 7.11 | 1.41 | 7.28 | 1.58 | 7.64 | 1.94 |
| **Cr(C$_6$H$_6$)$_2$** | 5.40 | 7.36 | 1.96 | 6.51 | 1.11 | 6.95 | 1.55 |
| **Cr(CO)$_3$(C$_6$H$_5$CH$_3$)** | 6.60 | 8.14 | 1.54 | 7.37 | 0.77 | 8.43 | 1.83 |
| **Cr(CO)$_3$C$_7$H$_8$** | 6.90 | 8.23 | 1.33 | 7.17 | 0.27 | 8.57 | 1.67 |
| **CrC$_{12}$H$_{12}$O$_3$ (1,3,5-Trimethylbenzene chromium tricarbonyl)** | 7.20 | 7.19 | -0.02 | 6.57 | -0.63 | 7.06 | -0.14 |
| **CrC$_{15}$H$_{18}$O$_3$ (Hexamethylbenzene chromium tricarbonyl)** | 6.40 | 7.94 | 1.54 | 7.04 | 0.64 | 8.18 | 1.78 |
| **Cr(CO)$_3$(C$_6$H$_5$-NMe$_2$)** | 7.38 | 8.05 | 0.67 | 7.35 | -0.03 | 8.28 | 0.90 |
| **Cr(CO)$_3$(Ph-O-Me)** | 7.38 | 8.15 | 0.77 | 7.40 | 0.02 | 8.51 | 1.13 |
| **CrC$_{10}$NH$_5$O$_5$ (Cr(CO)$_5$(Py))** | 7.30 | 8.10 | 0.80 | 6.68 | -0.62 | 8.42 | 1.12 |
| **Cr(CO)$_6$** | 8.20 | 8.87 | 0.67 | 8.05 | -0.15 | 9.54 | 1.34 |
| **Cr$_2$C$_{24}$N$_4$H$_{24}$O$_4$ (Tetrakis(mu-(6-methyl-2(1H)-pyridinato) dichromium))** | 6.50 | 8.14 | 1.64 | 6.03 | -0.47 | 8.12 | 1.62 |
| **Cr$_2$C$_8$H$_{12}$O$_8$ (Chromium diacetate dimer)** | 8.00 | 8.87 | 0.87 | 7.39 | -0.61 | 8.43 | 0.43 |
| **CrCl$_2$** | 9.40 | 8.43 | -0.97 | 8.13 | -1.27 | 10.75 | 1.35 |
| **CrF** | 9.30 | 8.18 | -1.12 | 8.04 | -1.26 | 7.68 | -1.62 |
| **CrF$_2$** | 10.60 | 9.05 | -1.55 | 8.16 | -2.44 | 9.93 | -0.67 |
| **CrO$_2$F$_2$** | 12.91 | 12.29 | -0.62 | 12.07 | -0.84 | 12.71 | -0.20 |
| **CrF$_3$** | 12.50 | 10.14 | -2.36 | 9.58 | -2.92 | 11.15 | -1.35 |
| **CrBr$_2$** | 9.30 | 9.33 | 0.03 | 8.81 | -0.49 | 10.33 | 1.03 |
| | | **AM1*** | | **PM6** | | **PM5** | |
| **N=18** | | | | | | | |
| **MSE** | | 0.37 | | -0.41 | | 0.76 | |
| **MUE** | | 1.10 | | 0.90 | | 1.20 | |
| **Dipole Moments for Chromium Compounds (Debye)** | | | | | | | |
| **CrF** | 3.71 | 3.15 | -0.56 | 2.00 | -1.71 | 4.06 | 0.35 |
| **CrO$_2$F$_2$** | 0.02 | 1.39 | 1.37 | 1.83 | 1.81 | 2.00 | 1.98 |
| **CrCl** | 4.55 | 3.73 | -0.82 | 8.92 | 4.37 | 6.78 | 2.23 |
| **CrCl$_2$O$_2$** | 0.76 | 1.19 | 0.43 | 2.24 | 1.48 | 1.48 | 0.72 |
| **CrBr** | 4.41 | 4.10 | -0.31 | 0.01 | -4.40 | 7.21 | 2.80 |
| **CrI** | 4.37 | 1.08 | -3.29 | 3.86 | -0.51 | 4.19 | -0.18 |
| | | **AM1*** | | **PM6** | | **PM5** | |
| **N=6** | | | | | | | |
| **MSE** | | -0.53 | | 0.17 | | 1.32 | |
| **MUE** | | 1.13 | | 2.38 | | 1.38 | |

The errors are color coded as follows: green up to 0.5 eV or 0.5 Debye; yellow between 0.5 and 1.0; pink larger than 1.0

**Table 7** Calculated AM1*, PM6 and PM5 bond lengths and angles for chromium-containing compounds

| Compound | Variable | Target | AM1* | Error | PM6 | Error | PM5 | Error |
|---|---|---|---|---|---|---|---|---|
| $Cr_2$ | Cr-Cr | 1.68 | 1.75 | 0.07 | 1.71 | 0.03 | 1.62 | -0.06 |
| $Cr_2^-$ | Cr-Cr | 1.68 | 1.71 | 0.03 | 1.67 | -0.01 | 1.66 | -0.02 |
| CrH | Cr-H | 1.67 | 1.67 | 0.00 | 0.97 | -0.70 | 1.51 | -0.16 |
| $CrH_2$ | Cr-H | 1.65 | 1.66 | 0.00 | 0.94 | -0.71 | 1.51 | -0.15 |
| $CrCp_2$ | Cr-C | 2.44 | 2.39 | -0.05 | 2.24 | -0.20 | 2.24 | -0.20 |
| $Cr(C_6H_6)_2$ | Cr-C | 2.17 | 2.20 | 0.03 | 2.16 | -0.02 | 2.21 | 0.04 |
| $Cr(CH_3)_6^{3-}$ (MCRLDX) | Cr-C | 2.30 | 2.20 | -0.10 | 2.11 | -0.19 | 2.02 | -0.28 |
| CrN | Cr#N | 1.58 | 1.66 | 0.08 | 1.42 | -0.16 | 1.31 | -0.28 |
| $Cr(NH_3)_6^{2+}$ | Cr-N | 2.21 | 2.10 | -0.11 | 2.13 | -0.08 | 4.74 | 2.53 |
| $CrN_6C_{12}H_{30}^{3+}$ (SUKFEJ) | Cr-N | 2.09 | 2.08 | -0.01 | 2.09 | 0.00 | 1.96 | -0.13 |
| | N-Cr-N | 82.9 | 85.7 | 2.9 | 85.9 | 3.0 | 85.04 | 2.2 |
| $CrC_6N_{15}H_{18}$ (BGUCRM) | Cr-N | 2.03 | 1.99 | -0.04 | 1.99 | -0.04 | 1.83 | -0.20 |
| CrO | Cr=O | 1.65 | 1.66 | 0.01 | 1.60 | -0.05 | 1.64 | -0.01 |
| $CrO^-$ | Cr=O | 1.67 | 1.68 | 0.01 | 1.69 | 0.02 | 1.70 | 0.02 |
| $CrO_2$ | Cr=O | 1.60 | 1.64 | 0.04 | 1.57 | -0.03 | 1.61 | 0.01 |
| | O=Cr=O | 130.8 | 99.2 | -31.6 | 150.6 | 19.8 | 116.3 | -14.5 |
| $CrO_2^-$ | Cr=O | 1.64 | 1.65 | 0.01 | 1.65 | 0.01 | 1.64 | 0.00 |
| $CrO_3$ | Cr-O | 1.63 | 1.61 | -0.02 | 1.61 | -0.02 | 1.61 | -0.02 |
| $CrO_3^-$ | Cr=O | 1.62 | 1.64 | 0.03 | 1.62 | 0.00 | 1.62 | 0.01 |
| | O=Cr=O | 120.0 | 101.7 | -18.3 | 120.0 | 0.0 | 120.0 | 0.0 |
| $HCrO_3^-$ | Cr-H | 1.59 | 1.67 | 0.08 | 1.03 | -0.56 | 1.51 | -0.08 |
| | Cr-O | 1.60 | 1.63 | 0.03 | 1.64 | 0.04 | 1.62 | 0.02 |
| | H-Cr=O | 103.3 | 112.0 | 8.6 | 92.6 | -10.7 | 104.4 | 1.1 |
| | O=Cr=O | 114.9 | 106.9 | -8.0 | 119.8 | 4.9 | 114.0 | -0.8 |
| $CrO_4^{2-}$ | Cr-O | 1.66 | 1.67 | 0.01 | 1.67 | 0.01 | 1.62 | -0.04 |
| $Cr(H_2O)_6^{3+}$ (TAPBUH) | Cr-O | 1.96 | 1.96 | 0.00 | 2.06 | 0.10 | 1.91 | -0.05 |
| $Cr(H_2O)_6^{2+}$ | Cr-O | 2.11 | 2.00 | -0.11 | 2.14 | 0.03 | 1.97 | -0.14 |
| $Cr_2O_7^{2-}$ | Cr-O | 1.75 | 1.78 | 0.03 | 1.81 | 0.06 | 1.62 | -0.13 |
| | O-Cr-O | 109.5 | 114.4 | 4.9 | 108.3 | -1.2 | 115.8 | 6.3 |
| $Cr_3O_{10}^{2-}$ | Cr-O | 1.83 | 1.84 | 0.01 | 1.88 | 0.05 | 1.85 | 0.02 |
| | Cr-O | 1.74 | 1.72 | -0.02 | 1.74 | 0.00 | 1.62 | -0.12 |
| $Cr(CH_3)_2O_2$ | Cr-C | 1.98 | 2.01 | 0.03 | 1.99 | 0.01 | 1.93 | -0.05 |
| | Cr=O | 1.59 | 1.60 | 0.01 | 1.58 | -0.01 | 1.58 | -0.01 |
| | O=Cr-C | 107.9 | 107.0 | -0.9 | 104.5 | -3.4 | 108.5 | 0.6 |
| $Cr(CO)_4$ | Cr-C | 1.91 | 1.95 | 0.04 | 1.89 | -0.03 | 1.94 | 0.03 |
| | C-Cr-C | 90.0 | 90.0 | 0.0 | 90.0 | 0.0 | 82.2 | -7.8 |
| $CrC_4H_4O_{10}^-$ (KOXACR) | Cr-O(-C) | 1.92 | 1.89 | -0.03 | 1.98 | 0.06 | 1.96 | 0.04 |
| | O-Cr-O | 83.4 | 87.6 | 4.2 | 81.5 | -1.9 | 91.4 | 8.0 |
| | Cr-O($H_2$) | 2.29 | 2.02 | -0.28 | 2.22 | -0.07 | 1.96 | -0.33 |
| $Cr(CO)_5$ | Cr-C(1) | 1.84 | 1.86 | 0.02 | 1.84 | -0.01 | 1.89 | 0.05 |
| | Cr-C(2) | 1.92 | 1.95 | 0.04 | 1.91 | 0.00 | 1.92 | 0.00 |
| | C-Cr-C | 90.0 | 90.0 | 0.0 | 90.0 | 0.0 | 89.6 | -0.4 |
| $Cr(CO)_6$ | Cr-C | 1.91 | 1.95 | 0.04 | 1.90 | -0.01 | 1.91 | 0.00 |
| | C-Cr-C | 90.0 | 90.0 | 0.0 | 90.0 | 0.0 | 90.0 | 0.0 |
| $Cr(C_2O_4)_3^{3-}$ (AMOXCR) | Cr-O | 2.01 | 1.91 | -0.10 | 2.03 | 0.02 | 1.96 | -0.05 |
| | O-Cr-O | 89.7 | 90.1 | 0.4 | 88.6 | -1.1 | 89.5 | -0.2 |
| $Cr(C_5H_5)(CO)_3$ | Cr-C(C=O) | 1.86 | 1.90 | 0.04 | 1.88 | 0.02 | 1.89 | 0.03 |
| | C-O | 1.15 | 1.18 | 0.03 | 1.16 | 0.01 | 1.15 | 0.00 |
| | Cr-C($C_4H_4$) | 2.23 | 2.22 | -0.01 | 2.26 | 0.03 | 2.21 | -0.02 |
| $Cr(CO)_3(C_6H_6)$ | Cr-Bz | 1.69 | 1.89 | 0.20 | 1.75 | 0.06 | 2.24 | 0.55 |
| | C-Cr-C | 90.0 | 90.2 | 0.2 | 91.9 | 1.9 | 92.5 | 2.5 |
| $Cr(CO)_3C_7H_8$ | Cr-C | 1.85 | 1.90 | 0.04 | 1.87 | 0.02 | 1.89 | 0.04 |
| $CrC_{10}H_{18}O_6^+$ (BAPWIZ) | Cr-O | 1.94 | 1.87 | -0.07 | 1.93 | -0.01 | 1.93 | -0.01 |
| $CrC_{14}H_{14}O_6^+$ (ATOLAW) | Cr-O(=C) | 1.96 | 1.85 | -0.11 | 1.99 | 0.03 | 1.91 | -0.05 |
| | Cr-O(-C) | 1.97 | 1.78 | -0.19 | 1.94 | -0.03 | 1.95 | -0.02 |
| | O-Cr-O | 92.3 | 112.2 | 19.9 | 90.5 | -1.8 | 89.4 | -2.9 |
| | Cr-O(H2) | 2.00 | 2.14 | 0.14 | 2.11 | 0.11 | 1.95 | -0.05 |
| $CrC_{15}H_{21}O_6$ (ACACCR) | Cr-O | 1.95 | 1.91 | -0.04 | 2.00 | 0.05 | 1.95 | 0.00 |
| | O-Cr-O | 91.7 | 92.1 | 0.4 | 93.3 | 1.6 | 88.5 | -3.2 |

**Table 7** (continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cr₂(CO)₁₀²⁻ | Cr-Cr | 3.22 | 2.94 | -0.28 | 3.05 | -0.17 | 2.91 | -0.31 |
| Cr₂C₁₂H₂₀O₁₂ (ACETCR) | Cr-O | 2.02 | 1.89 | -0.14 | 2.04 | 0.02 | 1.92 | -0.10 |
| | Cr-O' | 2.31 | 1.89 | -0.42 | 2.59 | 0.28 | 2.09 | -0.22 |
| Cr(NO)₄ | Cr-N | 1.75 | 1.76 | 0.01 | 1.69 | -0.06 | 1.64 | -0.11 |
| | N-O | 1.18 | 1.15 | -0.03 | 1.17 | -0.01 | 1.13 | -0.05 |
| CrC₁₀N₂H₁₂O₈⁻ (Chromium(III) EDTA) | Cr-N | 2.12 | 2.17 | 0.05 | 2.04 | -0.08 | 1.91 | -0.21 |
| | N-Cr-N | 86.5 | 83.1 | -3.3 | 87.9 | 1.4 | 92.4 | 5.9 |
| | Cr-O | 1.94 | 1.91 | -0.03 | 2.00 | 0.06 | 1.96 | 0.02 |
| Cr₂(Cp)₂(NO)₃(NH₂) | Cr-Cr | 2.65 | 2.59 | -0.06 | 2.44 | -0.21 | 3.24 | 0.59 |
| | Cr-N | 1.65 | 1.79 | 0.14 | 1.63 | -0.02 | 1.42 | -0.23 |
| | N-O | 1.20 | 1.16 | -0.04 | 1.19 | -0.01 | 1.18 | -0.02 |
| | Cr-N | 1.94 | 1.94 | 0.00 | 1.85 | -0.09 | 1.34 | -0.60 |
| | N-O | 1.12 | 1.15 | 0.03 | 1.20 | 0.08 | 1.23 | 0.11 |
| (Cp)₂Cr₂(NO)₄ | Cr-N(br) | 1.90 | 1.90 | 0.00 | 1.96 | 0.06 | 1.41 | -0.49 |
| | Cr-N(ter) | 1.71 | 1.74 | 0.03 | 1.94 | 0.23 | 1.41 | -0.30 |
| | Cr-C | 2.25 | 2.26 | 0.01 | 2.27 | 0.02 | 2.30 | 0.05 |
| CrF | Cr-F | 1.77 | 1.76 | -0.01 | 1.53 | -0.24 | 1.65 | -0.12 |
| CrF₆²⁻ | Cr-F | 1.72 | 1.75 | 0.03 | 1.75 | 0.03 | 1.80 | 0.08 |
| Cr₂F₉³⁻ (OCOLIB) | Cr-Cr | 2.77 | 2.80 | 0.03 | 2.66 | -0.11 | 2.86 | 0.09 |
| | Cr-F(t) | 1.85 | 1.82 | -0.03 | 1.82 | -0.03 | 1.72 | -0.13 |
| | Cr-F(br)-Cr | 121.9 | 124.1 | 2.2 | 125.3 | 3.4 | 121.9 | 0.0 |
| CrO₂F₂ | Cr-O | 1.57 | 1.60 | 0.03 | 1.58 | 0.01 | 1.61 | 0.04 |
| | Cr-F | 1.72 | 1.76 | 0.04 | 1.60 | -0.12 | 1.56 | -0.16 |
| | O-Cr-O | 107.8 | 99.8 | -8.1 | 106.3 | -1.5 | 107.5 | -0.3 |
| | F-Cr-F | 111.9 | 126.7 | 14.8 | 123.0 | 11.1 | 112.1 | 0.2 |
| CrF₅H₂O²⁻ (YASHAB) | Cr-F | 1.91 | 1.86 | -0.05 | 1.81 | -0.10 | 1.77 | -0.14 |
| | Cr-O | 1.99 | 3.86 | 1.87 | 4.24 | 2.25 | 2.36 | 0.37 |
| CrF₄N₂C₂H₈ (DIYFEW) | Cr-F | 1.89 | 1.77 | -0.13 | 1.82 | -0.07 | 1.70 | -0.20 |
| | F-Cr-N | 92.1 | 84.3 | -7.8 | 89.4 | -2.7 | 91.5 | -0.6 |
| CrC₂N₂H₁₂O₂F₂⁺ (BUTDAV) | Cr-F | 1.88 | 1.77 | -0.11 | 1.70 | -0.18 | 1.73 | -0.15 |
| | Cr-O | 2.00 | 2.04 | 0.04 | 2.21 | 0.21 | 2.04 | 0.04 |
| | Cr-N | 2.04 | 2.01 | -0.03 | 2.06 | 0.02 | 1.82 | -0.22 |
| CrCl | Cr-Cl | 2.17 | 2.18 | 0.01 | 1.97 | -0.20 | 2.27 | 0.10 |
| CrCl₂ | Cr-Cl | 2.19 | 2.24 | 0.05 | 1.95 | -0.24 | 2.23 | 0.04 |
| CrCl₄²⁻ (BAHVIP) | Cr-Cl | 2.43 | 2.37 | -0.06 | 2.39 | -0.04 | 2.14 | -0.29 |
| | Cl-Cr-Cl | 105.2 | 80.9 | -24.3 | 90.5 | -14.7 | 109.5 | 4.3 |
| Cr₂Cl₉³⁻ (ZEBRON) | Cr-Cr | 3.15 | 2.49 | -0.66 | 3.33 | 0.18 | 3.52 | 0.37 |
| | Cr-Cl(br) | 2.31 | 2.22 | -0.09 | 2.31 | 0.00 | 2.50 | 0.19 |
| | Cr-Cl(t) | 2.29 | 2.27 | -0.02 | 2.31 | 0.02 | 2.15 | -0.14 |
| CrCl₂O₂ | Cr-Cl | 2.13 | 2.17 | 0.04 | 1.94 | -0.19 | 2.13 | 0.00 |
| | Cr=O | 1.58 | 1.59 | 0.01 | 1.59 | 0.01 | 1.59 | 0.01 |
| Cr(CO)₄ClC₂H₃ (CATYOL) | Cr-Cl | 2.44 | 2.40 | -0.04 | 2.35 | -0.09 | 2.26 | -0.18 |
| | Cr-C(O) | 1.93 | 1.95 | 0.02 | 1.93 | 0.00 | 1.95 | 0.02 |
| | C-Cr-Cl | 86.3 | 109.2 | 22.9 | 83.2 | -3.1 | 91.4 | 5.1 |
| | Cr-C(H₃) | 1.71 | 1.81 | 0.10 | 1.72 | 0.01 | 1.94 | 0.23 |
| CrC₁₀H₁₅Cl₂O (AFEHIC) | Cr-Cl | 2.25 | 2.16 | -0.09 | 2.05 | -0.20 | 2.21 | -0.04 |
| | Cl-Cr-Cl | 96.5 | 86.3 | -10.1 | 94.7 | -1.8 | 95.5 | -1.0 |
| | Cr-O | 1.59 | 1.59 | 0.00 | 1.56 | -0.03 | 1.58 | -0.01 |
| | Cr-C | 2.24 | 2.22 | -0.02 | 2.27 | 0.03 | 2.29 | 0.05 |
| CrC₄N₃H₁₃Cl₃ (AMZCCR) | Cr-Cl | 2.33 | 2.20 | -0.13 | 2.23 | -0.10 | 2.32 | -0.02 |
| | Cr-N | 2.08 | 2.11 | 0.03 | 2.12 | 0.04 | 1.87 | -0.21 |
| CrAlH₂ | CrAl | 2.49 | 2.49 | 0.00 | 2.11 | -0.38 | 1.76 | -0.74 |
| HCrAlH₂ | CrAl | 2.63 | 2.54 | -0.09 | 2.11 | -0.52 | 1.90 | -0.73 |
| CrSiH₃ | Cr-Si | 2.44 | 2.46 | 0.02 | 2.85 | 0.41 | 1.93 | -0.51 |
| HCrSiH₃ | Cr-Si | 2.45 | 2.45 | 0.00 | 2.74 | 0.29 | 1.74 | -0.71 |
| HCrPH₂ | Cr-P | 2.35 | 2.24 | -0.11 | 2.20 | -0.15 | 2.47 | 0.12 |
| CrS | Cr=S | 2.11 | 2.09 | -0.02 | 1.80 | -0.31 | 2.43 | 0.32 |
| CrSH | Cr-S | 2.22 | 2.28 | 0.06 | 1.73 | -0.49 | 2.42 | 0.21 |
| HCrSH | Cr-S | 2.20 | 2.20 | 0.00 | 1.09 | -1.11 | 2.38 | 0.18 |
| CrC₁₂P₄H₃₄S₂ (JIYDOK) | Cr-S | 2.39 | 2.33 | -0.06 | 1.93 | -0.46 | 3.02 | 0.63 |
| | Cr-P | 2.36 | 2.17 | -0.19 | 2.41 | 0.05 | 2.48 | 0.12 |
| | S-Cr-P | 89.4 | 99.7 | 10.3 | 90.7 | 1.3 | 97.6 | 8.2 |
| CrS₄C₄H₈²⁻ (CUWLIP) | Cr-S | 2.39 | 2.28 | -0.11 | 2.28 | -0.11 | 2.69 | 0.30 |
| | S-Cr-S | 91.7 | 96.3 | 4.6 | 91.6 | -0.1 | 95.9 | 4.2 |

**Table 7** (continued)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| CrTi | Cr-Ti | 1.62 | 1.84 | 0.22 | 2.51 | 0.89 | 12.59 | 10.97 |
| CrNi | Cr-Ni | 2.13 | 2.17 | 0.04 | 2.67 | 0.54 | 1.39 | -0.74 |
| CrCu | Cr-Cu | 2.35 | 2.55 | 0.20 | 3.10 | 0.75 | 1.51 | -0.84 |
| CrZn | Cr-Zn | 2.37 | 2.60 | 0.23 | 1.91 | -0.46 | 1.84 | -0.54 |
| CrBr | Cr-Br | 2.43 | 2.25 | -0.18 | 2.42 | -0.01 | 2.41 | -0.02 |
| CrBr$_2$ | Cr-Br | 2.43 | 2.27 | -0.16 | 2.06 | -0.37 | 2.30 | -0.13 |
| CrZr | Cr-Zr | 1.98 | 2.16 | 0.18 | 2.31 | 0.33 | 2.21 | 0.23 |
| CrMo | Cr-Mo | 1.77 | 1.85 | 0.08 | 1.60 | -0.17 | 2.00 | 0.23 |
| CrI | Cr-I | 2.57 | 2.20 | -0.37 | 2.49 | -0.08 | 2.28 | -0.30 |
| CrI$_2$ | Cr-I | 2.41 | 2.41 | 0.00 | 2.45 | 0.04 | 2.24 | -0.16 |
| | | | | **AM1*** | | **PM6** | | **PM5** |
| *N*=110 | | | | | | | | |
| MSE bond length | | | | 0.00 | | -0.02 | | 0.06 |
| MUE bond length | | | | 0.09 | | 0.16 | | 0.29 |
| *N*=25 | | | | | | | | |
| MSE bond angle | | | | -0.6 | | 0.2 | | 0.7 |
| MUE bond angle | | | | 8.4 | | 3.7 | | 3.2 |

The coded-names within parentheses indicate the CSD-names of the compounds. The errors are color coded as follows: green up to 0.05 Å or 0.5°; yellow between 0.05–0.1 Å or 0.5–1.0°; pink larger than 0.1 Å or 1°

(−462.8 and −549 kcal mol$^{-1}$ for PM6 and PM5, respectively) for Cr$^{4+}$, −875.2 kcal mol$^{-1}$ (−1027.8 and −1098.1 kcal mol$^{-1}$ for PM6 and PM5, respectively) for Cr$^{5+}$ and −1673.9 kcal mol$^{-1}$ (−1871.6 and −1910.3 kcal mol$^{-1}$ for PM6 and PM5, respectively) for Cr$^{6+}$. Experimental heats of formation of these cations are given in Table S1 of the Supplementary Material. Once again, very large errors are given by the compounds that contain the original AM1 elements, as expected. The large errors for the compounds containing "pure" AM1* elements are likely to be a consequence of our sequential parameterization strategy.

Ionization potentials and dipole moments

A comparison of the calculated and experimental Koopmans' theorem ionization potentials and dipole moments for the compounds containing chromium are shown in Table 6.

AM1* and PM5 overestimate ionization potentials by 0.37 and 0.76 eV, respectively, whereas PM6 underestimate them by 0.41 eV. The performance of all three methods is comparable. The mean unsigned errors vary in a relatively small range from 0.90 (PM6) to 1.20 eV (PM5). The AM1* MUE, 1.10 eV, lies in the middle of this range. All the large errors (more than 1.0 eV) for AM1* are given by the compounds containing AM1 elements, C, N, O, F.

AM1* performs best for dipole moments with an MUE of 1.13 Debye. PM5 is slightly worse than AM1* with an MUE of 1.38 Debye. PM6 performs least well in reproducing dipole moments for chromium compounds with an MUE of 2.38 Debye. AM1* tends to underestimate dipole moments by 0.53 Debye, whereas PM6 and PM5 overestimate them by about 0.17 and 1.32 Debye, respectively. The largest

AM1* error is given by CrI (−3.29 Debye). That is not very surprising and reflects the known weakness [4] of AM1* parameterization for iodine in reproducing dipole moments.

Geometries

The geometrical parameters used to parameterize AM1* for chromium and a comparison of the AM1*, PM6 and PM5 results are shown in Table 7.

The mean unsigned errors for calculated bond lengths to chromium are found 0.09 Å for AM1*, 0.16 Å and 0.29 Å for PM6 and PM5, respectively. AM1* shows no systematic error. PM6 underestimates bond lengths to chromium by 0.02 Å, whereas PM5 systematically overestimates them by 0.06 Å.

None of the three methods shows significant systematic error in bond angles to chromium with the mean signed errors of −0.6° (AM1*), 0.2° (PM6) and 0.7° (PM5). Surprisingly, AM1* performs significantly (MUE of 8.4°) and PM6 slightly (MUE=3.7°) worse for bond angles than PM5 (MUE of 3.2°).

**Discussion**

The current AM1* parameterization for vanadium and chromium, for which the parameterization data have been extended and made more reliable by including results from DFT calculations, is of the standard expected for a modern NDDO-based method with *d*-orbitals. Parameters for vanadium and chromium provide important additional elements for catalytic chemistry and biochemistry applications. AM1* gives good results for both energetic and

electronic properties of the training set of molecules. AM1* also reproduces geometries well except that it gives larger errors for the bond angles of chromium compounds than the other PM5 and PM6.

Both AM1* and PM6 represent good, general purpose NDDO-based methods for these two elements. Their parameters will provide good starting points for reaction-specific local parameterizations of MNDO-like Hamiltonians and also extend the range of applicability of MNDO-like techniques.

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